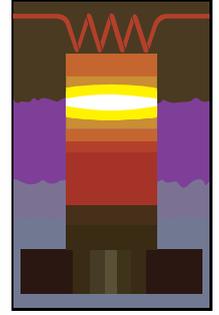


SHS XIII

INTERNATIONAL SYMPOSIUM ON SELF-PROPAGATING
HIGH TEMPERATURE SYNTHESIS

OCTOBER 12-15, 2015 ANTALYA / TÜRKİYE

WWW.SHS2015.ORG



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ABSTRACT BOOK

Let's propagate the future...

HELLO AND WELCOME TO SHS XIII !

Dear All,



On behalf of Organising Committee we would like to take this opportunity to express our pleasure to welcome you and your accompanies for the XIII. International Symposium on Self-Propagating High Temperature Synthesis which is being held October 12th to 15th, 2015 in the beautiful surroundings of Antalya, Turkey.

The general aim of SHS XIII is to integrate both the fundamentals and the applications on self-propagating high-temperature synthesis of materials and their processing.

Oral and poster contributions are invited in following areas:

1. Theory of SHS: combustion, structure formation, methods of modeling.
2. Mechanisms and kinetics of SHS processes.
3. SHS of powder materials (micron, submicron- and nano scale)
4. SHS of bulk materials (metal and alloys, intermetallics, ceramics, composites, advanced functional and constructional materials, biomaterials, nanomaterials, foams etc.)
5. Boron related SHS materials
6. Novel approaches and SHS related processes (SHS and shock waves, sol-gel auto-combustion synthesis, SHS in nano-systems etc.)
7. Application and Industrialization

Symposium Goals

- To share ideas, new SHS approaches and emerging SHS technologies to enable more effective SHS penetration in various fields of manufacture.
- To review the state of the art of SHS globally with regard to materials design, SHS processing and applications.
- To involve young scientists and engineers and promote continued development in the field of SHS, both in fundamental studies and in applied areas.
- To foster international collaboration among the communities of scientists, engineers, and technologists working on SHS.

The topics will be addressed in invited plenary lectures, keynote lectures, selected oral presentations and poster sessions.

We are looking forward to seeing all of you, who have their heart and soul in this society for an open discussion arena for all, in Antalya, home of tolerance, where different cultures merge in peace and harmony.

Sincerely yours,

Prof. Dr. Onuralp Yücel
SYMPOSIUM CHAIRMAN

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PROGRAMME

| Sunday, October 11 / 2015 | |
|---------------------------------|--|
| 09.00 - 17:00 | Registration |
| Monday, October 12 / 2015 | |
| 09:00 - 09:20 | OPENING CEREMONY |
| | Session Chairman: Onuralp Yucel |
| 09:20 - 10:20 | Plenary Report I Alexander S. Mukasyan RECENT ADVANCES IN COMBUSTION SYNTHESIS OF MATERIALS (OVERVIEW) ¹ Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana, USA, ² National University of Science and Technology, MISiS, Moscow, Russia |
| 10:20 - 11:00 | Coffee Break |
| 11:00 - 12:00 | Plenary Report II Giacomo Cao ENVIRONMENTAL AND SPACE APPLICATIONS OF SHS Department of Mechanical, Chemical and Materials Engineering University of Cagliari, 09123 Cagliari, Italy |
| 12:00 - 13:30 | Lunch |
| Session I | Session Chairman: Onuralp Yucel |
| 13:30 - 14:00 Abstract:1074 | Keynote I SYNTHESIS GAS GENERATION ON SHS AND SCS CATALYSTS FOR FUEL ECONOMY AND PURIFYING EXHAUST GASES OF INTERNAL COMBUSTION AND GAS TURBINE ENGINES <i>Galina Xanthopoulou</i> ¹ , Yuriy Knysh ² , Alexander Amosov ³ , Dmitriy Dmitriev ² NCSR "Demokritos" INN, Athens-Greece ¹ ; SSAU Department of Theory of Aircraft Engines, Samara-Russia ² ; Samara State Technical University ³ |
| 14:00 - 14:20 Abstract:1085 | SOLUTION COMBUSTION SYNTHESIS OF STABLE SUPPORTED NI AND Ni-Cu CATALYSTS FOR HYDROGEN PRODUCTION FROM ETHANOL Allison Cross ¹ , Khachatur Manukyan ² , Sergei Rouvimov ³ , Alexander Mukasyan ¹ , <i>Eduardo Wolf</i> ¹ University of Notre Dame, Department of Chemical and Biomolecular Engineering, Notre Dame -United States ¹ , University of Notre Dame, Department of Physics, Notre Dame -United States ² ; University of Notre Dame, Department of Electrical Engineering, Notre Dame -United States ³ |
| 14:20 - 14:40 Abstract:1134 | ACTIVITY OF SCS CATALYSTS ON HOLLOW SPHERES IN DRY REFORMING OF METHANE <i>Malik Matsuda</i> ¹ , Galina Xanthopoulou ² , H Wada ¹ , Osamu Odavara ¹ , George Vekinis ² Tokyo Institute of Technology, Department of Innovative and Engineered Materials, Yokohama-Japan ¹ ; NCSR "Demokritos", Institute of Nanoscience and Nanotechnology, Athens-Greece ² |
| 14:40 - 15:00 | Coffee Break |
| Session II | Session Chairman: Galina Xanthopoulou |
| 15:00 - 15:30 Abstract: 1135 | Keynote II SHS IN THIN FILMS <i>Alexander Rogachev</i> ¹ , Sergei Vadchenko ¹ , Florence Baras ² , Olivier Politano ² Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia ¹ ; Universite de Bourgogne, Laboratoire Interdisciplinaire Carnot de Bourgogne, Dijon-France ² |
| 15:30 - 15:50 Abstract: 1066 | REACTIVE NANOSTRUCTURED FOILS FABRICATED BY HIGH-ENERGY BALL MILLING AND COLD ROLLING <i>Andrey Nepapushev</i> ¹ , Alexander Rogachev ² , Alexander Mukasyan ³ National University of Science and Technology «MISIS», Moscow-Russia ¹ , Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia ² ; University of Notre Dame Department of Chemical & Biomolecular Eng., Notre Dame-United States ³ |

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| 15:50 - 16:10 Abstract: 1087 | NANOSTRUCTURED CERAMICS BY SPARK PLASMA SINTERING OF SHS SILICON CARBIDE NANOPOWDER <i>Dmitry Moskovskikh</i> ¹ , Alexander Rogachev ² , Alexander Mukasyan ³ National University of Science and Technology «MISIS», Center of Functional Nano-Ceramics, Moscow-Russia ¹ ; Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia ² ; University of Notre Dame, Department of Chemical & Biomolecular Eng., Notre Dame-United States ³ |
| 16:10 - 16:30 Abstract: 1096 | STRUCTURED COMPOSITE MATERIALS BY SHS METHOD: EXPERIMENTAL STUDY <i>Olga Kamynina</i> ¹ , Sergey Vadchenko ¹ , Alex Shchukin ¹ , Alexander Sytschev ² , Ivan Kovalev ³ Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia ¹ |
| 16:30 - 18:00 | <i>Poster Session I</i> |
| 18:30 - 19:30 | WELCOME RECEPTION |

Tuesday, October 13 / 2015

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| 09:00 - 10:00 | Plenary Report III <i>Florian Kongoli</i> ^{1 2 3} , <i>Edward Z. O'Brien</i> ³ , <i>Ian McBow</i> ³ SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) AND SUSTAINABLE DEVELOPMENT ¹ FLOGEN Technologies Inc. Montreal, QC, Canada, H3P 2T1, ² FLOGEN STARS OUTREACH, Montreal, QC, Canada, H3P 2T1, ³ FLOGEN Technologies Inc., Wilmington, De, 19808, USA Session Chairman: Vladimir Sanin |
| 10:00 - 10:20 | Coffee Break |
| Session III | Session Chairman: Vladimir Sanin |
| 10:20 - 10:50 Abstract: 1138 | Keynote III SHS-ENABLED REACTIVE BONDING FOR APPLICATION IN MICROSYSTEMS TECHNOLOGIES <i>Matthias P. Kremer</i> ¹ , Andreas Tortschanoff ² , Andreas E. Guber ³ CTR Carinthian Tech Research Heterogeneous Integraten Technologies, Villach-Austria ¹ ; CTR Carinthian Tech Research Microsystems Technologies, Villach-Austria ² ; Karlsruhe Institute of Technology, Institute of Microstructure Technology (IMT), Karlsruhe-Germany ³ |
| 10:50 - 11:10 Abstract: 1116 | CONSOLIDATION OF Cu-BASED NANOSTRUCTURED PSEUDO ALLOYS FOR ELECTRICAL CONTACT MATERIALS <i>Natalia Shkodich</i> ¹ , Alexander Rogachev ¹ , Alexander Mukasyan ² , Dmitry Moskovskikh ³ , Sergey Vadchenko ¹ , Kirill Kuskov ³ , Alexander Shchukin ¹ Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia ¹ ; University of Notre Dame, Department of Chemical and Biomolecular Engineering, Notre Dame-United States ² ; National University of Science and Technology "MISIS", Moscow-Russia ³ |
| 11:10 - 11:30 Abstract: 1055 | MA SHS OF SUBMICRON POWDERS AND NANOSTRUCTURED GRANULES BASED ON NiAl AND TiAl <i>Victoria Kurbatkina</i> , Evgeny Patsera, Evgeny Levashov National University of Science and Technology «MISIS», Moscow-Russia ¹ |
| 11:30 - 11:50 Abstract: 1168 | FORMATION OF NANOPARTICLES BY SHS <i>Erdem Camurlu</i> Akdeniz University Mechanical Eng. Dept.-Türkiye |
| 12:00 - 13:30 | Lunch |

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| Session IV | Session Chairman: Florian Kongoli |
| 13:30 - 14:00 Abstract: 1127 | Keynote IV THE CATALYSTS PREPARED BY SOLUTION COMBUSTION ON GLASS-FIBERS FOR SYNTHESIS OF CARBON NANOTUBES <i>Zulhair Mansurov</i> ¹ , Gaukhar Smagulova ¹ , Anvar Zakhidov ² Institute of Combustion Problems Chemistry and Chemical Technology, Almaty-Kazakhstan ¹ ; University of Texas at Dallas, Chemistry Richardson-United States ² |
| 14:00 - 14:20 Abstract: 1152 | CRYSTALLOGRAPHIC DEPENDENCE OF CATALYSTS ACTIVITY PREPARED BY SCS AND SHS METHODS IN DIFFERENT PROCESSES <i>Galina Xanthopoulou</i> ¹ NCSR "Demokritos", Institute of Nanoscience and Nanotechnology Athens-Greece ¹ |
| 14:20 - 14:40 Abstract: 1029 | ONE-STEP PREPARATION OF HIGHLY STABLE Ni-BASED SUPPORTED CATALYST BY SOLUTION COMBUSTION SYNTHESIS <i>S.I. Roslyakov</i> ¹ , Eduardo Wolf ² , Alisson Cross ² , A.S. Rogachev ³ , A.S. Mukasyan ² National University of Science and Technology «MISIS» Scientific Research Center "Advanced NanoCeramics" Moscow-Russia ¹ University of Notre Dame Department Chemical and Biomolecular Engineering Notre Dame-United States ² Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences Chernogolovka-Russia ³ |
| 14:40 - 15:00 | Coffee Break |
| Session V | Session Chairman: Alexander Mukasyan |
| 15:00 - 15:30 Abstract: 1109 | Keynote V 3-D RECONSTRUCTION OF HIGH ENERGY DENSITY MATERIALS: EFFECT OF NANOSTRUCTURE ON IGNITION CHARACTERISTICS <i>Christopher Shuck</i> ¹ , Alexander Mukasyan ¹ University of Notre Dame, Department of Chemical and Biomolecular Engineering, Notre Dame-United States ¹ |
| 15:30 - 15:50 Abstract: 1122 | CARBON ISOTOPE 13C LABELLING IN SiC NANOFIBER SYNTHESIS USING SHS APPROACH <i>Andrzej Huczko</i> ¹ , Michał Soszyński ¹ , Balram Pokhrel ² Warsaw University, Department of Chemistry, Warsaw-Poland ¹ ; Kathmandu University, School of Science, Dhulikhel-Nepal ² |
| 15:50 - 16:10 Abstract: 1143 | SUPPRESSION EFFECT OF REACTION TEMPERATURE ON COMBUSTION SYNTHESIS OF TITANIUM CARBOSULFIDE <i>Ryuichi Tomoshige</i> ¹ , Kazushi Kai ¹ , Yuuki Furu-ichi ¹ , Kiyohito Ishida ² Sojo University Nanoscience, Kumamoto-Japan ¹ ; Tohoku University Materials Science, Sendai-Japan ² |
| 16:10 - 16:30 Abstract: 1057 | QUANTITATIVE ENVIRONMENTAL ASSESSMENT OF SOLUTION COMBUSTION SYNTHESIS OF OXIDE NANOMATERIALS <i>Roberto Rosa</i> ¹ , Martina Pini ² , Paolo Neri ² , Anna Maria Ferrari ² University of Modena and Reggio Emilia Department of Engineering "Enzo Ferrari" Modena-Italy ¹ University of Modena and Reggio Emilia Department of Sciences and Methods for Engineering Reggio Emilia-Italy ² |
| 16:30 - 16:50 Abstract: 1111 | SOLUTION COMBUSTION SYNTHESIS OF PEROVSKITE OXIDE NANOPARTICLES: CONVENTIONAL VS. MICROWAVE IGNITION <i>Roberto Rosa</i> ¹ , Chiara Ponzone ¹ , Paolo Veronesi ¹ , Isabella Natali Sora ² , Veronica Carrara ² , Valeria Felice ² , Cristina Leonelli ¹ University of Modena and Reggio Emilia Department of Engineering Enzo Ferrari Modena-Italy ¹ University of Bergamo Department of Engineering and Applied Science Bergamo-Italy |
| 16:50 - 18:30 | Poster Session II |

| Wednesday, October 14 / 2015 | |
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| 09:00 - 10:00 | <p>Plenary Report III Igor Smurov, M. Doubenskaia SELECTIVE LASER MELTING AND DIRECT METAL DEPOSITION: FROM PROCESS FUNDAMENTALS TOWARDS ADVANCED PRODUCTS LTDS Laboratory Université de Lyon, ENISE Saint-Etienne, France Session Chairman: Dominique Vrel</p> |
| 10:00 - 10:20 | Coffee Break |
| Session VI | Session Chairman: Dominique Vrel |
| 10:20 - 10:50 Abstract: 1006 | <p>Keynote VI CONTRIBUTION OF SHS TO ADDITIVE TECHNOLOGY OF SELECTIVE LASER AND ELECTRON BEAM SINTERING <i>Evgeny Levashov</i>¹, Yury Pogozhev¹, Vladimir Sanin², Vladimir Yukhvid², Dmitry Andreev², Aleksander Zaitsev¹, Zhanna Sentyurina¹, Alla Logacheva³, Anatoly Timofeev³ National University of Science and Technology "MISIS", Moscow-Russia¹; Institute of Structural Macrokinetics and Materials Science, Russian Academy of Science, Chernogolovka- Russia²; "Kompozit" Research, Development & Production Corp., Korolev-Russia³</p> |
| 10:50 - 11:10 Abstract: 1073 | <p>WORLD FIRST 3D PRINTED CATALYSTS BLOCKS ALSO ASSISTED BY SHS AND SCS <i>Galina Xanthopoulou</i>¹, Yurii Knysh², Dmitriy Dmitriev², Vitaliy Smelov³ NCSR "Demokritos" INN, Athens-Greece¹; SSAU Department of Theory of Aircraft Engines, Samara-Russia²; SSAU Department of Aircraft Engines production Samara-Russia³</p> |
| 11:10 - 11:30 Abstract: 1076 | <p>CENTRIFUGAL METALLOTHERMIC SHS OF CAST CHARGED MATERIALS FOR FOLLOWING METALLURGICAL TREATMENT <i>Vladimir Sanin</i>¹, Denis Ikornikov¹, Dmitrii Andreev¹, Vladimir Yukhvid¹, Evgeny Levashov², Yury Pogozhev², Zhanna Sentyurina² Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹; National University of Science and Technology "MISIS", Moscow- Russia.</p> |
| 11:30 - 11:50 Abstract: 1050 | <p>HIGH PERMITTIVITY OF BARIUM TITANATE PREPARED BY SHS/QP <i>Jinyong Zhang</i>¹, Chongjun Xu¹, Fan Zhang¹, Zhengyi Fu¹ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing Wuhan University of Technology Wuhan-China¹</p> |
| 12:00 - 13:30 | Lunch |
| Session VII | Session Chairman: Alexander Rogachev |
| 13:30 - 14:00 Abstract: 1038 | <p>Keynote VII CENTRIFUGAL SHS OF CAST 'HIGH-ENTROPY' METAL ALLOYS <i>Vladimir Sanin</i>¹, Denis Ikornikov¹, Dmitriy Andreev¹, Nina Sachkova¹, Yuriy Kovalev¹, Vecheslav Borshch¹, Vladimir Yukhvid¹ Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹</p> |
| 14:00 - 14:20 Abstract: 1115 | <p>MICROSTRUCTURE AND PROPERTIES OF Al₂O₃/ZrO₂ EUTECTIC COMPOSITE BY COMBUSTION SYNTHESIS MELT-CASTING UNDER LOW PRESSURE <i>Yongting Zheng</i>¹, Pan Yang¹, Shui Wang¹, Xiaodong He¹ Harbin Institute of Technology Center for Composite Materials and Structure, Harbin-China¹</p> |
| 14:20 - 14:40 Abstract: 1148 | <p>PRODUCTION OF NICKEL BASED SUPERALLOYS BY SHS PRODUCTION METHOD <i>Murat Alkan</i>¹, Dmitrii E. Andreev², M. Seref Sönmez³, Vladimir N. Sanin², Bora Derin³, Vladimir I. Yukhvid², Onuralp Yücel³ MTA Mineral Research & Exploration Gen. Direct. Dept. of Mining Analysis and Tech. Ankara-Turkey¹ Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia²; Istanbul Technical University Metallurgical and Materials Eng. Dept., Istanbul-Turkey³</p> |
| 14:40 - 15:00 | Coffee Break |

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| Session VIII | Session Chairman: Zulkhair Mansurov |
| 15:00 - 15:30 Abstract: 1162 | Keynote VIII ONGOING DEVELOPMENT ACTIVITIES OF BORON LOADED PROPELLANT AT ROKETSAN <i>Serhat Ozturk</i> ¹ ROKETSAN Propellant Technology Department , Ankara-Turkey |
| 15:30 - 15:50 Abstract: 1140 | SEMI-COMMERCIAL PRODUCTION OF TiB₂ BY SHS: SYNTHESIS, CHARACTERIZATION AND SINTERING BEHAVIOR <i>Mehmet Suat Somer</i> ¹ , Meltem Ipekci ² , Selcuk Acar ³ , Mustafa Elmadagli ⁴ , Jürgen Hennicke ⁵ Koç University College of Science Department of Chemistry, Istanbul-Turkey ¹ ; Koç University Graduate School of Sciences & Engineering, Department of Materials Science and Engineering Istanbul-Turkey ² ; Pavezyum Kimya San. Dis. Tic., Istanbul-Turkey ³ ; Roketsan Roket Sanayii ve Ticaret A.S. Malzeme ve Balistik Koruma Teknolojileri Mudurlugu, Ankara-Turkey ⁴ ; FCT Systeme GmbH, Frankenblick-Germany ⁵ |
| 15:50 - 16:10 Abstract: 1002 | COMBUSTION SYNTHESIS OF BORON NITRIDE VIA MAGNESIUM REDUCTION USING ADDITIVES <i>Shyan-Lung Chung</i> ¹ , Yu-Hsiang Hsu ¹ , Kuan-Ying Tseng ¹ National Cheng Kung University, Department of Chemical Engineering, Tainan-Taiwan ¹ |
| 16:10 - 16:30 Abstract: 1078 | CENTRIFUGAL SHS HARDFACING WITH Mo₂NiB₂/Ni COMPOSITE <i>Dmitrii Andreev</i> ¹ , Denis Ikornikov ¹ , Vladimir Sanin ¹ , Vladimir Yukhvid ¹ , Bora Derin ² , Onuralp Yucel ² Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia ¹ ; Istanbul Technical University Metallurgical and Materials Engineering, Istanbul-Turkey ² |
| 16:30 - 16:50 Abstract: 1008 | FABRICATION OF MgB₂ BY COMBUSTION SYNTHESIS UNDER HIGH GAS PRESSURE <i>Sanat Tolendiuly</i> ¹ , Sergey Fomenko ² , Roza Abdulkarimova ¹ , Zulkhair Mansurov ³ , Karen Martirosyan ⁴ al-Farabi KazNU Chemical and Chemical Technology, Almaty-Kazakhstan ¹ ; Institute of Combustion Problems, SHS-laboratory, Almaty-Kazakhstan ² ; Institute of Combustion Problems, Almaty-Kazakhstan ³ ; University of Texas at Brownsville Physics and Astronomy, Brownsville-United States ⁴ |
| 16:50 - 17:10 Abstract: 1167 | INVESTIGATION OF Mo-Ni-B TERNARY ALLOYS FOR PRODUCTION OF BORIDE-BASED CERMETS BY SHS METHOD Bora Derin ¹ , <i>S. R. Moghaddam</i> ¹ , Onuralp Yucel ¹ , S. Sonmez ¹ , M. Bugdayci ¹ , M. Sezen ² , F. Bakan ² , Vladimir Sanin ³ , Dmitrii Andreev ³ Istanbul Technical University, Metallurgical and Materials Eng. Dept., Istanbul-Turkey ¹ ; Sabanci University, Nanotechnology Research and Application Center, Istanbul-Turkey ² ; Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka-Russia ³ |
| 17:10 - 18:30 | Poster Session III |
| 20:00 - 23:00 | GALA DINNER |

| Thursday, October 15 / 2015 | |
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| 09:00 - 10:00 | <p>Plenary Report IV <u>Alexander Rogachev</u>, M.I.Alymov, I.P.Borovinskaya Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences (ISMAN), 142432 acad. Osipyana str., 8, Chernogolovka Moscow region, Russia CARRYING ON MERZHANOV TRADITIONS: NEW ACHIEVEMENTS ON SHS IN ISMAN Session Chairman: Paola Bassani</p> |
| 10:00 - 10:20 | Coffee Break |
| Session IX | Session Chairman: Paola Bassani |
| 10:20 - 11:00 Abstract:1142 | <p>Keynote IX ENERGETIC COMBUSTION AND SHS: COMPARATIVE ANALYSIS OF THE ACHIEVEMENTS AND UNSOLVED PROBLEMS Giorgi Tavadze ¹, <u>Alexander Shteinberg</u> ² Ferdinand Tavadze Institute of Metallurgy and Materials Science, Tbilisi-Georgia ¹; N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow-Russia ²</p> |
| 11:00 - 11:20 Abstract:1048 | <p>INFLUENCE OF PHASE TRANSFORMATIONS ON THE SPIN COMBUSTION <u>Vadim Prokofyev</u> ¹, Victor Smolyakov ² Tomsk State University, Faculty of Physics and Engineering, Tomsk-Russia ¹; Tomsk Scientific Center, Department of Structural Macrokinetics, Tomsk-Russia ²</p> |
| 11:20 - 11:40 Abstract:1139 | <p>IN-SITU TRANSMISSION ELECTRON MICROSCOPY AND ELECTRON DIFFRACTION INVESTIGATIONS OF SOLID-STATE REACTIONS IN Fe₃Si(111)/Si(111) FILMS <u>Sergey Zharkov</u> ¹, Roman Altunin ¹, Evgeny Moiseenko ¹, Sergey Varnakov ¹, Ivan Yakovlev ¹, Ivan Tarasov ¹, Sergey Ovchinnikov ¹ Kirensky Institute of Physics, Russian Academy of Sciences, Krasnoyarsk-Russia ¹</p> |
| 11:40 - 12:00 Abstract:1158 | <p>PRODUCTION OF ZrB₂-B₄C-ZrC COMPOSITE POWDER MIXTURES VIA SHS <u>Kağan Benzeşik</u> ¹, Mehmet Buğdaycı ¹, Onuralp Yücel ¹, Filiz Cinar Sahin ¹, Ahmet Turan ² Istanbul Technical University, Metallurgical and Materials Engineering, Istanbul-Turkey ¹; Yalova Uni. Chemical and Process Engineering, Yalova-Turkey ²</p> |
| 12:00 - 12:10 | CLOSING CEREMONY |
| 12:10 - 13:30 | Lunch |
| 13:30 - 17:30 | ANTALYA CITY TOUR |

Tuesday, October 13 / 2015

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| Session X | Session Chairman: Filiz Şahin |
| 10:20 - 10:50 Abstract No : 1062 | Keynote X SHS PRESSING ALUMINUM-CERAMIC SKELETON COMPOSITES ON THE BASE OF Ti₂AlC MAX PHASE <i>Aleksandr Amosov^{1,2}, Aleksandr Fedotov^{1,2}, Evgeniy Latukhin^{1,2}, Vladislav Novikov^{1,2}</i> ¹ Samara State Technical University, 244 Molodogvardeyskaya Str., Samara, 443100, Russia ² Samara State Aerospace University, 34 Moskovskoe Shosse, Samara, 443086, Russia |
| 10:50 - 11:10 Abstract No : 1007 | SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF MULTICOMPONENT CERAMICS BASED ON Zr-Si-Al-B. PECULIARITIES OF COMBUSTION AND STRUCTURE FORMATION <i>Yury Pogozhev¹, Artem Potanin¹, Evgeny Levashov¹, Ivan Yatsuk¹, Dmitry Kovalev², Nikolay Kochetov²</i> National University of Science and Technology "MISIS", Moscow-Russia ¹ , Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka-Russia ² |
| 11:10 - 11:30 Abstract No : 1149 | PRODUCTION OF ZIRCONIUM DIBORIDE POWDER BY SHS <i>Murat Alkan¹, Burcu Akkas², M. Seref Sönmez², Bora Derin², Onuralp Yücel²</i> MTA Mineral Research & Exploration Gen. Direct. Dept. of Mining Analysis and Tech. Ankara-Turkey ¹ Istanbul Technical University Metallurgical and Materials Eng. Dept. Istanbul-Turkey ² |
| 11:30 - 11:50 Abstract No : 1130 | SYNTHESIS, KINETICS AND MECHANICAL PROPERTIES OF Mn+1AX_n BY SHS AND SHS/PHIP <i>Guobing Ying¹, Xiaodong He², Shanyi Du²</i> Hohai University Department of Materials Science and Engineering Nanjing-China ¹ Harbin Institute of Technology Center for Composite Materials and Structures Harbin-China ² |
| 11:50 - 12:10 Abstract: 1165 | PROCESSING OF MAX PHASES WITH USE OF SHS TECHNIQUES - ACHIEVEMENTS, PROBLEMS AND PROSPECTS <i>Jerzy Lis¹</i> AGH UST Faculty of Materials Science and Ceramics Ceramics and Refractories Kraków-Poland ¹ |
| 12:10 - 13:30 | Lunch |
| Session XI | Session Chairman: Şeref Sönmez |
| 13:30 - 14:00 Abstract No : 1067 | Keynote XI AUTOWAVE CHEMICAL CONVERSION IN MULTICOMPONENT MIXTURES THERMITE TYPE WITH ACTIVE METALS <i>Vladimir Yuxhvid¹, Dmitrii Andreev¹, Vladimir Sanin¹</i> I Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka-Russia ¹ |
| 14:00 - 14:20 Abstract No : 1155 | A COMPARATIVE STUDY ABOUT PRODUCTION OF CHROMIUM CONTAINING IRON BASED ALLOYS FOR 3 DIFFERENT CONDITIONS BY METALLOTHERMIC PROCESS <i>Mehmet Bugdayci¹, Ahmet Turan², Murat Alkan³, Onuralp Yucel¹</i> İ.T.Ü. Metallurgical and Materials Eng. Istanbul-Turkey ¹ Yalova University Chemical and Process Engineer Yalova-Turkey ² MTA Metallurgy Ankara-Turkey ³ |
| 14:20 - 14:40 Abstract No :1070 | CENTRIFUGAL SHS METALLURGY OF CAST TiAL BASED ALLOYS AND APPROACHES TO IMPROVE STRUCTURE AND CHEMICAL COMPOSITION <i>Dmitrii Andreev¹, Vladimir Yuxhvid¹, Denis Ikornikov¹, Vladimir Sanin¹</i> Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka-Russia ¹ |
| 14:40 - 15:00 | Coffee Break |

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| Session XII | Session Chairman: Evgeny Levashov |
| 15:00 - 15:20 Abstract No :1166 | THERMOCHEMICAL CALCULATIONS OF SHS-PRODUCED NiTi SMA'S BY FACTSAGE Bora Derin ¹ , <u>Berk Keskin</u> ¹ , Meltem Sezen ² , Feray Bakan ² , Paola Bassani ³ Istanbul Technical University Metallurgical and Materials Eng. Dept. Istanbul-Turkey ¹ Sabanci University Nanotechnology Research and Application Center Istanbul-Turkey ² CNR-IENI National Research Council-Institute for Energetics and Interphases Milano-Italy ³ |
| 15:20 - 15:40 Abstract No :1120 | THERMODYNAMIC ANALYSIS FOR COMBUSTION SYNTHESIS OF AL₂O₃/ZrO₂ EUTECTIC MELT UNDER HIGH PRESSURE AND CRYSTALLIZATION MORPHOLOGY IN RAPID SOLIDIFICATION Yongting Zheng ¹ , Wei Ye ¹ , <u>Xiaodong He</u> ¹ , Yangyang Guo ¹ , Xiaonang Zhang ¹ Harbin Institute of Technology Center for Composite Materials and Structure Harbin-China ¹ |
| 15:40 - 16:00 Abstract No :1061 | FABRICATION OF COMPOSITE POWDERS BASED ON TITANIUM CARBIDE AND IRON BY SHS WITH REDUCING STAGE <u>Aleksandr Amosov</u> ¹ , Anatoliy Samboruk ^{1,2} , Igor Yatsenko ² , Vladimir Yatsenko ² ¹ Samara State Aerospace University, 34 Moskovskoe Shosse, Samara, 443086, Russia ² Samara State Technical University, 244 Molodogvardeyskaya Str., Samara, 443100, Russia |
| 16:00 - 16:20 Abstract No :1153 | ETI ELEKTROMETALURJI LOW CARBON FERROCHROME PRODUCING PROCESS Yahya Öcal ¹ , <u>A.Cüneyt Dönmezyürek</u> ² , Baran Yönter ³ , Alpaslan Durusan ⁴ Eti Elektrometallurgy Director Antalya-Turkey ¹ Elektrometallurgy Process Antalya-Turkey ² Elektrometallurgy Purchasing Antalya-Turkey ³ Elektrometallurgy Sales Antalya-Turkey ⁴ |
| 16:20 - 16:40 Abstract No:1039 | PRODUCTION OF ULTRA-HIGH TEMPERATURE CARBIDE (Ta,Zr)C BY SHS OF MECHANICALLY ACTIVATED MIXTURES <u>Evgeny Patsera</u> ¹ , Viktoriya Kurbatkina ¹ , Evgeny Levashov ¹ , Dmitriy Kovalev ² , Nikolay Kochetov ² National University of Science and Technology "MISIS", Moscow-Russia ¹ , Institute of Structural Macrokineics and Materials Science, Russian Academy of Science, Chernogolovka-Russia ² |
| 16:50 - 18:30 | Poster Session II |

Wednesday, October 14 / 2015

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| Session XIII | Session Chairman: Vladimir Yuhvid |
| 10:20 - 10:40 Abstract:1004 | SHOCK WAVE ASSISTED SHS PROCESS AND CONSOLIDATION OF Ta-Al -B₄C PRECURSORS <i>Akaki Peikrishvili</i> ¹ , Bagrat Godibadze ² , Vakhtang Peikrishvili ³ , Elguja Chagelishvili ² , Metab Tsiklauri ² Ferdinand Tavadze Institute of metallurgy and materials science & G.Tsulukidze Mining Institute Blasting Technologies Department. High-Tech Materials Laboratory. Tbilisi-Georgia ¹ G.Tsulukidze Mining Institute Blasting Technologies Department. High-Tech Materials Laboratory. Tbilisi-Georgia ² Ferdinand Tavadze Institute of metallurgy and materials science Laboratory of Self-propagating High Temperature Synthesis Problems Tbilisi-Georgia ³ |
| 10:40 - 11:00 Abstract:1123 | EFFECT OF ALUMINIUM ADDITION ON SHS SYNTHESIS OF Ti₂AlN POWDERS WITH USE OF INTERMETALLIC PRERSCURSORS Ti₃Al <i>Leszek Chlubny</i> ¹ , Jerzy Lis ¹ , Mirosław M. Bućko ¹ , Czesław Kapusta ² , Paulina Chachlowska ¹ , Katarzyna Chabior ¹ , Kaja Zieleńska ¹ AGH University of Science and Technology Faculty of Materials Science and Ceramics Kraków-Poland ¹ AGH University of Science and Technology Faculty of Physics and Applied Computer Science Kraków-Poland ² |
| 11:00 - 11:20 Abstract:1012 | CONVERSION OF MILL SCALE WASTE INTO VALUABLE IRON-CHROMIUM ALLOY USING ALUMINO-THERMIC AND ALUMINO-SILICO-THERMIC PROCESSES <i>Mamdouh Eissa</i> ¹ , Azza Ahmed ¹ , Mohamed Kamal El-Fawakhry ¹ , Rabab Abo-Shohba ² , Seham Shahein ² Central Metallurgical R & D Institute (CMRDI) Steel and Ferroalloys Department Cairo-Egypt ¹ Al-Azhar University Faculty of Science Cairo-Egypt ² |
| 11:20 - 11:40 Abstract:1164 | COMPOSITES IN THE ALUMINUM OXYNITRIDE - MeN (Me=Ti, Ta, Nb, Cr) SYSTEM PREPARED FROM SHS-DERIVED POWDERS Alan Wilmański ¹ , Jerzy Lis ¹ , <i>Mirosław M. Bućko</i> ¹ AGH-University of Science and Technology Faculty of Materials Science and Ceramics Krakow-Poland ¹ |
| 12:00 - 13:30 | Lunch |
| Session XIV | Session Chairman: Bora Derin |
| 13:30 - 13:50 Abstract:1144 | SYNTHESIS OF TUNGSTEN NANOPOWDERS: COMPARISON OF MILLING, SHS, MASHS AND MECHANO-CHEMICAL PROCESSES Sarah Dine ¹ , Sara Aïd ¹ , Karim Ouaras ¹ , Véronique Malard ² , Nathalie Herlin-Boime ³ , Michaël Odorico ² , Aurélie Habert ³ , Adèle Gerbil-Margueron ³ , Christian Grisolia ⁴ , Jacques Chêne ⁵ , Gregory Pieters ⁵ , Bernard Rousseau ⁵ , <i>Dominique Vrel</i> ¹ CNRS LSPM Villetaneuse-France ¹ CEA IBEB Bagnols-sur-Cèze-France ² CEA IRAMIS-NIMBE Gif-sur-Yvette-France ³ CEA IRFM Saint-Paul-lez-Durance-France ⁴ CEA Ibitec-S Gif-sur-Yvette-France ⁵ |
| 13:50 - 14:10 Abstract:1035 | COMBUSTION SYNTHESIS OF NANO-SIZED AMORPHOUS BORON POWDERS <i>Weimin Wang</i> ¹ Wuhan university of Technology State Key Lab Wuhan-China ¹ |
| 14:10 - 14:30 Abstract:1141 | PARAMETRIC STUDIES ON TITANIUM-STAINLESS STEEL EXPLOSIVE CLADDING SUBJECTED TO UNI-LOADING RATIO <i>Saravanan S</i> ¹ Annamalai University Mechanical Engineering Annamalai Nagar-India ¹ |

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| 14:30 - 14:50 Abstract:1010 | MULTI TEMPERATURE MODELING OF ELECTRICAL FIELD GENERATION DURING COMBUSTION SYNTHESIS OF ZnS Andrey Markov ¹ , Igor Filimonov ² , A Poletaev ² , <i>Karen Martirosyan</i> ³ Institute for Problems in Mechanics Mechanics Moscow-Russia ¹ ISMAN Combustion synthesis Chernogolovka-Russia ² University of Texas at Brownsville Physics Brownsville-United States ³ |
| 14:50 - 15:00 | Coffee Break |
| Session XV | Session Chairman: Alexander Steinberg |
| 15:00 - 15:20 Abstract:1027 | SOLUTION COMBUSTION SYNTHESIS OF La- AND Cr- DOPED SrTiO₃ PHOTOCATALYSTS FOR SUSTAINABLE AIR POLLUTANT REMOVAL Ivan Davila ¹ , Vladimir Yefremov ² , <i>Karen Martirosyan</i> ¹ University of Texas at Brownsville Physics Brownsville-United States ¹ Institute of Combustion Problems Advanced Materials Almaty-Kazakhstan ² |
| 15:20 - 15:40 Abstract:1005 | SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS OF RARE-EARTH OXIDE NANOPOWDERS FOR TRANSPARENT CERAMICS Stanislav Balabanov ¹ , Evgeny Gavrishchuk ¹ , Oksana Klyusik ² , <i>Dmitry Permin</i> ¹ G.G. Devyatykh Institute of Chemistry of High-Purity Substances RAS laboratory of high-pure optical materials Nizhny Novgorod-Russia ¹ Nizhny Novgorod State University chemical department Nizhny Novgorod-Russia ² |
| 15:40 - 16:00 Abstract:1013 | RARE EARTH IRON NANOSTRUCTURED GARNETS: COMBUSTION SYNTHESIS AND MAGNETOELECTRIC PROPERTIES <i>Almaz Saukhimov</i> ¹ , Gabit Almanov ¹ , Chamath Dannangoda ² , Mkhitar Hobosyan ² , Serik Kumekov ¹ , Karen Martirosyan ² KazNTU Physics Almaty-Kazakhstan ¹ UTB Physics Brownsville-United States ² |
| 16:00 - 16:20 Abstract:1022 | COMBUSTION SYNTHESIS OF NANO STRUCTURED CATALYTIC ACTIVATORS FOR REDUCTION OF SOOT ACTIVATION ENERGY <i>Zhimart Ualiev</i> ¹ , Karen Martirosyan ² Institute of Combustion Problems Physics Almaty-Kazakhstan ¹ University of Texas at Brownsville Physics Brownsville-United States ² |
| 16:20 - 16:40 Abstract:1021 | Abstract No : 1021 PLASTIC DEFORMATION AS MECHANISM FOR RAPID SINTERING OF NANO CERAMICS WITHOUT GRAIN GROWTH BASED SHS REACTION <i>Zhengyi Fu</i> ¹ , Weimin Wang ¹ , Hao Wang ¹ , Yucheng Wang ¹ , Jinyong Zhang ¹ Wuhan University of Technology State Key Lab of Advanced Technology for Materials Synthesis and Processing Wuhan-China ¹ |
| 17:10 - 18:30 | Poster Session III |
| 20:00 - 23:00 | GALA DINNER |

SHS 2015 POSTER SESSIONS

Monday, October 12 / 2015 - 16:30-18:00

Tuesday, October 13 / 2015 - 16:50-18:30

Wednesday, October 14 / 2015 - 17:10-18:30

1.Theory of SHS: combustion, structure formation, methods of modeling.

Abstract No : 1003

GASLESS COMBUSTION OF THERMALLY COUPLED LAYERS

*Vadim Prokofyev*¹, Victor Smolyakov¹

Tomsk Scientific Center, Siberian Branch Russian Academy of Sciences Tomsk-Russia¹

Abstract No : 1033

SPECIALTY PRESS-MOLD PROVIDING CONTROL OF COOLING AND CRYSTALLIZATION OF SHS PRODUCT: DESIGN AND CAPABILITIES

*David Sakhvadze*¹, Alexander Shteinberg², Gigo Jandieri¹

LEPL Ferdinand Tavadze Institute of Metallurgy and Materials Science 8 laboratory Tbilisi-Georgia¹ ALOFT, Chem. Eng. and Mater. Sci. Consulting Inc. ALOFT, Chem. Eng. and Mater. Sci. Consulting Inc Berkeley-United States²

Abstract No : 1060

STRUCTURE OF SHS PRODUCTS: NUMERICAL SIMULATION

*Serguey Konovalikhin*¹, Vasiliy Ponomarev¹, Aleksandr Sytshev¹, Serguey Vadchenko², Dmitriy Kovalev¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1088

MATHEMATICAL SIMULATION OF SOLID-PHASE PLUNGER EXTRUSION WITH DOUBLE COMPRESSION OF COMPOSITE MATERIALS

*Lyubov Stelmakh*¹, Alexander Stolin¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1097

SYNTHESIS AND REACTION MECHANISM OF Ti₂SnC FROM Ti/Sn/C POWDER BY SELF-PROPAGATION HIGH-TEMPERATURE TECHNIQUE

*Chuncheng Zhu*¹, Hexin Sun¹, Hong Lin¹

Harbin Normal University Department of chemistry Harbin-China¹

Abstract No : 1117

COMBUSTION OF Ti - B MIXTURES UNDER QUASI-STATIC PRESSURE

*Valery Barinov*¹, Vladimir Shcherbakov¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1156

A STUDY ABOUT THERMOCHEMICAL SIMULATION OF ZrB₂-B₄C-ZrC SYSTEM

*Mesut Yilmazoglu*¹, Mehmet Bugdayci², Candemir Uysal², Kagan Benzesik², Onuralp Yucel²

Yalova University Chemical and Process Engineering Yalova-Turkey¹ İ.T.Ü. Metallurgy and Materials Engineer Istanbul-Turkey²

2. Mechanisms and kinetics of SHS processes.

Abstract No : 1014

IN SITU SYNCHROTRON INVESTIGATION IN THE Ti-C-Ni AND Ti-C-NiO-Al SYSTEMS

*Hafida Boutefnouchet*¹, Caroline Curfs²

University of Annaba Metallurgy Annaba-Algeria¹ ESRF ID31 Grenoble-France²

Abstract No : 1025

COMBUSTION OF MARTIAN REGOLITH SIMULANTS WITH MAGNESIUM

Armando Delgado¹, Sergio Cordova¹, *Evgeny Shafirovich*¹

The University of Texas at El Paso Mechanical Engineering El Paso-United States¹

Abstract No : 1034

UNSTABLE GAS-FREE COMBUSTION OF DISC-SHAPED SYSTEMS

*Yuriy Maksimov*¹, Oleg Lapshin¹

Tomsk Scientific Center, Siberian Branch Russian Academy of Sciences Tomsk-Russia¹

Abstract No : 1051

STUDY OF FERROSILICOALUMINIUM NITRIDING

*Konstantin Bolgaru*¹, Ludmila Chukhlomina¹, Yuriy Maksimov¹

Tomsk Scientific Center, Siberian Branch Russian Academy of Sciences Tomsk-Russia¹

Abstract No : 1092

THERMOCHEMICAL CONVERSION OF IRON COMPOUNDS IN A WAVE OF FLAMELESS COMBUSTION

Yuriy Mikhailov¹, Victor Aleshin¹, Alexandra Kolesnikova¹, Larisa Zhemchugova¹, *Dmitry Kovalev*²

IPCP Laboratory of energy polymer systems Chernogolovka-Russia¹ Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia²

Abstract No : 1093

GAS EVOLUTION DURING SHS OF TiC

Alexandr Shchukin¹, *Sergey Vadchenko*¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1098

ACOUSTIC EMISSION METHOD APPLICATION FOR SHS PROCESSES STUDIES

Anatoly Kuznetsov¹, Sergey Kunavin¹, Pavel Berezhko¹, Vyacheslav Yaroshenko¹, *Maxim Tsarev*¹, Sergey Mityashin¹, Evgeny Zhilkin¹

Russian Federal Nuclear Centre - All-Russia Research Institute of Experimental Physics Rosatom Sarov, Nizhny Novgorod region-Russia¹

Abstract No : 1121

INVESTIGATION OF PHASE FORMATION DURING SHS OF MATERIALS WITH FLUORINE PHLOGOPITE MATRIX

*Ivan Kovalev*¹, Vazgen Loryan², Alexander Kachin², Inna Borovinskaya¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1161

COMBUSTION SYNTHESIS OF METAL SULFIDE CERMETS: COMBUSTION CHARACTERISTICS, AND MECHANICAL PROPERTIES

*Atefeh Nabavi*¹, Samuel Goroshin¹, David Frost¹, Francois Barthelat¹

McGill University Mechanical Eng Montreal-Canada¹

Abstract No : 1016

THE EFFECT OF PRELIMINARY MECHANICAL ACTIVATION ON STRUCTURAL CHARACTERISTICS OF THE REACTION MIXTURE Ti + Ni

*Olga Shkoda*¹, Oleg Lapshin¹

Tomsk Science Centre Structural Macrokinetics Tomsk-Russia¹

Abstract No : 1046

THE INFLUENCE OF 'L - S' ENVIRONMENT SYSTEM ON PHASE FORMATION DURING COMBUSTION OF THE SHS SYSTEM 'W - Ti - N'

Larisa Raskolenko¹, *Olga Shkoda*¹

Tomsk Science Centre Structural Macrokinetics Tomsk-Russia¹

3.SHS of powder materials (micron, submicron- and nano scale)

Abstract No : 1037

COMBUSTION SYNTHESIS AND DIELECTRIC PROPERTIES OF THE DOPED BARIUM TITANATE

*Aleksandr Khort*¹, Evgeniya Dyatlova¹, Kirill Podbolotov¹

Belarusian State Technological University Glass and Ceramic Technologies Minsk-Belarus¹

Abstract No : 1056

PHASE EVOLUTION OF YAG POWDERS OBTAINED BY GEL COMBUSTION COMBINED WITH FIELD-ASSISTED RAPID SYNTHESIS TECHNIQUE

Rongrong Wang¹, *Yucheng Wang*¹

Wuhan University of Technology State Key Lab of Advanced Technology for Materials Synthesis and Processing Wuhan-China¹

Abstract No : 1058

DEVICE OF MOLTEN GRANULATION FOR OBTAINING THE POWDER MATERIALS FOR SHS

*David Sakhvadze*¹, Ivan Gorbenko¹, Teimuraz Tsirekidze¹, Gigo Jandieri¹, Alexander Shteinberg²

LEPL Ferdinand Tavadze Institute of Metallurgy and Materials Science 8 laboratory Tbilisi-Georgia¹ ALOFT, Chem. Eng. and Mater. Sci. Consulting Inc., Berkeley ALOFT, Chem. Eng. and Mater. Sci. Consulting Inc., Berkeley Tbilisi-United States²

Abstract No : 1059

SOLUTION COMBUSTION SYNTHESIS OF LUMINESCENT PIGMENTS ON THE BASES OF Co-Al-Mg-Ba-O, Co-Al-B-O, Co-Ba-B-O FOR INK APPLICATIONS

*EIRINI PAVLOU*¹, GALINA Xanthopoulou², MARIOS Tsigonias³, GEORGE Vekinis²

Technological Educational Institute of Athens/NCSR DEMOKRITOS Department of graphic arts technology/Institute of nanoscience and nanotechnology ATHENS-Greece¹ NCSR DEMOKRITOS Institute of nanoscience and nanotechnology ATHENS-Greece² Technological Educational Institute of Athens Department of graphic arts technology ATHENS-Greece³

Abstract No : 1063

HYDROTHERMAL SYNTHESIS OF ONE DIMENSIONAL TiO₂ POWDERS

*Nursev Bilgin*¹, Jongee Park², Abdullah Ozturk¹

METU Metallurgical and Materials Engineering Ankara-Turkey¹ Atilim University Metallurgical and Materials Engineering Ankara-Turkey²

Abstract No : 1071

Ni-Al INTERMETALLICS DISPERSION-STRENGTHENED WITH CR2O3: SYNTHESIS AND CHARACTERIZATION

A.E. Sytshev, O.D. Boyarchenko, S.G. Vadchenko, A.S. Shchukin, and I.D. Kovalev

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka-Russia

Abstract No : 1081

PHYSICO-CHEMICAL PROPERTIES OF COMBUSTION SYNTHESIS CATALYSTS AND THEIR ACTIVITY IN LIQUID PHASE HYDROGENATION

*Olga Thoda*¹, Galina Xanthopoulou², Alexander Chronesos³, George Vekinis¹

NCSR "Demokritos" INN Athens-Greece¹ NCSR "Demokritos" INN Athens-Greece² Coventry University Faculty of Engineering and Computing Coventry-United Kingdom³

Abstract No : 1082

INFLUENCE OF SCS CONDITIONS ON PROPERTIES OF NANOSTRUCTURED METALS AND ALLOYS

Dimitris Tzavellas¹, *Galina Xanthopoulou*², George Vekinis³

NTUA School of Chemical Engineering Athens-Greece¹ NCSR "Demokritos" INN Athens-Greece² NCSR "Demokritos" INN Athens-Greece³

Abstract No : 1107

EVALUATION OF SHS POWDER COMPOSITION UNIFORMITY USING SPECTRAL ANALYSIS METHODS

Alexey Postnikov¹, Valery Mokrushin¹, *Andrey Potekhin*¹, Irina Tsareva¹, Olga Yunchina¹, Maxim Tsarev¹, Pavel Berezhko¹

Russian Federal Nuclear Centre - All-Russia Research Institute of Experimental Physics Rosatom Sarov, Nizhny Novgorod region-Russia¹

Abstract No : 1118

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF TITANIUM NITRIDE OVER AMMONIUM CHLORIDE

*Vladimir Zakorzhevsky*¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1129

COBALT CATALYSTS SYNTHESISED BY SOLUTION COMBUSTION FOR DRY REFORMING OF METHANE

Kostas Karanasios¹, *Galina Xanthopoulou*¹, George Vekinis¹

NCSR "Demokritos" INN Athens-Greece¹

Abstract No : 1015

SYNTHESIS OF SINGLE-PHASE NIOBIUM SILICIDE BY SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS WITH USING PRELIMINARY MECHANICAL ACTIVATION

*Olga Shkoda*¹, Olga Terekhova¹

Tomsk Science Centre Structural Macrokinetics Tomsk-Russia¹

4. SHS of bulk materials (advanced functional and constructional materials, including biomaterials, intermetallic alloys, composites, foams etc.)

Abstract No : 1011

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF BIOCERAMIC MATERIALS IN THE Ti-C-Ca₃(PO₄)₂ SYSTEM

*Artem Potanin*¹, Evgeniy Levashov¹, Yuriy Pogozhev¹, Nataliya Shvindina¹, Dmitriy Kovalev²

National University of Science and Technology "MISIS", Moscow-Russia¹; Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia²

Abstract No : 1017

SYNTHESIS OF MATERIALS IN Ti-Cr-C-Me SYSTEM

*George Oniashvili*¹, Zurab Aslamazashvili¹, Garegin Zakharov¹, Giorgi Tavadze², George Mikaberidze¹

F.Tavadaze Institute of Metallurgy and Materials Science Laboratory of SHS problems Tbilisi-Georgia¹ F.Tavadaze Institute of Metallurgy and Materials Science Director Tbilisi-Georgia²

Abstract No : 1018

SYNTHESIS OF GRADIENT MATERIALS ON THE BASIS OF INTERMETALLICS

*Giorgi Tavadze*¹, George Oniashvili², Zurab Aslamazashvili², Garegin Zakharov², Mikheil Chikhradze²

F.Tavadaze Institute of Metallurgy and Materials Science Director Tbilisi-Georgia¹ F.Tavadaze Institute of Metallurgy and Materials Science Laboratory of SHS problems Tbilisi-Georgia²

Abstract No : 1019

TECHNOLOGY FOR SYNTHESIS OF MULTIFUNCTIONAL CERAMIC MATERIALS

*Zurab Aslamazashvili*¹, George Oniashvili¹, Garegin Zakharov¹, Giorgi Tavadze¹, Gulnara Urushadze¹

F.Tavadaze Institute of Metallurgy and Materials Science Laboratory of SHS problems Tbilisi-Georgia¹

Abstract No : 1020

SHS-HEAT INSULATORS BASED ON THE MODIFIED TECHNOGENIC RAW MATERIALS

Zulhair Mansurov¹, Nina Mofa², *Bakhtiyar Sadykov*², Zhandarbek Sabayev²

The Institute of Combustion Problems The Institute of Combustion Problems Almaty-Kazakhstan¹ The Institute of Combustion Problems Laboratory of mechanochemical processes Almaty-Kazakhstan²

Abstract No : 1026

FABRICATION OF MAGNESIUM SILICIDE VIA MECHANICALLY ACTIVATED SHS FOLLOWED BY SHOCKWAVE CONSOLIDATION

Armando Delgado¹, Sergio Cordova¹, David Nemir², *Evgeny Shafirovich*¹

The University of Texas at El Paso Mechanical Engineering El Paso-United States¹ TXL Group Inc. N/A El Paso-United States²

Abstract No : 1032

EVALUATION OF COMBUSTION TEMPERATURE AND COMBUSTION SPEED OF THE PROCESS OF SH-SYNTHESIS OF TITANIUM OXIDE BRONZE

*Margarita Kotvanova*¹, Nadezhda Blinova¹, Yuri Gulyaev², Alexey Dolmatov², Svetlana Pavlova¹

Yugra State University Institute of Nature Khanty-Mansiysk-Russia¹ Yugra State University Polytechnic Institute Khanty-Mansiysk-Russia²

Abstract No : 1042

STRUCTURAL CHARACTERIZATION AND SUPERCONDUCTING PROPERTIES OF Nb₃Al BY COMBUSTION SYNTHESIS

*Ali HAFS*¹, Abdel AZIZ Benaldijia², Badis BENDJEMIL³

University of El Tarf DEPARTEMENT SCIENCE DE LA MATIERE B.P. 73, El Tarf, 36000 Algeria-Algeria¹ University of Annaba mecanique B.P. 12, Annaba, 23000 Algeria-Algeria² University of Guelma MECANIQUE B.P. 401, Guelma, 24000 Algeria-Algeria³

Abstract No : 1043

FABRICATION OF Cu-20At.% Sb SEMICONDUCTING PROPERTIES BY COMBUSTIONSYNTHESIS METHOD

*Ali HAFS*¹, Abdel AZIZ Benaldijia², Badis BENDJEMIL³

University of El Tarf DEPARTEMENT SCIENCE DE LA MATIERE B.P. 73, El Tarf, 36000 Algeria-Algeria¹ University of Annaba mecanique B.P. 12, Annaba, 23000 Algeria-Algeria² University of Guelma MECANIQUE B.P. 401, Guelma, 24000 Algeria-Algeria³

Abstract No : 1044

MICROSTRUCTURE EVOLUTION AND MANGNETIQUE PROPRIETIES OF NANOCRYSTALLINE Fe₆₀Cu₃₀Al₁₀ PREPARED BY COMBUSTION PROCESSES

*Ali HAFS*¹, Abdel AZIZ Benaldijia², Badis BENDJEMIL³

University of El Tarf DEPARTEMENT SCIENCE DE LA MATIERE B.P. 73, El Tarf, 36000 Algeria-Algeria¹ University of Annaba mecanique B.P. 12, Annaba, 23000 Algeria-Algeria² University of Guelma MECANIQUE B.P. 401, Guelma, 24000 Algeria-Algeria³

Abstract No : 1053

ULTRA-FAST DENSIFICATION OF BORON CARBIDE CERAMICS BASED ON SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

*Fan Zhang*¹, Zhengyi Fu¹

Wuhan University of Technology State Key Lab of Advanced Technology for Materials Synthesis and Processing Wuhan-China¹

Abstract No : 1065

SHS-PRODUCED TRANSITION METAL SILICIDES: SYNTHESIS AND SINTERING

Vladimir Gorshkov¹, Pavel Miloserdov¹, *Dmitrii Andreev*¹

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia¹

Abstract No : 1068

STRUCTURAL HEREDITY OF ALLOYS OBTAINED BY CENTRIFUGAL SHS: INFLUENCE OF REMELTING TEMPERATURE

Vitalii Sanin¹, Yurii Anikin¹, *Vladimir Yukhvid*², Michael Filonov¹

National University of Science and Technology "MISIS", Moscow-Russia¹; Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka- Russia²

Abstract No : 1072

SHS OF COMPOSITE MATERIALS BASED ON Ti-Co

Sytshev A.E., Kamynina O.K., Umarov L.M., Schukin A.S., Zhidkov M.V

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Abstract No : 1077

SHS OF POLYMETALLIC CATALYSTS WITH MULTIFUNCTIONAL PROPERTIES

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Abstract No : 1084

NOVEL SHS INDUSTRIAL REFRACTORIES BASED ON CHROMITE AND FERROUS WASTES

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Abstract No : 1094

IMPROVEMENT IN THE DURABILITY OF ALUMINIDE INTERMETALLIC COATINGS BY MICROWAVE-ASSISTED COMBUSTION SYNTHESIS STRATEGIES

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Abstract No : 1095

SHS OF CAST NiCrCoFeMnAlX NANO-STRUCTURED HIGH ENTROPY ALLOYS AND COATINGS OF THEM

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Abstract No : 1100

STRUCTURE FORMATION IN THIN LAYERS OF BALLS AT AXIAL COMPACTION. I. CYLINDRICAL MATRIX

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Abstract No : 1102

STRUCTURE FORMATION IN THIN LAYERS OF BALLS AT AXIAL COMPACTION. II. MATRIX OF SQUARE SECTION

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Abstract No : 1104

STRUCTURE FORMATION IN THIN LAYER OF BALLS AT AXIAL COMPACTION. III. MATRIX OF HEX-TYPE CROSS SECTION

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Abstract No : 1105

SHS OF COMPOSITE MATERIALS BASED ON Ti+2B MIXTURE CONTAINING TITANIUM PARTICLES OF SPHERICAL AND DENDRITE SHAPE

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Abstract No : 1106

SHS OF Ti-Al-B SYSTEM FROM Ti+2B MIXTURE WITH ALUMINUM-CLAD TITANIUM SPHERICAL PARTICLES

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Abstract No : 1108

MECHANICALLY ACTIVATED SHS OF TARGET MATERIALS IN Ti-Al-C AND Si-B-C SYSTEMS FOR PVD OF TRIBOLOGICAL COATINGS

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Abstract No : 1112

SHS SURFACING WITH THERMITE NiO-Al MIXTURE

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Abstract No : 1113

SYNTHESIS OF CAST OXIDE MATERIALS IN THE Al-O-N SYSTEM

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Abstract No : 1119

FORMATION OF ULTRAFINE GRAIN STRUCTURE IN THE SHS-PRODUCED CAST Co-Cr-Mo-ALLOY BY PLASTIC DEFORMATION

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Abstract No : 1132

INFLUENCE OF MECHANOCHEMICAL TREATMENT OF Ni+Al POWDER MIXTURES ON PHYSICAL AND CATALYTIC PROPERTIES OF COATINGS PRODUCED BY "CAFSY" METHOD

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Abstract No : 1133

STUDY OF CATALYTIC ACTIVITY OF COATINGS PRODUCED BY CAFSY METHOD IN DRY REFORMING OF METHANE

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Abstract No : 1146

EFFECT OF MECHANICAL ACTIVATION OF Ta-Zr-C MIXTURES ON PHASE COMPOSITION OF SHS-PRODUCTS

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Abstract No : 1150

OPTIMIZATION OF PARAMETERS OF FERROMOLYBDENUM PRODUCTION VIA METALOTHERMIC REDUCTION PROCESS

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Abstract No : 1151

PRODUCTION AND IMPROVEMENT OF THE Ni-Cr-B ALLOYS VIA SHS

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Abstract No: 1169

DIFFERENT IGNITION STRATEGIES IN THE COMBUSTION SYNTHESIS OF Ni-Ti INTERMETALLICS

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Abstract No: 1170

INFLUENCE OF LASER PARAMETERS ON POROUS NiTiNi SHAPE MEMORY ALLOY PRODUCED BY SHS

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Abstract No: 1171

FORMATION OF (Ti,Zr)B₂ SOLID SOLUTIONS BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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5. Boron related SHS materials

Abstract No : 1023

MECHANICALLY ACTIVATED SHS OF MOLYBDENUM BOROSILICIDE BASED MATERIALS FOR ULTRAHIGH-TEMPERATURE STRUCTURAL APPLICATIONS

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Abstract No : 1028

OBTAINING OF BORON CONTAINING MATERIALS BY SHS

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Science Laboratory of Pressure Processing of Metal Materials Tbilisi-Georgia³

Abstract No : 1031

SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS OF COMPOSITES ON THE BASIS OF ZrB₂ - Al₂O₃

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Abstract No : 1045

EFFECTS OF BORONIZING COMPOSITION ON AISI 8620 STEEL CAM SHAFT

Saban Gezer¹, Mehmet Kul¹, Kürşad Oğuz Oskay¹, Bahadır Karaca², Fatih Özyayın³, Oğuz Han Bolat¹, Ahmet Emre
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Abstract No : 1047

EFFECTS OF BORONIZING COMPOSITION ON AISI 1045 STEEL CAM SHAFT

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Abstract No : 1049

EFFECTS OF BORONIZING COMPOSITION ON GGG 60 CAM SHAFT

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Abstract No : 1090

INFLUENCE OF SYNTHESIS CONDITIONS ON BORON CARBIDE SHS

Ivan Kovalev¹, Vasiliy Ponomarev¹, Sergey Konovalikhin¹, Dmitriy Kovalev¹, Vladimir Vershinnikov¹
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Abstract No : 1114

CAST Mo₂NiB₂ AND Mo₂FeB₂ METAL-MATRIX COMPOSITES BY COMBINED CENTRIFUGAL CASTING-SHS PROCESS

Denis Ikornikov¹, Vladimir Sanin¹, Vladimir Yukhvid¹, Dmitrii Andreev¹, Onuralp Yucel², Bora Derin²
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Abstract No : 1145

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF BORON SUBPHOSPHIDE B₁₂P₂

Vladimir Mukhanov¹, Petr Sokolov¹, Ovidiu Brinza¹, Dominique Vrel¹, Vladimir Solozhenko¹
CNRS LSPM Villetaneuse-France¹

6. Novel approaches and SHS related processes (SHS and shock waves, sol-gel auto-combustion synthesis, SHS in nano-systems etc.)

Abstract No : 1024

COMBUSTIBLE MIXTURES FOR HYDROGEN AND IODINE GENERATION BASED ON MECHANICALLY ALLOYED REACTIVE MATERIALS

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Abstract No : 1052

FEATURES OF SYNTHESIS OF MATERIALS DURING ALUMINOTHERMIC PROCESS IN CONDITIONS OF ROTATION

Georgy Ksandopulo¹, Anna Baideldinova¹, Ludmila Mukhina¹, *Elena Ponomareva*¹, Bagzhan Nurahmetov²

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Abstract No : 1054

INFLUENCE OF DISPERSITY ON EXPLOSIVE SOLID-STATE SYNTHESIS IN THE AI-S SYSTEM

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Abstract No : 1075

CATALYSTS PRODUCED BY SOLUTION COMBUSTION SYNTHESIS FOR LOW TEMPERATURE CO OXIDATION

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Abstract No : 1101

THE INFLUENCE OF ELECTRON IRRADIATION ON THE OXIDATION AND BURNING OF METAL NANOPOWDERS

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Abstract No : 1124

NANOSTRUCTURED MATERIALS FROM IMMISIBLE METALS BY A COMBINATION OF HIGH-ENERGY BALL MILLING AND SPARK PLASMA SINTERING

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Abstract No : 1125

HIGH ENERGY BALL MILLING AND SPARK PLASMA SINTERING OF NANOSTRUCTURED W-Cu-Cr COMPOSITE AND ITS CHARACTERIZATION

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Abstract No : 1126

A NOVEL PREPARATION TECHNIQUE OF METAL AND METAL OXIDE MICROSPHERES BY SOLUTION COMBUSTION IN ULTRASOUNDIC - GENERATED AQUEOUS AEROSOLS

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Abstract No : 1128

THE SYNTHESIS OF NANOSIZED COBALT AND CERIUM OXIDES BY «SOLUTION COMBUSTION»

Daniyar Khusainov¹, Solgen Kim¹, Gaukhar Smagulova¹, *Zulhair Mansurov*¹

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Abstract No : 1136

SYNTHESIS OF NANOCRYSTALLINE ALPHA-HEMATITE (α -Fe₂O₃) MICROSPHERES BY SOLUTION COMBUSTION IN ULTRASOUNDIC - GENERATED AQUEOUS AEROSOLS

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Abstract No : 1137

ONE-STEP SYNTHESIS OF NICKEL-BASED CATALYSTS COMPOSITIONS BY SOLUTION COMBUSTION METHOD IN ULTRASOUNDIC - GENERATED AQUEOUS AEROSOLS

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Abstract No : 1160

OBTAINING CERMET MATERIALS IN Ti-Si-C SYSTEM

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7. Application and Industrialization

Abstract No : 1030

PLASMA SPRAY OF METAL AND CERMET COATINGS FROM Ni-Al ALLOYS PREPARED BY SHS PROCESS

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Abstract No : 1064

THE METALLURGICAL SHS PROCESS

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Abstract No : 1083

SOLUTION COMBUSTION SYNTHESIS OF LUMINESCENT PIGMENTS BASED ON THE SYSTEMS Co-Al-Mg-Ba-O, Co-Al-B-O AND Co-Ba-B-O FOR INK APPLICATIONS

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Abstract No : 1131

REFRACTORY AND HEAT INSULATING SHS-MATERIALS

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Abstract No : 1163

ANTIMONY PRODUCTION BY USING NIEDERSCHLAG PROCESS

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PLENARY LECTURES

Plenary Report I

Alexander S. Mukasyan

RECENT ADVANCES IN COMBUSTION SYNTHESIS OF MATERIALS (OVERVIEW)



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The review involves the analysis of recent (2013-2015) achievements in the field of combustion synthesis (CS) of advanced materials, including self-propagating high-temperature synthesis (SHS). The topics comprise the traditional directions, such as SHS of powders and bulk materials, as well as novel routes, containing implementation of CS concept for 3D-fabrication, spark plasma sintering and high energy density materials. Special attention is paid for the CS in nanostructured systems, encompassing the mechanically induced composite particles and reactive nano-foils. Accomplishments in solution combustion synthesis are discussed, focusing on such applications as catalysis, solar-energy systems, super-capacitors and etc. Using of CS approaches for fabrication of 2D one atomic layer crystals, embracing graphene, is also considered. Finally, based on the above analysis and taking into account state-of-art venues in material science, promising future directions in the field of CS are outlined.

Plenary Report II

Giacomo Cao

ENVIRONMENTAL AND SPACE APPLICATIONS OF SHS



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The major achievements obtained in the field of self-propagating reactions when exploited for environmental protection and space applications are taken into account. In particular, the fixation and consolidation of high level radioactive wastes, the treating and recycling of a highly toxic solid waste from electrolytic zinc plants, the recycling of silicon sludge and aluminum dross produced by semiconductor industries and aluminum foundries, respectively, the degradation of chlorinated aromatics and the treatment of wastes containing asbestos are addressed. In addition, low-gravity experiments performed by various research groups on several self-propagating reactions systems are discussed. Such experiments are able to permit the general mechanism of combustion and structure formation to be revealed without the disturbing effect of gravity. Future scientific and technological directions related to these promising fields of scientific and technological applications are also foreseen.

Plenary Report III

Florian Kongoli^{1,2,3}, Edward Z. O'Brien³, Ian McBow³

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) AND SUSTAINABLE DEVELOPMENT



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Self-propagating high-temperature synthesis (SHS) are used to produce inorganic compounds with specific properties such as powders, metallic alloys and ceramics with high purity, corrosion-resistance at high-temperature and/or super-hardness. The key of this process is the use of exothermic energy at high temperatures and this establish a direct relation of this processes with sustainability since one of the most important dimensions of sustainability is the efficient use of energy.

However, some prefabricated misconceptions and confusions exist in evaluating this technology and in general high temperature processes including extraction of metals and materials in terms of sustainability. These processes and extraction and processing of metals in general are perceived by the public as old and not sustainable while waste processing technologies as still dangerous and not sustainable. Misconceptions also widely exist in the society about the role that engineers and scientists dealing with these processes play on the development of the society. This paper will give an overview of various aspects of sustainability related to SHS as well as extraction and processing technologies concentrating on the primary important role that scientists and engineers play in the environmentally balanced development of the world and on the need for better and broader recognitions at the level of the society of scientists and engineers as one of the best ways to assure a sustainable development.

Plenary Report IV

Igor Smurov, M. Doubenskaia

SELECTIVE LASER MELTING AND DIRECT METAL DEPOSITION: FROM PROCESS FUNDAMENTALS TOWARDS ADVANCED PRODUCTS



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Selective Laser Melting (SLM) is a powder-based and laser assisted additive manufacturing technology capable to produce parts layer-by-layer from a 3D CAD model. Nowadays SLM is used in various industrial domains including aerospace, automotive, electronic, chemical and biomedical, as well as other high-tech areas. Industrial interest is focused on manufacturing of fully functional objects with high geometrical complexity and excellent mechanical properties. Properties of the manufactured parts depend strongly on each single laser-melted track and each single layer, as well as the strength of the connections between them.

SLM comprises the following physical phenomena: absorption and scattering of laser radiation, heat transfer, phase transformation, fluid flow within the molten pool caused by surface-tension gradient, evaporation and emission of material, and chemical reactions. The SLM process is also defined by a large number of parameters including the processing parameters such as laser power, scanning speed, scan line spacing (hatch distance), thickness of layer, scanning strategy, working atmosphere, temperature of powder bed, and material-based input parameters. The nature of the effective heat source produced by laser irradiation of a powder layer considerably differs from the case of laser irradiation of an opaque metallic body. During laser treatment, only a part of radiation is absorbed by the particles at the outer surface of the loose powder layer. The rest of the radiation penetrates through the pores containing gases and interacts with the underlying particles. Further, the heat distribution into the powder layer is done by the usual heat transfer mechanisms. The essential operation at SLM is the laser beam scanning over the surface of a thin powder layer previously deposited on a substrate or previously remelted layer, which is a substrate for the following layer. Each cross-section (layer) of the part is sequentially filled with elongated tracks of melted powder. Line-by-line, a laser beam melts the material along a row of powder particles, thereby forming a molten pool. Under the effect of surface tension, the molten pool takes the shape of a circular or segmental cylinder. Fragmentation of the remelted tracks is a well-known drawback of SLM referred to as the "balling" effect. The features of the tracks' instability depend of laser power, scanning speed, powder layer thickness, substrate material, physical properties and granulomorphometry of the powder used. The properties of a part produced by SLM technology depend strongly on the properties of each single track and each single layer, as well as the strength of the connections between them.

The analysis of the mechanical properties of the samples manufactured by SLM technique from Inconel 625, SS grade 316L and Co212-F powder has shown their mechanical strength equivalent to the wrought materials. Based on the obtained results, several 3D models and functional prototypes with a complex geometry were fabricated from metal powders for different industrial applications: from aerospace and automotive to biomedical and chemical.

Robotic laser cladding with coaxial powder injection is often referred to as Direct Metal Deposition (DMD). Modern DMD technology progressively occupies a number of rapidly growing fields in various applications where thick protective coatings are used, where repairing of large and small size and complex geometry parts, as for example moulds, is needed, and also in the field of direct near-net-shape manufacturing. In the field of elaboration of protective coatings, one of the basic objectives of DMD is to improve wear, abrasive and corrosion resistance of a mechanical component, to apply advanced surface engineering including deposition of functionally graded composites, multilayered, etc.

It is shown that optical diagnostics and numerical simulation may sufficiently improve our understanding of mutual interrelated phenomena in DMD and to define an appropriate way to reach a given industrial objective.

Plenary Report V

M.I.Alymov, I.P.Borovinskaya, A.S. Rogachev

CARRYING ON MERZHANOV TRADITIONS: NEW ACHIEVEMENTS ON SHS IN ISMAN



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Academician A.G.Merzhanov, a “father” of SHS and founder of the Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences (ISMAN), formulated some general directions of the future research and developments in the field of SHS [1,2]. Among them: creating of general theory of the flame propagation in heterogeneous medium; investigation of mechanism and kinetics of high-temperature interaction in combustion waves; development of technologies based on thermally conjugate SHS processes (simultaneous production of two or more products); development of technological approaches with strong energy and mechanic effects; development technologies of direct production of inorganic materials strengthened by nano-sized grains, and others.

In this work, we make analysis of new results obtained in ISMAN during the period 2013 – 2015, from the viewpoint of A.G.Merzhanov’s predictions. It is shown that new phenomena have been found for the unsteady propagating of “solid flame”, that allow significant expanding of the combustion theory. Study of mechanisms of heterogeneous interactions under extreme conditions of combustion wave shed light on the ways of microstructure control of SHS products.

A wide variety of morphologies, including nanoparticles, nano-whiskers and tubes have been obtained. Most promising technological and industrial applications developed in ISMAN are also considered.

It is shown that many of the predicted research directions have led to notable scientific results; some other predictions are still waiting for their realization.

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A.G.Merzhanov 40 years of SHS: A Lucky Star of a Scientific Discovery (A presentation with elements of a scientific lecture). Bentham Science Publishers Ltd., 2009.

ORAL PRESENTATIONS

HALL A - Monday, October 12 / 2015

Keynote I - Abstract:1074

SYNTHESIS GAS GENERATION ON SHS AND SCS CATALYSTS FOR FUEL ECONOMY AND PURIFYING EXHAUST GASES OF INTERNAL COMBUSTION AND GAS TURBINE ENGINES

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Efficiency of modern internal combustion engines (ICE) are 30-40% on stable regime and 10-15% in the conditions of city cycle, gas turbine engine (GTE) efficiency is 30 -38%. This means that main transport and gas turbines modernization tasks are: development more effective engines with minimum possible exhausted gases. It is well known that the addition of a small concentration of hydrogen to a main fuel of Internal Combustion Engine (ICE) or gas turbine engine (GTE) leads to its operation on lean mixtures /1-2/. The presence of hydrogen also reduces the formation of NO_x and CO. The problem is how to get hydrogen on board of a vehicle or in turbine. Additives of synthesis gas mixture to fuel (methane) has the same effect (improving of combustion quality) as pure hydrogen (hydrogen is 3-5 times more expensive than synthesis gas), which leads to fuel economy, reduction of exhausted gases and possibility to work on poor mixtures /1/. For this purpose, catalysts can be used for partial oxidation of methane to synthesis gas and for CO₂ steam and dry reforming of methane. This approach significantly improves both the economic and environmental characteristics of ICE and GTE. SHS method is very promising for the catalysts synthesis for partial oxidation of methane /3/ and dry reforming of methane /4/ because the method allows obtaining heat-resistant, active, block catalysts with a given structure and properties (because doping of ions in crystal lattice of spinels can be done during SHS in simple way).

Catalysts for generating hydrogen-containing gas from methane were prepared by solution combustion method (SCS) and SHS method on the base of systems: Ni-Al, Ni-Al-O, Co-Al-O, Ni-Co, Ni skeleton/Al-Mg-Si-O, Ni-Mg-Zr-Ca-O, Ni-Al-Mg-Si-O, Ni-Ce-La-O, Co-Al-Zr-O. Block catalysts of honeycomb structure were prepared and impregnated by mixture of nitrates and reducer with further drying and synthesis in SCS regime. It was found that catalysts produced by SHS and SCS method are very active in methane partial oxidation and CO₂ dry reforming of methane. Fig.1 demonstrates results of methane partial oxidation on Co-Al-O catalyst. Best result received at 800°C: conversion of methane is 99.7%, hydrogen selectivity 99.6%, CO selectivity 80%.

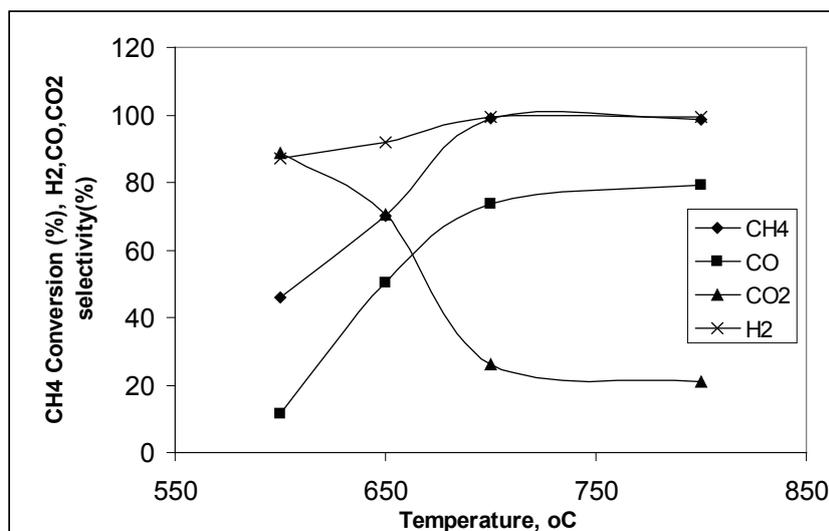


Fig.1 CH₄ conversion and H₂, CO, CO₂ selectivity over Co-Al-O SHS catalyst in partial methane conversion

The application of novel nano-structured catalytic systems and innovative structural concepts made it possible to design a simple device with catalysts for in-situ synthesis gas generation.

Acknowledgement.

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Abstract:1085

SOLUTION COMBUSTION SYNTHESIS OF STABLE SUPPORTED NI AND Ni-Cu CATALYSTS FOR HYDROGEN PRODUCTION FROM ETHANOL

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Introduction

The long-term activity of several catalysts will be presented and discussed. The causes of deactivation will also be discussed to design novel highly active stable catalysts for long time on stream. A major drawback of Ni catalysts is deactivation due to carbon formation, sintering of the active metal, and oxidation.[1] Oxidation of the catalyst can be minimized when using the ethanol decomposition reaction; however, carbon formation leads to catalyst deactivation. To produce stable catalysts, several solutions were attempted here: adding Cu as a promoter, using an active support such as ceria, and preparing partially encapsulated active particles by combustion synthesis. The effectiveness of these solutions to provide high activity for long time on stream (TOS) will be characterized by activity vs. TOS experiments, and textural, TEM, and UHV-XPS characterization before and after the reaction.

Materials and Methods

The catalysts studied were prepared by standard solution combustion synthesis (SCS). Aqueous solutions of nickel nitrate hexahydrate, copper nitrate trihydrate, and glycine with a fuel to oxidizer stoichiometric ratio, ϕ , of 1.75 was used to produce 10 wt.% of Ni, 10 wt.% Cu and 10-10 wt.% NiCu on each support of cerium (IV) oxide (Aldrich, 99.95%) and silicon dioxide (Aldrich, 99.8%) powders. The SCS method was also modified here to combust the precursors under pressures above atmospheric and under inert gases. We prepared 20% Ni on silica (Aldrich, fumed powder, 0.007 μ m) and combust it under 5 atm Ar atmosphere. Also for comparison, a 10% Ni on silica catalyst was prepared by standard wet impregnation techniques where Ni nitrate is dissolved and dispersed onto the silica and then calcined. All SCS catalysts and the impregnated catalyst were reduced at 300°C prior to reaction studies.

Catalytic activity was measured in a continuous flow fixed bed quartz reactor at atmospheric pressure as previously described.[2] The catalysts were imaged using a transmission electron microscope (FEI Titan 80-300 TEM). UHV powder X-ray photoelectron spectra (XPS) measurements were obtained under high power mode in a Kratos XSAM 800. A Multipak software package was used to determine the surface oxidation states and concentrations of the catalysts.

Results and Discussion

When comparing Ni/CeO_x and Ni/SiO₂ by the same synthesis method, the Ni/SiO₂ catalyst is stable for over 30 hours without any deactivation while Ni/CeO_x begins deactivating almost instantly due to massive carbon formation on the surface as detected by UHV-XPS. Ceria has been reported elsewhere to be able to remove residual surface carbon based

on its redox and oxygen storage capacity properties. With the model reaction of ethanol decomposition (no added oxygen), we do not see the same effect, instead more carbon formation on the ceria supported catalysts is observed when compared to Ni/SiO₂. We hypothesize that the significant increase in stability is due to the Ni becoming partially encapsulated by the small silica particles during SCS, so that carbon formation is inhibited. By alloying Ni with Cu, the stability increases due to a slower rate in carbon formation over the bimetallic catalysts. The alloying of Ni prevents the metastable metal carbide formation, which is an intermediate stage of the growth of carbon.

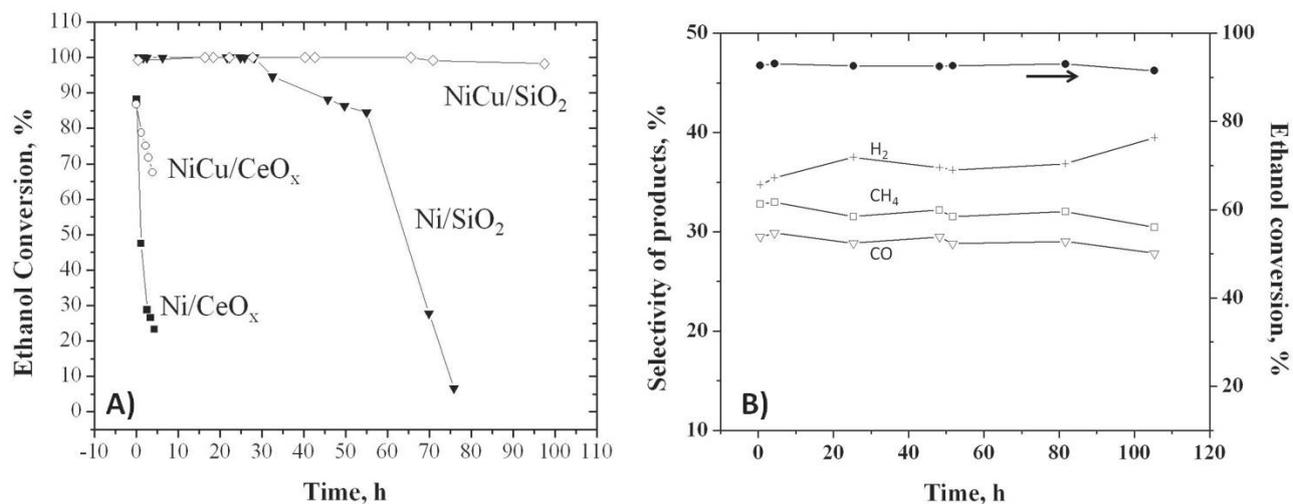


Figure 1. Ethanol conversion over A) standard SCS prepared single and bimetallic catalysts and B) Ni/SiO₂ prepared by SCS under 5 atm inert atmosphere

SCS in an inert atmosphere produces partially encapsulated Ni particles by the support particles. This produces highly stable catalysts that resist deactivation for 100 h TOS of the ethanol decomposition reaction. TEM results show that these stable catalysts exhibit no change in structure and size, and decreased carbon formation during 100 h TOS. Under 5 atm of an inert atmosphere and with slightly higher porosity of the silica support, the active Ni particles can be more fully encapsulated than during standard SCS, protecting fully from any deactivation during reaction.

Significance

Partial encapsulation, the surrounding of the metal by the support preventing agglomeration and carbon deposition on surface Ni while still allowing the reactants to reach the active surface, is demonstrated to prevent catalyst deactivation. Ni/SiO₂ prepared by CS under 5 atm inert atmosphere demonstrates no change after 100 h TOS reaction.

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Abstract:1134

ACTIVITY OF SCS CATALYSTS ON HOLLOW SPHERES IN DRY REFORMING OF METHANE

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Ceramic hollow spheres are being developed for electronic uses in piezoelectric transducers and low dielectric constant substrates, for structural applications in syntactic and metal foams, for fluid transport uses in filters and radiant burners, and for acoustic insulation. In this work, hollow spheres were used as carriers for catalysts. Fabrication of coarse hollow spheres (1-10 mm) is done by nozzle or sacrificial core processes and fine sizes (1-100 μ m) are fabricated using sol-gel techniques.

Ceramic hollow spheres can be formed by sintering of spherical organic template covered with a mixture of ceramic powders and organic binder. Smaller ceramic powders via a milling process made coating the mixture homogeneous and higher intrinsic viscosity binder had good ability to retain a spherical shape of ceramic hollow spheres. Size, thickness and porosity which are primary structural characteristics and affect the properties of ceramic hollow spheres were found to vary with binder type, binder weight ratio, weight ratio of ceramic powders and organic template and sintering temperature.

The controllability of the structure is influential for the application with specific qualification. Strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$) powders which are the permanent magnetic material as ceramic component. Polyoxyethylene lauryl ether (POE) and polyvinyl pyrrolidone (PVP) as well as polyvinyl alcohol (PVA) as organic binder and expanded polystyrene (EPS) spheres which are 870 μ m in average diameter as the sacrificial template were selected. Firstly, binder was mixed with small amount of pure water and stirred until the binder was dissolved well, and ceramic powders milled for 1 hour were added in the solution and stirred to make homogenous slurry. Secondly, EPS spheres are added in the slurry and stirred until the spheres were coated with the mixture of ceramic powders and binder through the evaporation of water. The amount of ceramic powders was 20 times of the EPS in weight which is enough for the coating according to an approximate calculation and the binder ratio was 2 wt% in all components including ceramic powders, EPS and binder. Binder ratios of POE, PVP and PVA were 5.5 wt%, 2 wt% and 2 wt%, respectively. The coated spheres were heated around from 373 K to 773 K with an infrared image furnace in atmospheric condition. The temperature was increased by 0.5 K/s in heating rate from room temperature and kept for 60 s at every 100 K. The weight of coated spheres and organic components and the appearance of coated spheres after heating at each temperature were investigated. Maximum heating temperature was varied from 1373 K to 1523 K. Diameter of ceramic hollow spheres sintered at different temperature was measured by the optical microscope. Compressive strength was also measured on an Instron universal tester at a displacement rate of 1.7 μ m/s. The compression test was conducted using about 100 spheres in 1 cm^2 . Diameter of the hollow spheres is around 0.9 - 1.1 mm, and the thickness of $\text{SrFe}_{12}\text{O}_{19}$ layer is around 0.7-1.0 mm.

Under similar conditions (as second stage) were prepared catalysts on the base of systems: Ni-Co-O, Ni-Co-Ce-O, Ni-Co-Mg-O, Ni-Co-Mg-Al-O, Co-Mg-Al-Fe-O and Fe-Mg-Al-O, in this case total layer thickness is 45-90 microns. Catalysts were produced by solution combustion synthesis method (SCS). XRD, SEM/EDS, BET methods were used for composition analysis and catalysts characterization.

Catalyst activity were studied in the process of dry (CO_2) reforming of methane (all tests were conducted at atmospheric pressure in gas mixture ($\text{CH}_4:\text{CO}_2:\text{O}_2$ (1:1:1)), flow 0.24 l/s at temperatures 1023, 1073, 1123 and 1173K in a fixed-bed free flow quartz reactor. Conversion of CH_4 , CO_2 , yield of H_2 and CO measured, ratio H_2/CO and activity of catalysts calculated. Surface area of SCS catalysts on hollow spheres varied from 6 to 20 m^2/g . The gas products were analyzed in a gas chromatograph with thermal conductivity detector using column filled with HayeSep Q 80 / 100 mesh.

It was found that $\text{SrFe}_{12}\text{O}_{19}$ has low catalytic properties, but during reaction at high temperatures and presence of hydrogen (as product of reaction) reduction reaction take place and in some cases iron originates (as small drops on the surface as shown by SEM analysis). There is good catalytic activity (up to 95% conversion of CO_2 and CH_4) and stability for Ni-Co-Ce-O, Ni-Co-Mg-O and Ni-Co-Mg-Al-O catalysts on hollow spheres. These catalysts show origination of Fe during

catalysis and this iron works as dehydrogenation catalyst and increase catalyst thermal conductivity which is good for stability of catalyst (there is no local overheating).

In case of iron spinels-containing catalysts there is no origination of metallic iron after catalysis. This could be because of exchange of oxygen between $\text{SrFe}_{12}\text{O}_{19}$ spinel structure and iron containing spinel, because of their similar parameters. Introduction in the catalyst composition of cerium oxide stabilizes the carrier, protecting its particles and pores from sintering at high temperatures. The work is continuing.

Keynote II - Abstract: 1135

SHS IN THIN FILMS

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Exothermic reaction waves in thin nanostructured films [1,2], so-called “thin film SHS”, still provide puzzling tasks for experimental, theoretical and modelling research [3]. Unusual properties of the process, such as extremely high rate of temperature rise $\sim 10^6$ K/s; high velocity of the reaction front propagation $\sim 10 - 100$ m/s; temperature $\geq 1500-1900$ K, rise many questions concerning mechanisms of the combustion reaction and exothermic reaction wave propagation. In this work we report our new results obtained by experimental diagnostics of the thin film SHS and by molecular dynamic simulation, in comparison with newest results reported in the literature. The heterogeneous nanostructured foils, produced by magnetron deposition or mechanical processing, represents new class of reactive materials. They are composed of layers or clusters of the different phases with typical size $10 - 100$ nm, which can react with each other, releasing high amount of heat. Thus the reaction, being initiated locally, spontaneously propagates across the whole foil in the form of high-temperature wave.

Our experimental results based on high-speed video recording, micro-pyrometry, time-resolved X-ray diffraction, quenching of the reaction waves and other contemporary methods, show that this wave has complex, multi-stage structure, including stages of chemical and physical transformations. The first stage relates to nano-heterogeneous chemical reaction. Mechanisms of this reaction cannot be described by well-known models of solid-state reactive diffusion or direct dissolution and diffusion in the melt. Combination of the experimental data and molecular dynamic simulation [4] allows formulation of new “solid-liquid-solid” mechanism of the crystal grain growth that explains extremely fast (microseconds) formation of the crystal grains of the reaction products in intermetallic systems. This mechanism becomes possible because the solid product does not form the continuous layer along the boundary between the metals layers but rather grow as separate spherical grains, permitting refractory compound to dissolve in the melt during the whole duration of the process, and precipitate on the “external” surface of the growing crystal. This mechanism predicts also that systems with high solubility of refractory metal reactant into molten reactant (Ni-Al, Pt-Al, etc.) should possess higher rates than systems with low solubility (Ti-Al, Zr-Al), weakly depending on the solid-state or liquid-state diffusivities.

Second wave, wave of physical transformations, propagates behind the first wave of chemical transformation. Duration of the second wave is from milliseconds to seconds. We suppose that the nano-grains growth provide heat generation for the second wave due to decrease of the specific surface of grain boundaries. Specially designed quenching technique allows splitting of the SHS wave in the thin multilayer reaction film, and organize propagation of two-stage exothermic chemical + physical wave (figure 1, left), or solely firsts chemical stage (figure 1, right). Propagation of the solely physical waves are also considered, and

Promising practical applications of these foils in the advanced technologies, e.g., joining of dissimilar materials, are demonstrated.

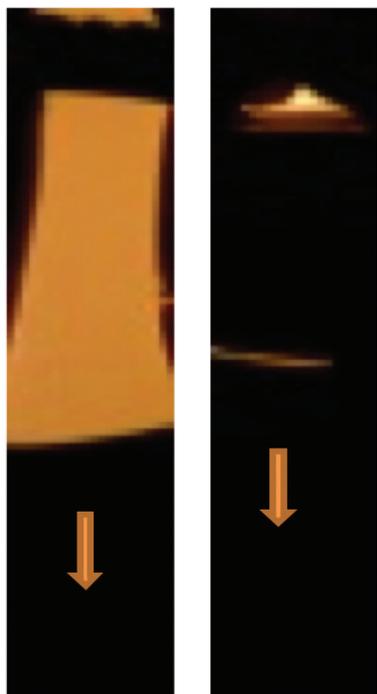


Figure 1. High-speed video frames of the SHS wave propagation in the Ni/Al multilayer reactive nanofoil: left - free standing Ni/Al reactive multilayer nanofoil, two-stage wave; right - the same on the Cu substrate, propagates only the first stage. (recording rate 40000 frames per second).

This work is supported by RFBR grant No.13-03-01043.

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Abstract: 1066

REACTIVE NANOSTRUCTURED FOILS FABRICATED BY HIGH-ENERGY BALL MILLING AND COLD ROLLING

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Magnetron sputtered multilayer nanofoils, which consist of regularly alternating nanolayers of solid reactants, is a new class of functionally graded materials. Since such materials possess a set of unique properties, including low temperature of reaction initiation, high velocity of a combustion wave propagation and high rate of heat release, they found a variety of applications including joining of dissimilar materials [1]. However, due to the technological complexities, which are related to the sputtering of some elements, the range of compositions for such reactive nano-foils is not broad. To overcome these shortcomings and expand composition ranges a novel method for fabrication of reactive nanostructured foils (ribbons) by means of the high-energy ball milling (HEBM) followed by cold rolling is suggested [2].

The powder mixture of titanium and silicon (Ti + 0.6Si) were subjected to HEBM in a planetary ball mill Activator 2S (Activator, Russia), that have the independent drives for a sun wheel and the jars, thus allowing to change their rotation speeds separately. Varying the ratio between the rotation speeds of the sun wheel (W) and the jars (w) one can obtain qualitatively different ball motion regimes inside the jar [3]. More specifically five different milling regimes have been

found. The most efficient HEBM regime was achieved when the ratio between the rotating speed of the milling vials, w , and the sun disk, W , was $K = w/W = 1.5$, which corresponds to predominantly rolling trajectories of the moving balls and a large fraction of stagnant balls inside the jar. At these regimes, the fastest transformation of crystal structure and morphology of the particles was observed, along with the most significant changes in the reactive properties, e.g., a decrease of the self-ignition temperature. According to X-ray analysis optimal milling time was chosen at which the reaction has not yet been detected in the jar.

Analysis of data obtained using a scanning electron microscope showed that such treatment leads to the formation of composite particles in which the silicon and titanium are presented in the form of nanoscale layers. In addition, it was demonstrated that for the composite Ti +0,6Si particles fabricated under optimal conditions the ignition temperature could be as low as 820 K. Thus obtained nanostructured reactive powder was subjected to the cold rolling. The process allows us to produce the ribbons with length up to 10 mm, width ~ 2 cm and a thickness of $\sim 250 \mu\text{m}$.

Reactive properties of such ribbons were also investigated. In order to use such ribbon as an energy source it was positioned between two carbon/carbon (C/C) composites to be joined. The stack was placed between two electrodes of spark plasma sintering (SPS) apparatus and heated up to $1600 \text{ }^\circ\text{C}$ with the heating rate of 100 K/min under the load of 3 kN .

Figure 1 shows typical SEM images of a cross-section of a joined C/C samples at the vicinity of the joint layer. It can be seen that a crack-free joined layer $\sim 150\text{-}200 \mu\text{m}$ in thickness was produced. It was also observed that part of the bonding media infiltrated to the depth of $\sim 100 \mu\text{m}$ into the porous skeleton of the C/C composites. Thus, it was shown that combination of the HEBM and cold rolling is a promising method for production of reactive nanostructured foils (ribbons) that can be used for joining of refractory materials.

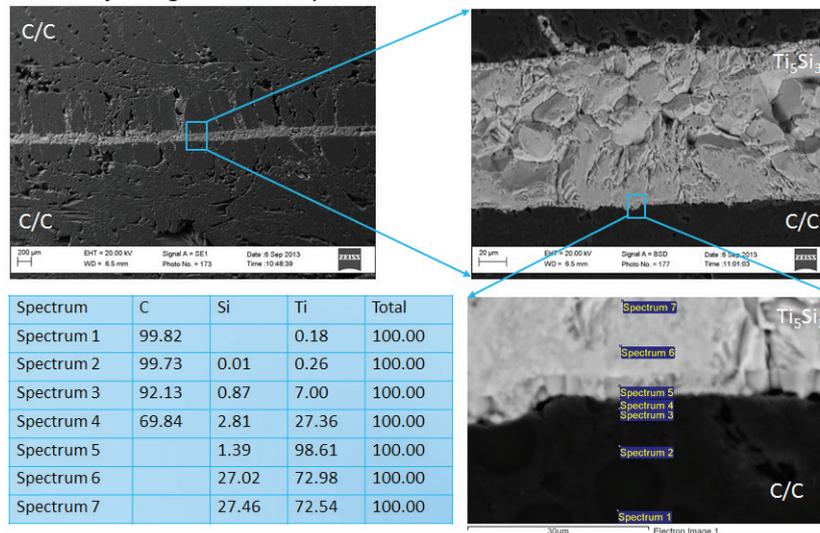


Figure 1. Typical SEM image of C/C composite joined with reactive ribbon of Ti+0.6Si.

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Abstract: 1087

NANOSTRUCTURED CERAMICS BY SPARK PLASMA SINTERING OF SHS SILICON CARBIDE NANOPOWDER

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Silicon carbide (SiC) based ceramics has a set of unique properties, such as thermal and chemical durability, refractoriness and high hardness. Due to these properties, SiC has a wide variety of applications, including abrasives and cutting tools, structural ceramics and crystals for microelectronics, catalysts, and coatings.

A systematic study was conducted to verify the influence of various spark plasma sintering (SPS) parameters (heating rate, temperature, duration and applied load), on the densification and grain-growth kinetics of a silicon carbide nanopowder produced by self-propagating high temperature synthesis (SHS) [1-2]. The direct *in situ* SHS+SPS method for fabrication of SiC ceramics was also investigated. It was shown that SiC powders could be fully densified by SPS at lower temperature and within shorter time, as compared to the conventional sintering. It is suggested that the densification is enhanced in the initial part of the sintering cycle by a local spark-discharge process in vicinity of the contacts between the particles, and that both grain-boundary diffusion and grain-boundary migration are enhanced by the electrical field originating from the pulsed direct current used for heating the sample. Both the diffusion and the migration that promote the grain growth were found to be strongly dependent on temperature, implying that it is possible to retain the original particle nano-structure in fully densified materials. Thus sintered pore-free SiC nanostructured ceramics has a micro-hardness around 25 GPa and fracture toughness of 5 MPa·m^{1/2}.

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Abstract: 1096

STRUCTURED COMPOSITE MATERIALS BY SHS METHOD: EXPERIMENTAL STUDY

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As is known, the heat released in SHS reactions can be spent not only on further processing of combustion product or its structuring but also as a source of extra thermal energy to be used for joining (welding) of dissimilar materials [1-3]. SHS technology offers a challenging possibility for in-situ synthesis of transition layers (including graded ones) that would provide reliable joining between dissimilar materials, which is impossible to get by standard methods of soldering or welding. SHS-produced transition layers can be expected to consist of a wide range of materials, such as intermetallics, metals, alloys, ceramics, and composites, whose combined use would ensure the formation of strong joint between incompatible materials. This technique finds its application in aerospace industry to produce materials for use both on the ground and in space (in space stations and interplanetary missions).

This work aimed at finding out specific SHS reactions that would yield combustion products suitable for in-situ fabricating of strong joining between ceramic materials and other materials. Our experiments were performed with the following reactive mixtures:

| | |
|--|-------|
| (Ti + 0.5C) + (Ti + Si) | (I) |
| (Ti + 0.65C) + (5Ti + 3Si) | (II) |
| (5Ti + 3Si) + (NiAl + W) + (5Ti + 3Si) | (III) |

As a result, we managed to obtain the functionally graded materials (shown in Fig. 1) exhibiting varied composition and porosity gradients and demonstrated good perspectives of the above method for deposition of graded heat-resistant coatings. In reactions I and II, joining takes place due to formation of a Ti-Si-C MAX-phase. This technique was found applicable not only to joining similar (ceramic/ceramic) but also dissimilar materials (ceramic/intermetallic).



Fig. 1. Overall view of combustion products derived from mixtures I-III.

In the case of melting within the combustion wave, the effect of joining is reached due to reactive infiltration of the melt to the pores in both materials under the action of external and capillary forces [4].

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HALL A - Tuesday, October 13 / 2015

Keynote III - Abstract: 1138

SHS-ENABLED REACTIVE BONDING FOR APPLICATION IN MICROSYSTEMS TECHNOLOGIES

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Most modern bonding techniques in microsystems technologies make use of high temperatures. While this is necessary to establish strong bonding forces, it can cause significant problems. Especially when dealing with delicate microelectromechanical systems (MEMS), high temperatures can destroy the functional structures. Furthermore, it is often required to bond different materials, which can lead to intrinsic tensions caused by differences in the material's coefficients of thermal expansion.

Integrated reactive material systems have gained attention throughout the last years as an internal heat source for bonding, as they promise a feasible way to join heterogeneous materials without applying too much thermal stress to the whole device [1]. These concepts usually comprise multiple alternating layers of reactive materials such as Al, Ti, Ni, Co, Zr, Pd or Pt which undergo an SHS-reaction [2, 3].

We propose a novel concept for reactive bonding based on a single layer of a reactive nanocomposite (RNC), containing intermixed metal nanoparticles [4]. Figure 1 shows a drawing of the joining concept: The nanoparticles are dispersed in a volatile organic solvent to enhance handling properties and prevent unintended ignition. After deposition of the dispersion, the solvent evaporates, leaving a dry layer of intermixed reactive nanoparticles. A second substrate is aligned on top of the reactive layer and while applying pressure, the reactive nanocomposite layer is ignited by a laser pulse. The resulting self-sustaining exothermic reaction creates a sufficient amount of heat to establish a bond between the substrates.

Composites of aluminum-nickel and aluminum-titanium were produced by dispersing dry metal nanoparticles in a solvent. The used particles were spherical with diameters ranging from 18 nm to 100 nm. After manual deposition of single droplets of the dispersions, the solvent evaporated at room temperature. Pressure was applied to the sample, while ignition was executed with a laser pulse at $\lambda = 808$ nm, $\text{Spot}_{\varnothing} = 100$ μm and $p = 130$ mW.

The RNC layers were analyzed prior and post ignition via scanning electron microscopy, energy-dispersive x-ray spectroscopy, scanning white light interferometry, x-ray powder diffraction (XRD) and optical microscopy. Analysis shows, that passivation layers of the nanoparticles can constrain self-sustaining reactions. Figure 2 shows an SEM micrograph of a reacted

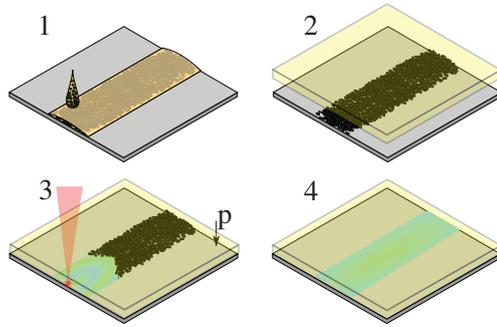


Fig. 1: Drawing of the concept: (1) Deposition of the nanocomposite dispersion. (2) Alignment of top substrate after solvent evaporation. (3) Ignition of SHS reaction while applying pressure. (4) Finished bond.

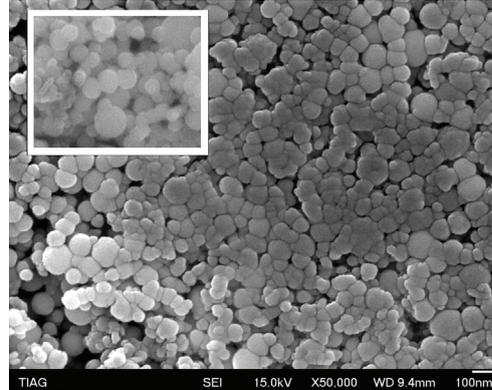


Fig. 2: SEM micrograph of a reacted AlTi sample. The initially spherical nanoparticles formed one layer comprising non-spherical grains. The insert shows the unreacted RNC layer.

AlTi sample and an unreacted sample in the insert. The initially spherical nanoparticles formed one layer comprising non-spherical grains. Using XRD the chemical composition of the sample was evaluated, showing the presence of titanium(II) oxide, which is formed at 1600 °C.

Our novel nanoparticle based approach for reactive nanocomposites is a highly promising technique for applying reactive bonding without the need to use texturing methods like lithography, as the dispersion can be deposited in virtually any pattern. Current work focuses on enhancing the layer homogeneity and minimizing oxygen contamination. As methods for depositing the RNC layer, inkjet-printing and screen printing are evaluated as alternatives to manual deposition.

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Abstract: 1116

CONSOLIDATION OF Cu-BASED NANOSTRUCTURED PSEUDO ALLOYS FOR ELECTRICAL CONTACT MATERIALS

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Nanostructured matrix composites such as Cu-Cr, Cu-W, Cu-Mo (also called pseudo- alloys) have been of current interest due to unique combination of their mechanical, electrical, and thermo-physical properties. The combination of a refractory and typically hard metals such as Cr, Mo, W with a low-melting metal Cu exhibits high mechanical strength, high electric/thermal conductivities, affords tailoring composite materials for a wide variety of applications, including heat-sink elements in microelectronic devices, contacts in high-voltage circuit breakers, as well as plasmatron nozzles and rocket engines.

One of the essential aspects to produce high quality Cu based pseudo alloys require that initial components should be mixed in a submicron- and nanostructural level. Namely, Cr, W or Mo phase must be uniformly distributed in a Cu matrix and the particle size of refractory metals should be in a nanometer range. Analysis of the available literature shows that nanostructured pseudo-alloys may have advantages for electrotechnical applications as compared to conventional micro-sized composites [1-4].

However, the difficulty in production of such composites is low mutual solubility, high difference between their melting points and densities, and high wetting angle. And it cannot be overcome completely through the conventional melting and casting methods. Moreover these methods are expensive, power-consuming and multistage.

In the present study a set of nanocomposite Cu-Cr, Cu-Mo, Cu-W powders were prepared by high-energy ball milling. The powders were then consolidated by short-term (5-10 min) spark plasma sintering at 700-950°C under pressure (50 MPa) to obtain essentially pore-free pseudo-alloys.

Microstructure, crystal structure, and local atomic structure were characterized by XRD, high-resolution SEM, and high-resolution TEM. It has been shown that the Cu-Cr powder mixture after 60 min of ball milling consists of Cr with the grain size is in the range of only 3-5 nm which is uniformly distributed in Cu matrix. Same behavior of nanocomposite formation during high energy ball-milling was observed for Cu-W and Cu-Mo powder mixtures.

A typical time for fabrication of pseudoalloys in the Cu-Cr system by other techniques ranges between 20 and 80 h [5-7]. The grain sizes in the produced bulk materials remained within the ranges 5-60 nm for refractory metal-based phase and 200-300 nm for Cu-based matrix.

Consolidated Cu-Cr nanocomposites have a Vickers microhardness up to 5.12 GPa and a specific electrical resistivity in the range 6-9.6 $\mu\Omega$ cm. As for Cu-W and Cu-Mo bulk nanocomposites, values of Vickers microhardness reach 6,19 GPa and 3,88 respectively. GPa. These nanocomposites could be promising candidates for the application in high-voltage circuit breakers.

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Abstract: 1055

MA SHS OF SUBMICRON POWDERS AND NANOSTRUCTURED GRANULES BASED ON NiAl AND TiAl

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Due to the unique combination of their physicochemical properties, NiAl and TiAl intermetallides and alloys based on them are given close attention by researchers designing materials for gas turbine, aircraft, space, ship building engineering, etc.

Narrow-fraction powders (several micrometers in size) are required for modern technologies such as SPS and selective laser sintering. Metal matrix composites produced using mechanical activation (MA) followed by SHS are characterized by improved physico-mechanical properties compared to those of materials of close composition prepared using the conventional methods.

This study was aimed at preparing submicron powders and nanostructured granules based on NiAl and TiAl using MA SHS.

Several variants were tested when optimizing the process of preparing powders from alloys based on NiAl- and TiAl + Ti₃Al with a nanoblock structure: MA of reaction mixtures followed by layerwise SHS combustion or the thermal explosion mode of SHS, as well as mechanochemical synthesis (MCS) of an intermetallide in the planetary ball mill drum. Ni-Al mixtures were prepared in a planetary ball mill in the modes preventing formation of synthesis products in the drum. In order to reduce the NiAl grain size and increase porosity of the target product (to make grinding easier), synthesis was conducted in a reactor under argon atmosphere in the thermal explosion mode. TiAl + Ti₃Al powders were synthesized in the thermal explosion mode in a vacuum furnace from the mechanically activated reaction mixture. MCS in planetary mill drums was an alternative method for synthesizing powders.

The effect of MA parameters on the structure and phase composition of the reaction mixtures and the resulting SHS products, NiAl and TiAl + Ti₃Al, were studied by optical and electron microscopy, X-ray diffraction and X-ray spectroscopy, laser diffraction, and BET measurement of specific surface area. The optimal modes of treatment of the reaction mixtures were determined.

It was found that 100% NiAl phases can be produced using either the MA + SHS method or MCS. MA SHS gives rise to porous sintered products with the large grain size (60-70 μm) and a nanoblock (less than 50 nm) structure of the intermetallide phase, which require further milling to obtain desired grain size. In the latter case (MCS), long-term treatment in a ball mill results in contamination of the powder with impurities from container and grinding media, which has a negative effect on properties of the products. NiAl powders contain 4.9% Fe and 0.9% Cr as impurities. Furthermore, the MCS method is inefficient and energy-consuming. The grain morphology of these powders is extremely heterogeneous both in terms of their shape and size. The share of the small fraction (< 15 μm) is less than 80-90%. The size of the coherent scattering region (CSR) is less than 50 nm.

An analysis of the phase composition and structure of mechanically activated Ti-Al mixtures demonstrated that the total amount of TiAl+ Ti₃Al formed after 2 h of MA was less than 80%. Synthesis in the thermal explosion mode in a vacuum furnace at temperatures above the melting point of aluminum is the optimal method for producing TiAl+ Ti₃Al powders. In order to increase the degree of fineness of NiAl powder, functional additives and pore-forming agents were introduced to the blend. These agents also inhibit grain growth in the SHS wave when products are cooled down and increase the porosity of sintered products, thus facilitating further grinding. It was demonstrated that functional additives require additional heat to be heated and melted, which reduces the reactivity of the mixture, decreases the combustion temperature and rate, and has a positive effect on composition and structure of the combustion product. Thus, the grinding time for synthesizing NiAl powder with grain size less than 5 μm was reduced twofold by using salts of pore-forming agents and grain growth inhibitors.

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Abstract: 1168

FORMATION OF NANOPARTICLES BY SHS

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There is an increasing attention on the production of ultrafine or nanosize ceramic particles and in addition, on the sintered articles comprising of nanoparticles. The stimulus for this attention mainly arises from the possibility of sintering at lower temperatures and to higher densities due to the increased surface area of the nanosize powder as compared to micron-scale powder. In addition, enhanced mechanical properties are gained from the sintered articles of nanoparticles [1]. Furthermore in Al matrix composites, addition of ceramic nanoparticles is reported to enhance both strength and ductility [2]. Although, nanoparticles have the potential of exhibiting superior properties, there are a limited number of studies in the literature on formation of nanoparticles by SHS.

Inherently, formation of nanoparticles through SHS is a challenging task, since very high temperatures are involved and this leads to extensive coarsening of the particles. Present study deals solely with formation of nanoparticles through SHS from solid reactants and thus sol-gel combustion synthesis is left out of scope.

There are mainly two approaches in the literature on formation of nanoparticles by SHS: utilization of active and inert diluents. They both make use of the reduction in the exothermicity of the SHS reactions. In the approach of active diluents, one exothermic reaction and one parallel endothermic reaction are utilized in order to form the desired product. The extent of the endothermic reaction determines the attained combustion temperature in the reaction zone of the pellet. Wang et al. [3] obtained amorphous boron nanopowder through SHS by using boron oxide, Mg (for exothermic reaction) and KBH₄ (for endothermic reaction).

In the inert dilution technique, salts that evaporate at the reaction temperature or product of the reactions or metal powder has been added into the starting mixture. For example, near nano WC particles were obtained from WO₃, C and Mg mixtures by using NH₄Cl, MgO, (NH₄)₂CO₃, CO(NH₂)₂, NaF, NaCl, NaBr, NaI as diluents [4]. Nano sized TiB₂ particles were formed by SHS from H₃BO₃, Mg and TiO₂, and NaCl as the diluent [5]. NaCl was also utilized as a diluent in the formation of nano TiC particles from Ti and C [6].

Addition of some of the expected products as diluents into the reactant mixture has some drawbacks. First of all, it may require acid leaching for purification of the desired products. Secondly, it may react with one of the reactants and so that it may form side products such as borates that are difficult to leach, as in the case of utilizing MgO as diluent in magnesiothermic formation reactions of borides. Thus, the advantage of NaCl is that it is possible to remove it from the products by simply dissolving it in water and also it usually does not react with product and reactant phases during SHS. In the present study, SHS of two systems was investigated with NaCl addition as diluent in order to obtain nano size particles. The products were subjected to XRD, SEM and particle size analyses. One of the investigated systems is Zr + B, which yielded single phase ZrB₂ [7]. Second investigated system is TiO₂ + BN + Al, which yielded a mixture of TiB₂, TiN and Al₂O₃ particles. NaCl was added into the starting mixture in 0-40wt% range. Increase in the diluent amount resulted in a decrease in the combustion temperature, velocity of the SHS wave front and particle size of the obtained products. A stable SHS reaction could not be obtained in the 40% NaCl added mixtures of both systems and mixtures could not be ignited when higher amounts of NaCl were used. The role of NaCl in decreasing the particle size of the product particles is suggested as reduction of the combustion temperature, isolation of the formed particles and hindrance of mass transport among the formed crystals [6,7].

Broadening of the peaks on the XRD patterns of the products indicated that the crystallite size of the products decreased with the increasing amount of NaCl. XRD analyses revealed that intended reaction products were obtained in the TiB₂, TiN and Al₂O₃ system with no cross reaction products. ZrB₂ system was composed of mostly near nano size particles with some particles finer than 100nm [7]. TiB₂, TiN and Al₂O₃ system resulted in near nano size particles.

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Keynote IV - Abstract: 1127

THE CATALYSTS PREPARED BY SOLUTION COMBUSTION ON GLASS-FIBERS FOR SYNTHESIS OF CARBON NANOTUBES

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This work is devoted to the development of nanosized catalysts of oxides of metal (Co, Ni) on glass fiber support by a "solution combustion" (SC) method [1]. The chosen method of preparation allows uniform heating of the catalyst at low temperature (400 °C) initiating the combustion front on the surface of catalyst, and the low content of active components will limit the development of a high temperature wave by preventing the overheating of the catalyst.

Glass fibers (GF) of a definite size were impregnated with a solution of cobalt or nickel nitrates and glycine, after that they were dried for 30 minutes in air at 100°C and then calcinated in air atmosphere at 400°C. As a result of the reaction, the formation of nanoparticles with sizes ranging from 10 to 50 nm was achieved [2, 3].

Synthesis of CNT carried on the installation for chemical vapor deposition. Gas flow: He-650 cm³/min, H₂-150 cm³/min, C₂H₂-19.5 cm³/min. Temperature -710°C, time of synthesis - 20 min.

To establish a structure derived metal oxides was carried out SEM analysis of glass fibers with nanoparticles of metal oxides, X-ray analysis of glass fibers with nanoparticles of metal oxides (Fig. 1a for Co₃O₄) and TEM analysis of carbon nanotubes grown on glass fibers with metal oxides (Fig. 1b CNT@GF-Co₃O₄).



Fig. 1. a) X-ray analysis of glass fibers with nanoparticles of Co₃O₄; b) TEM image of carbon nanotubes grown on glass fiber fabrics with Co₃O₄ (5 wt. %); c) current-voltage characteristics of "array" of CNT grown on glass fiber fabrics with Co₃O₄ (5 wt. %) at different temperatures

As can be seen from the TEM images carbon nanotubes have diameters of 25 - 35 nm, and are all intertwined, forming a three-dimensional disordered structure. Current-voltage characteristics of "array" of CNT (Fig. 1c) and fiberglass with CNTs were measured. The use of composite of a glass cloth - CNT has a number of advantages. If there is no sunlight is possible to heat the water by feeding the small current (10 - 20 V). As can be seen from the above data CNT are good conductors of electrical current, which gives an effective Joule heating.

Co and Fe nano-catalysts prepared by combustion on glass fiber textile substrates allows to grow various types of CNT and carbon fibers standard by CVD method. This type of conductive CNT@fiberglass textiles can be used for various functional applications, such as selective black coatings for solar water heaters and flexible heating elements. Such CNT@GF coatings have advantages of Joule heating by externally applied current in the absence of sun.

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Abstract: 1152

CRYSTALLOGRAPHIC DEPENDENCE OF CATALYSTS ACTIVITY PREPARED BY SCS AND SHS METHODS IN DIFFERENT PROCESSES

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Identifying the structure sensitivity of catalysts in chemical reactions to achieve the maximum and stable reactivity is one of the most challenging goals in heterogeneous catalysis. A growing number of studies are conducted to understand the nature of the structure sensitivity, supported by well-defined preparation methods, in situ characterizations, surface science studies and calculations.

Over the years, notable structure sensitivities have been observed for SHS catalysts and recently for solution combustion synthesis (SCS) catalysts. On the base of results of study the catalysts on the base of cobalt, alumina, manganese, nickel, chromium, iron, copper, magnesium and etc. activity produced by SHS and SCS were found regularities of crystallographic dependence of catalysts activity.

A prime example of this complex structure sensitivity is the CO₂ dry reforming of methane converting CO₂ and CH₄ to synthesis gas and dehydrodimerization of methane with ethene and propene as main product. Other processes as CO oxidation and soot oxidation are also sensitive to catalysts structure, which depends from method of preparation (SHS or SCS) and conditions of synthesis. Process of synthesis of SHS catalysts can be controlled by number of parameters (initial batch components particle size, forming parameters, preheating temperatures, cooling conditions), in case of SCS by preheating and cooling conditions and temperature. The process of SCS catalyst on carriers synthesis may be controlled by the transport of the compound through the pores of the catalyst or support. Role of impregnation and diffusion in the synthesis and structure of supported catalysts will be discussed. A procedure is developed for determining the exact specific activity-size dependence. The importance of the pore structure of the supports used in these catalyst systems has been noted. Process of SHS catalysts on carriers synthesis during CAFSY process can be controlled by in flight SHS thermal coating (CAFSY) parameters [1]. It was found that the most active catalysts were made using "open-pored" alumina and spinels carriers. An average pore radius can be estimated for these optimal supports. SHS and SCS technology permit "tuning" catalysts to have desired properties (particle size, surface area, parameters of crystal planes) and it is demonstrating, that the size of metal catalyst "nanoparticles" deposited on a surface as also parameters of crystal planes and surface area affects the catalyst's level of activity.

Over the years, structure sensitivities have been observed for SHS catalysts, i.e., crystallographic structure and particle size. It is noted that some of phases of SHS catalysts can exist in different crystallographic structures, for example the hexagonal closepacked phase and the face-centered cubic phase, and both phases can be found in catalyst. There are a number of data on the effect of particle size of SCS and SHS catalysts on activity. Nevertheless, it is clear that one cannot increase the mass-specific activity of SHS and SCS catalysts simply by decreasing the particle size.

Also in a number of works [2-5] the influence of the non-stoichiometry was studied for the different SHS and SCS catalysts on their activity in different processes. In many cases a lack of stoichiometry leads to a very substantial increase of the catalysts overall activity. An apparent correlation has been obtained between the non-stoichiometric structures of the catalysts and their activities in the dehydrodimerization of methane, pyrolysis of diesel fuel, CO oxidation, dry reforming of methane, soot oxidation, hydrogenation and others.

In summary, we identify theoretically that the great influence of crystallographic structure and corresponding morphology effect on formation of the various active sites with higher activity and density is illustrated. This data might open up a new avenue for the design of better, stable catalysts with maximum specific reactivity, in which material synthesis would play an essential role.

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Abstract: 1029

ONE-STEP PREPARATION OF HIGHLY STABLE Ni-BASED SUPPORTED CATALYST BY SOLUTION COMBUSTION SYNTHESIS

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Nickel-based catalysts are active and selective for a range of chemical reactions such as those occurring in petroleum refining including hydro-treating, hydro-cracking, and hydro-processing [1-3]. Nickel-based catalysts are also used for hydrogen production from ethanol (decomposition, steam reforming, and oxidative steam reforming). Ethanol is nontoxic, easily transported through the current infrastructure, and is considered as a potential hydrogen generation source [4,5]. The stability of catalysts, however, is the most important challenge in all pathways for hydrogen production from ethanol. Recently, deactivation aspects of catalysts during ethanol conversion were thoroughly reviewed [6]. Catalyst deactivation is generally attributed to the deposition of carbonaceous species, as well as the sintering and oxidation of metallic particles.

Various approaches are reported for the synthesis of Ni-supported catalysts, including incipient wetness, impregnation, coprecipitation and sol-gel methods, which produce catalysts with a high specific surface area [7,8]. Nickel nitrates are often used as a precursor throughout these preparation techniques, although nickel hydroxides and acetates can also be used. However, these synthesis methods typically require an additional calcination to obtain the desired phase composition, which could lead to significant sintering.

Solution combustion synthesis (SCS) is another viable method for catalyst preparation. SCS is typically a redox based reaction that takes place in a homogeneous aqueous solution of oxidizing (e.g., metal nitrates) and reducing agents (fuels) [9]. These mixtures react exothermically after ignition, generating high-energy output, which is sufficient to produce crystalline materials in a single self-sustained step. This form of combustion offers some unique features for material synthesis. The reaction is completed within seconds with maximum temperatures as high as ~1500 °C. Such high temperatures facilitate formation of crystalline material and usually no calcination is required to obtain the desired phase composition. More importantly, the mixing of precursors on the molecular level and release of large quantities of gases, such as carbon dioxide, water, and nitrogen, result in the formation of nanoscaled solid porous products.

SCS is used to prepare nanosized materials for various applications, including bulk and supported catalysts [10]. SCS is also used to produce supported catalysts as a porous support can further improve the dispersion of the active phase and enhance the structural and thermal stability of the catalysts. Indeed, an inert support used in SCS facilitates formation of smaller and dispersed particles.

In this work, we report one-step SCS of silica supported active metal (nickel) catalysts in an argon atmosphere. The thus prepared Ni/SiO₂ supported catalyst possesses high activity during ethanol decomposition to produce hydrogen at low temperatures (200 °C) and it has excellent stability toward deactivation with essentially no change of catalyst activity over 100 hours of operation Figure 1 (see details in [11]).

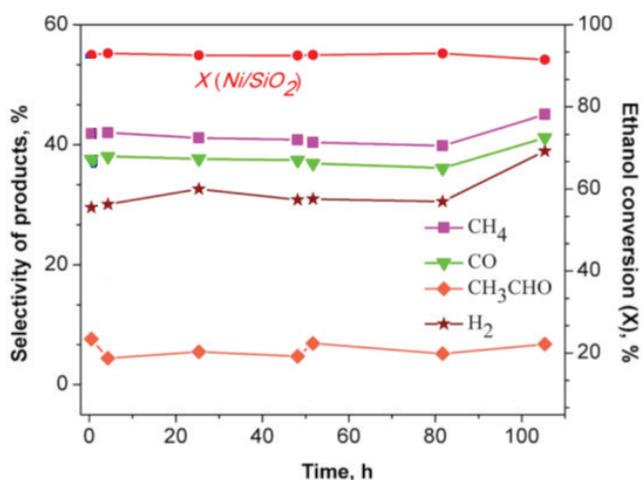


Figure 1: Conversion ($X(\text{Ni}/\text{SiO}_2)$) and selectivity of methane, carbon monoxide, hydrogen, and acetaldehyde during the ethanol decomposition over Ni/SiO_2 catalyst, 200 °C.

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Abstract: 1109

Keynote V

3-D RECONSTRUCTION OF HIGH ENERGY DENSITY MATERIALS: EFFECT OF NANOSTRUCTURE ON IGNITION CHARACTERISTICS

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Through use of High-Energy Ball Milling (HEBM), specifically Arrested Reactive Milling (ARM), oxygen free Ni/Al composite particles were prepared with a variety of HEBM times. As the milling time is increased, up until the critical time, it is known that the internal nanostructure of the particles becomes more intermixed in thin tortuous lamellar structures [1,2]. These structures have increased surface area contact and lower reactant diffusive distances. It is well known that solid-phase reactivity is related to the surface area contact between the reactants. However, to date, there has not been a statistically valid study that accurately controls both the ignition characterization and nanostructural evaluation simultaneously. In the majority of studies, few ignition experiments were conducted, resulting in nonstatistical datasets; the trends and relationships could be due to noise or observed extreme cases. Additionally, it is commonplace to qualitatively evaluate the nanostructure; nearly every publication depicts the nanostructure with analysis of few 2D cross-sectional SEM or TEM images [3]. The goal of this work is to provide statistically proven quantitative data on the nanostructural characteristics of the HEBM-induced high energy density materials (HEDM), utilizing 3D reconstruction of the complete sample volume (Figure 1). Correlations of these nano-features with statistical, experimentally proven values of HEDM ignition characteristics in the Ni-Al system are also investigated.

Experimental datasets from Ni/Al composite particles of each investigated HEBM time are collected until statistical convergence is reached. Each dataset is digitized using 3D reconstruction software and analyzed using distance-ordered thinning algorithms combined with the determined diffusive distance maps. Using the 3D reconstructions, accurate analysis relating to diffusive layer thickness of both Ni and Al, surface area contact between reactants, along with a multitude of other nanostructural features can be determined. Utilizing quantitative nanostructural data, an accurate relationship was determined that relates the ignition characteristics to the nanostructural properties.

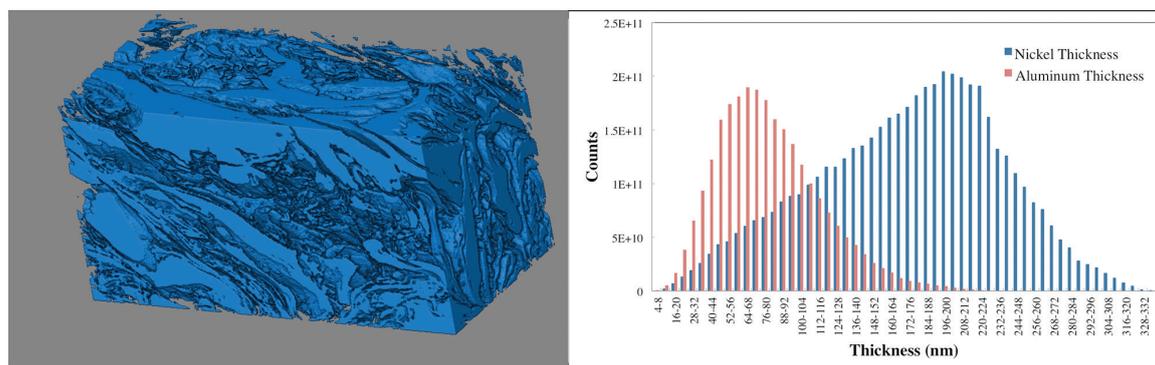


Figure 1: a) 3D reconstruction of Ni/Al composite particle, b) Layer thickness distribution obtained with 3D reconstruction.

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Abstract: 1122

CARBON ISOTOPE ¹³C LABELLING IN SiC NANOFIBER SYNTHESIS USING SHS APPROACH

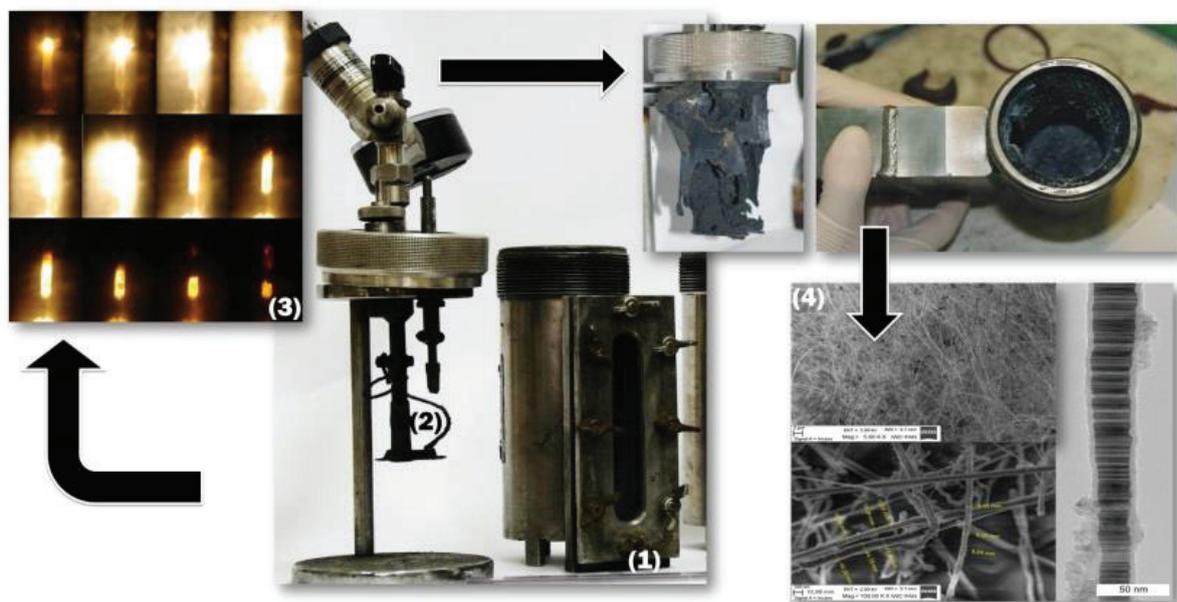
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An important group of pyrolants are those constituted from metallic or non-metallic reducer and halocarbon compounds [1]. We found earlier [2] that SiC nanofibers (SiCNFs) can be efficiently SHS-produced using the following scheme



The parametric studies of this process showed [3] its yield depended on combustion variables, i.e., atmosphere and initial pressure. A partial departure of the reaction from the thermodynamic equilibrium was suggested, too. Further optimization of SiCNFs production calls for the knowledge of the reaction mechanism. We present here the combustion of the powdered stoichiometric mixture of Si ($\leq 64 \mu\text{m}$, Aldrich)/PTFE ($\leq 1 \mu\text{m}$, Aldrich) = 34/64, either in air or in argon (initial pressure equal to 10 atm.). Pure SiCNFs were isolated following the wet chemistry protocol outlined elsewhere [3]. The carbon originated from PTFE in the starting combusted mixture was in the following runs steadily substituted (50, 80 and 90 wt% percent) either with powdered ¹²C or ¹³C carbon black still keeping the initial C/Si ratio constant. In case of the leanest composition (10 wt% of carbon from PTFE) the combustion proceeded only in the vicinity of the igniting tape. For 20 wt% substitution the combustion took place only within the crucible volume (with relatively high content of 3-D microcrystallites of SiC), without the expansion of the products within the entire reactor volume. For the content of C (originated from PTFE) higher than 20 wt% %, the system behaves in a typical way as for pure PTFE: the gas-phase expansion of the products to the whole volume of the reactor results in the fast and abundant formation of sponge-like product containing SiCNFs, following the VLS growth mechanism. Thus, we showed the solid starting carbon can partially participate in gas-phase reactions leading towards SiCNFs growth. Those findings were in line with SEM observations of product morphology and the content of un-reacted Si obtained from chemical analyses. Raman and/or NMR analyses of the product (both before and after purification) resulting from the runs with solid ¹³C isotope helped to establish the extent of solid carbon participation in gas-phase reactions of SiCNF formation.



Experimental setup: high-pressure stainless-steel reactor with optical follow-up of the combustion (extremely fast process, within 1 s) and SEM/HR TEM images of products (SiCNFs with diameter $50 \text{ nm} \pm 20 \text{ nm}$ and length up to several microns).

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Acknowledgement: This research has been supported by NCN grant No. 2012/05/B/ST5/00709.

Abstract: 1143

SUPPRESSION EFFECT OF REACTION TEMPERATURE ON COMBUSTION SYNTHESIS OF TITANIUM CARBOSULFIDE

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MAX Phases with the general formula $M_{n+1}AX_n$ ($n=1\sim3$) and unique properties are expected to bridge the gap between properties of metals and ceramics [1,2]. Our research group has exhibited to be possible to prepare some MAX phases, e.g. Ti_2AlC and Ti_2SC , by combustion synthesis [3-5]. In the preparation of Ti_2SC , we have revealed to be effective to cool a reaction container before combustion synthesis for suppressing drastically active reactivity [4]. The purpose of this study is to investigate addition effect of NaCl as a cooling agent on reactivity of Ti_2SC , microstructures and some properties of the materials.

We prepared mixtures of titanium, sulfur and graphite powders as raw materials for synthesis of Ti_2SC . In addition, NaCl powder as the cooling agent were added into the above mixtures to be compositions of Ti: C: S: NaCl: 2:1:1:0.25 ~ 1.0 in molar ratio. They were wet-mixed with ethanol for 1 hour. The mixture was dried fully, followed by molding into a pellet by a hydraulic press. Combustion synthesis was performed in air by using nichrome wire coil. NaCl was washed away after combustion synthesis.

As a consequence, we could get Ti_2SC successfully in all compositions. Measured maximum temperatures lowered from 1300 to 1100 °C as increasing the quantity of NaCl. When the reaction temperature was high, flame generated from the specimen during the reaction and the specimen became hard. On the other hand, when the reaction temperature was low, the specimen was brittle. From XRD patterns, it was revealed that the specimens consisted of mainly Ti_2SC phase, accompanied with slight TiC phase. Though the formation of Ti-S system phases has been suggested in another study [6], we could not detect them in this study. Results of TG-DTA showed that oxidation weight change of Ti_2SC was inhibited up to 350 °C in air as well as MoS_2 , and 650 °C in argon. TEM micrographs show that Ti_2SC has thin film and band-like structures (see Fig. 1). Their bandwidth is several tens of nanometers. The observations reveal that Ti_2SC phase is crystal with strong anisotropy and has similar microstructures to those in another study [7].

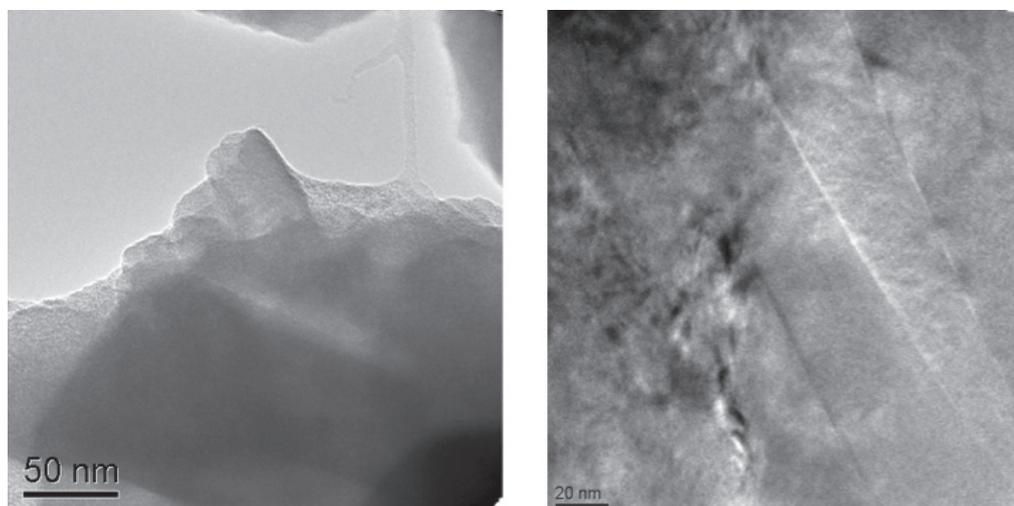


Fig. 1 TEM images of Ti_2SC phase: (a) thin film-like and (b) band-like structures.

Acknowledgment

This work was supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Number 20560695.

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Abstract:1057

QUANTITATIVE ENVIRONMENTAL ASSESSMENT OF SOLUTION COMBUSTION SYNTHESIS OF OXIDE NANOMATERIALS

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Among soft chemistry strategies for the preparation of advanced functional oxide nanomaterials, solution combustion synthesis (SCS) can be easily considered the most appealing one. Indeed, with respect, for example, to sol-gel (both hydrolytic and non-hydrolytic) and hydrothermal (or solvothermal) techniques, SCS is significantly less energy and time consuming, the reason of which mainly relies in its self-sustaining character [1, 2]. However, although SCS advantages have been widely recognized and accepted worldwide, contributing to make this synthetic route well fitting in the green inorganic chemistry field [3, 4], quantitative data related to its environmental as well as human health impact is missing in the scientific literature.

Therefore, starting from a previous work from our group [5], in which the green metrics evaluation of a hydrolytic sol-gel synthesis of TiO₂ nanoparticles was accurately investigated, a similar approach was applied in the present work to quantitatively assess the impact of SCS of similar oxide material.

Particularly SCS of anatase nanoparticles consists in the following three reaction steps [6]: hydrolysis (eq. 1), nitration (eq. 2) and CS employing glycine as fuel (eq. 3).



A first evaluation, from a mere chemical point of view, was realized by means of the software EATOS (Environmental Assessment Tool for Organic Syntheses [7]). This software allows calculating some important environmental parameters, by considering data, which are easily available from the material safety data sheets.

Moreover, in order to take into consideration other potentially impacting categories such as transportation, energy and time requirements, thus realizing a cradle to the grave environmental evaluation, the Life Cycle Assessment (LCA, [8]) of the SCS of anatase TiO₂ nanoparticles has been realized.

The obtained results will allow for the first time to quantitatively determine the widely recognized "greenness" of SCS technique, and, concurrently, to compare this synthetic strategy to those more conventionally employed. The quantitative environmental parameters obtained by the combined EATOS-LCA methodology, will be extremely useful to inorganic chemists and material scientists with a strong environmental awareness.

The potential applicability, of the here proposed quantitative environmental assessment to further combustion synthesis-based processes and products will be discussed as well.

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Abstract: 1111

SOLUTION COMBUSTION SYNTHESIS OF PEROVSKITE OXIDE NANOPARTICLES: CONVENTIONAL VS. MICROWAVE IGNITION

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Perovskite oxide-based nanomaterials and nano-structured materials find emerging high technological applications practically on a daily basis, including Solid Oxide Fuel Cells (SOFCs), catalysts, sensors and microelectronic devices. Although conventional soft chemistry routes allow obtaining these materials at lower temperatures with respect to the "ceramic" one (which still remains the method of choice for industries), most of these strategies still suffers from requiring rather long reaction times, tedious work-up procedures, considerable amount of energy and the use of large volumes of organic solvents [1-3].

On the opposite, solution combustion synthesis (SCS) surely represents a more energy and time efficient alternative [4-6] being the energy required limited to the ignition step and being the reaction rate greatly increased as a consequence of the high exothermicity of the reaction itself.

In the present work SCS of lanthanum ferrites (LaFeO₃) as well as of bismuth ferrites (BiFeO₃) perovskite nanoparticles has been investigated in detail. Particularly, results obtained by conventional ignition of exothermic reactions have been fully compared with those achieved by exploiting microwave (MW) energy irradiation, as ignition source. Indeed this latter innovative heating technique has been recently recognized [7, 8] as a process intensification promoting ignition strategy due to its unquestionable enhancements in energy transfer efficiency and rapidity due to the strong MW-absorbing abilities of most of the reactive salty solutions.

Indeed, for both the oxide systems studied, the use of microwaves allowed a significant reduction of the ignition time. Moreover, particles size distribution resulted depending on the heating technique employed, mainly as a result of volumetric nature of microwave heating and the dielectric properties of the as synthesised products [9].

On the opposite, typically, the ignition strategy neither affected the obtained phases nor the particles morphology.

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HALL A - Wednesday, October 14 / 2015

Keynote VI - Abstract: 1006

CONTRIBUTION OF SHS TO ADDITIVE TECHNOLOGY OF SELECTIVE LASER AND ELECTRON BEAM SINTERING

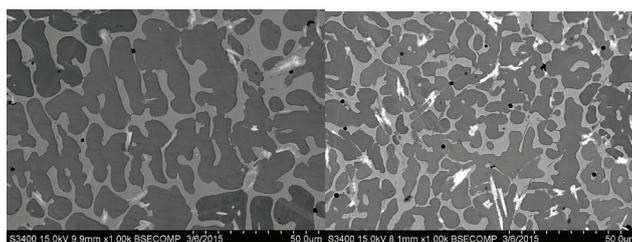
*Evgeny Levashov*¹, Yury Pogozev¹, Vladimir Sanin², Vladimir Yukhvid², Dmitry Andreev², Aleksander Zaitsev¹, Zhanna Sentyurina¹, Alla Logacheva³, Anatoly Timofeev³

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Designing refractory materials (RMs) based on TiAl and NiAl aluminides, which are capable of ensuring high strength, corrosion resistance, and thermodynamic stability under high loads, in aggressive environments, and at high temperatures up to 1100°C, while being characterized by low specific weight ($\sim 5 \text{ g/cm}^3$) is a promising trend in research. One of problem includes structure heterogeneity (in particular, due to liquation phenomena, poor sinterability and low plasticity), which impedes production of intermetallic-based alloys and may cause impermissible variability in performance parameters. Additive 3D technologies of selective electron beam melting (SEBM) and selective laser melting (SLM) are widely used over the world. However, granular powder materials having regular spherical shape and specific grain size are needed to manufacture geometrically complex parts using additive technologies. In this connection, integral technology are currently developing and include: 1- centrifugal SHS casting of a RM semi-product based on NiAl and TiAl using oxide raw material; 2- vacuum remelting of the RM semi-product with alloy structure modification using nanopowder containing master alloys and further electrode molding; 3- centrifugal sputtering of electrodes and classification of granules to the specified grain size. SHS of cast semi-products (ingots) from promising NiAl- and TiAl-based alloys under centrifugal forces was performed, including searching for the optimal modes to provide the greatest degree of phase separation in the target product from the slag phase and formation of the specified alloy composition with the allowable impurity content. The features of structural phase transformations of the synthesis products were studied during centrifugal SHS casting. Optimization of temperature-time modes of vacuum induction remelting of SHS semi-products, concentration of alloying and functional additives, and crystallization conditions were carried our in order to obtain electrodes with satisfied quality on criteria of chemical homogeneity, grain size of the main phases, amount of impurities, residual porosity. Fig. 1 demonstrate electrode ingot based on NiAl produced by integral technology and his microstructure before and after modification by ZrO_2 nanoparticles. Grain size of NiAl, $\text{Ni}_{20}\text{Al}_3\text{B}_6$ phases became smaller in 2,5-3 times.



a



b

c

Fig. 1. Overview of electrode ingot based on NiAl produced by induction remelting in optimal conditions (a) and his microstructure: before (b) and after modification by nanoparticles (c)

Electrodes obtained were tested in centrifugal sputtering of granules. Granules based on TiAl alloy (a), their structure (b) and size distribution 40-100 μm are shown on Fig. 2.

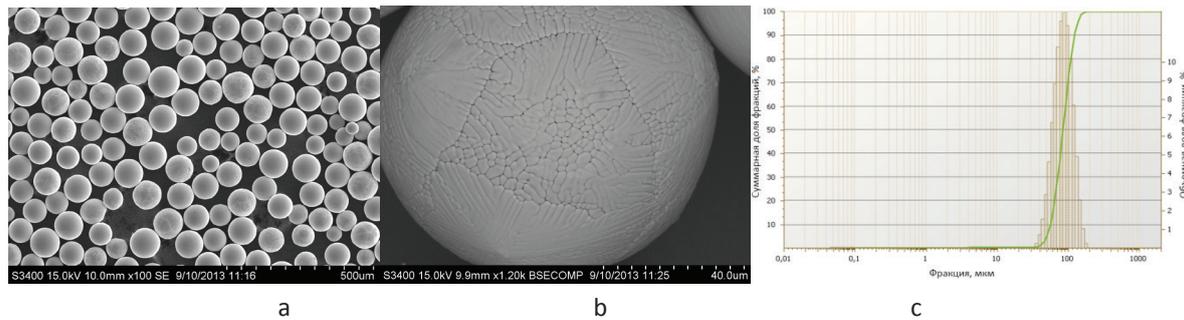


Fig. 2. Granules based on TiAl alloy produced by centrifugal sputtering (a) and his microstructure (b) and grain size (c)

Authors gratefully acknowledge the support from the Ministry of Education and Science of the Russian Federation in the framework of Federal Target Program on Priority Directions of R&D in 2014-2020 (agreement 14.578.21.0040, project RFMEFI57814X0040).

Abstract: 1073

WORLD FIRST 3D PRINTED CATALYSTS BLOCKS ALSO ASSISTED BY SHS AND SCS

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The thermal efficiency of gas-turbine power plants could be dramatically increased by the development of new structural materials based on molybdenum silicides, which can operate at temperatures higher than 1300 °C with no need for cooling [1-3]. A major challenge, however, is to simultaneously achieve high oxidation resistance and acceptable mechanical properties at high temperatures. For example, molybdenum disilicide (MoSi_2) has excellent oxidation resistance and poor mechanical properties, while Mo-rich silicides such as Mo_3Si and Mo_5Si_3 have much better mechanical properties but poor oxidation resistance. The addition of boron to Mo-rich silicides improves their oxidation resistance through the formation of a borosilicate surface layer. In particular, Mo_5SiB_2 (called T_2) phase and alloys based on this phase are promising materials that offer favorable combinations of high temperature mechanical properties and oxidation resistance.

The synthesis of Mo-Si-B multi-phase alloys is usually difficult because of their extremely high melting temperatures. Mechanical alloying has been considered as a promising method for manufacturing these materials [4-6]. This method, however, requires long milling times, leading to large energy consumption and contamination of the product by grinding media.

In the present paper, alloys of T_2 phase and TiB_2 have been fabricated from Mo, B, Si, and Ti using mechanically activated self-propagating high-temperature synthesis (MASHS). Mo/Si/B mixtures for the formation of Mo_5SiB_2 - TiB_2 materials exhibited spin combustion. XRD analysis has shown that along with the desired Mo_5SiB_2 and TiB_2 , the products contain Mo_5Si_3 , Mo_3Si , and MoSi_2 phases.

The chemical oven technique, recently used for synthesis of a single T_2 phase [7], has enabled fabrication of α -Mo/ Mo_5SiB_2 / Mo_3Si (Mo-12Si-8.5B) alloys (Fig. 1), which are promising materials for ultrahigh-temperature structural applications.

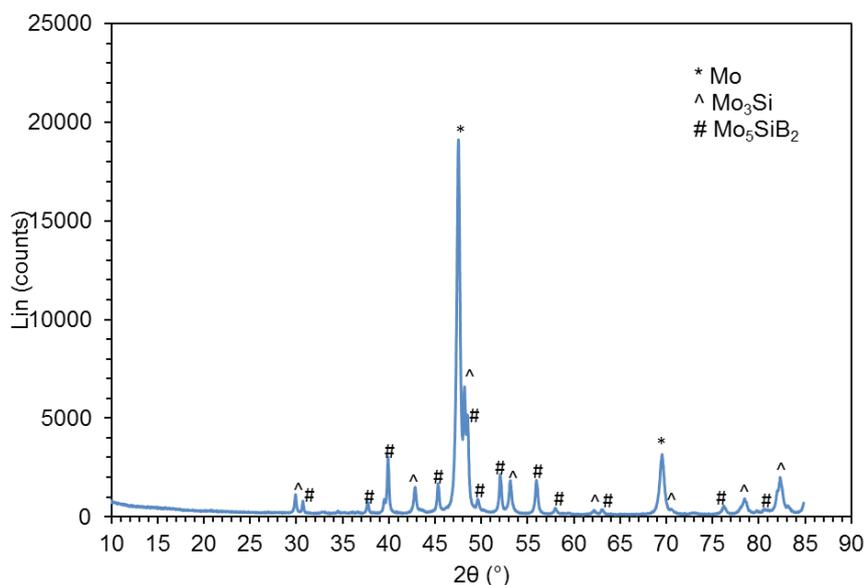


Figure 1: XRD pattern of products obtained by combustion of Mo-12Si-8.5B mixture.

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Abstract: 1076

CENTRIFUGAL METALLOTHERMIC SHS OF CAST CHARGED MATERIALS FOR FOLLOWING METALLURGICAL TREATMENT

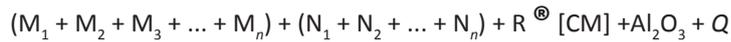
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Heavy-duty items for operation at 700-1100°C are normally fabricated from ductile wrought and cast alloys of nickel, cobalt or iron [1]. The work on their improvement and design new alloying systems and improving casting technology is ever in progress [2]. A key problem here a fine-grain structure and specified level properties the cast items. Modern methods for production of cast items from high alloys (superalloys) generally include (a) fabricating of charged materials (CMs), or alloys for subsequent casting with desired composition and microstructure and (b) subsequent casting of CMs into machine parts of desired configuration. The quality of CMs can have a significant impact on both parameters of casting process and properties of target products.

Marked advance in service parameters of final components can be achieved by using the following approach to manufacturing cast materials: (1) synthesis of cast CMs by centrifugal SHS [3] and (2) their remelting under reduced pressure or in an inert atmosphere followed by casting into a mold with desired geometry.

The SHS reactions yielding cast CMs can be represented by the following scheme:



where M_n stands for oxides of Cr, Ni, Co, Nb, W, Mo, Mn, etc.; N_n stands for nonmetals such as C, B, etc.; and R is reducing agent (Al).

The combustion temperature of such mixtures exceeds 3000-3500 K, which makes it possible to obtain composite materials and alloys in the cast form. Short synthesis time (tens of seconds) and the protection of the upper melt surface by oxide melt (Al_2O_3) allows to synthesis the materials in air, which is impossible for electrometallurgical production of such alloys.

SHS process was performed at centrifugal accelerations $a = 10\text{-}400\text{ g}$. In this way, we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product structure more uniform. Thus synthesized CMs exhibited a uniform distribution of the elements over the entire ingot.

Metallothermic SHS was used to fabricate the following three composites: Ni-based **(I)** Ni-Mo-Al-Hf-Mn-B, **(II)** Ni-Al-Co-Cr-B **■** Co-based **(III)** Co-Nb-Cr-W-Mo-Al-C. Their microstructures are presented in Fig. 1.

On the first stage, the synthesis process of cast SHS alloys (cast charged materials) under the action of centrifugal forces, including the optimal conditions search promotes deepest phase separation between target metal products and slag phase, formation of required alloy composition with an acceptable level of impurities were carried out.

On the second stage, time-temperature regimes for the CMs remelting and structural studies produced castings of the alloys we studied.

Our results can be expected to provide a technological background for a new cost-effective two-stage process: (a) SHS fabrication of cast high alloys with a desired composition and (b) their metallurgical remelting for production of castings specified configuration.

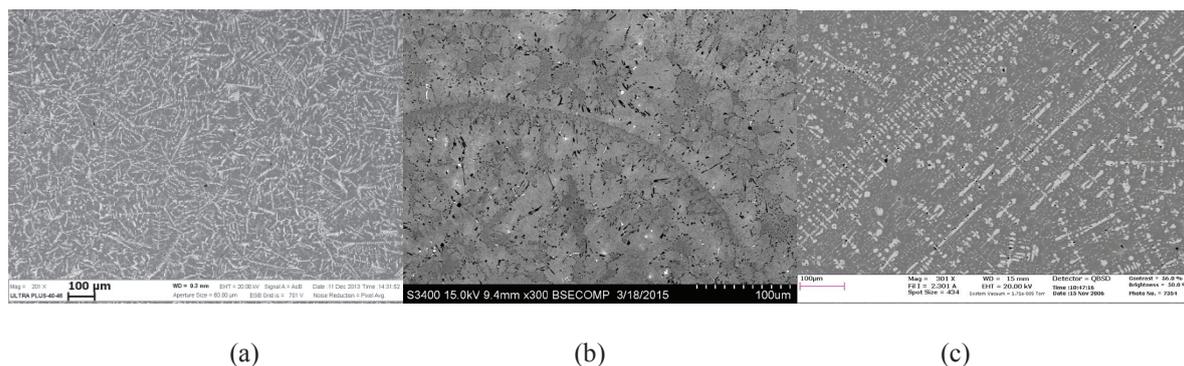


Fig. 1. The microstructure of SHS-produced CMs: (a) Ni-Mo-Al-Hf-Mn-B, (b) Ni-Al-Co-Cr-B), and (c) Co-Nb-Cr-W-Mo-Al-C.

This work was supported by the Russian Ministry for Education and Science in the framework of Program on Priority Directions of R & D in the years 2014-2020 (agreement no. 14.578.21.0040, project code RFMEFI57814X0040).

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Abstract: 1050

HIGH PERMITTIVITY OF BARIUM TITANATE PREPARED BY SHS/QP

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Recently, several methods have been studied in order to obtain BaTiO₃ with high permittivity and low dielectric loss [1-2]. According to the internal barrier layer capacitance (IBLC) model, with the nanograined interface as the internal barrier layer, Valdez-Nava and colleagues produced nanograined BaTiO_{3-x} ceramic with a very high permittivity (up to 10⁶ at 1 kHz) by spark plasma sintering (SPS) [3]. However, its dielectric loss is too high (more than 50% at ambient temperature). To control the dielectric loss of BaTiO₃ ceramics with high permittivity, Chung and co-workers [4] utilized core@shell technology and successfully optimized the high permittivity of BaTiO₃. Here, the initial core particles were coated [5] by a highly insulating shell as the grain boundary.

In this abstract, BaTiO₃ ceramics with high permittivity were fabricated with BaTiO₃ and SiO₂ by the ball-milling method. An in-situ formed fresnoite (Ba₂TiSi₂O₈, BTS for short) interface was formed around the semi-conductive BaTiO₃ grains after sintering the ball-milled powders. The ball-milled powders have an improved sintering capacity and increase in density after sintering.

In order to investigate the microstructure of interfaces (BST-glass and crystallized BST-grain) and the related permittivity property, an ultra-fast sintering method termed self-propagating high-temperature synthesis plus quick pressing (SHS/QP) was used to fabricate the BaTiO₃/SiO₂ ceramic. The green specimen is heated during an exothermic reaction of sacrificial powders around the specimen. The sacrificial powders are used for a self-propagating high temperature synthesis (SHS) in which an ultra-fast heating rate (more than several thousand centigrade per minute) can be achieved. After SHS combustion, the green specimens are in a high-temperature heating state and a large mechanical pressure is applied. Then, the nearly full dense ceramics can be obtained in several minutes [6]. The SHS/QP technique is conducive to preserving the high-temperature microstructure [7] because of the ultra-fast heating rate and quenching conditions. The interface microstructure at high temperature can be preserved for additional detailed study. The dielectric property of BaTiO₃/SiO₂ before and after annealing was measured. Results shows the newly formed BST (Ba₂TiSi₂O₈, fresnoite) interface acts as a dielectric barrier in the final ceramics and an oxidation barrier during the annealing process.

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Keynote VII - Abstract: 1038

CENTRIFUGAL SHS OF CAST ‘HIGH-ENTROPY’ METAL ALLOYS

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Because of valuable properties, high-entropy alloys (HEAs), or multi-component alloys with equiatomic or close-to-equiatomic compositions, are becoming new hot spots in the materials science and engineering community [1, 2]. Depending on their composition, HEAs may exhibit valued physicochemical properties, especially in such applications as high-temperature and coating materials with high hardness and wear resistance.

Nevertheless preparation of multicomponent materials is not an easy task. Such materials should be highly homogeneous and their production requires complicate facilities and expensive mold materials so as many of the alloys content has high chemical active component (Ti, Al, Zr, Hf *etc.*)

In this work, we explored a cost-effective SHS process for fabricating cast high-entropy alloys—NiCrCoFeMnAl_x (**I**), NiCrCoFeAlCu_x (**II**), NbTiMoZrCrAl_ySi_x (**III**), *etc.*—through the following aluminothermic reaction:



where (MeO)_i = NiO, Cr₂O₃, Fe₂O₃, Co₃O₄, *etc.*; FA is some functional additive facilitating phase segregation; and *Q* the reaction heat.

Since combustion temperature of typical thermite-type SHS mixtures is in the range of 2500–3500 K, this technique affords fabrication of cast materials (alloys, composites, *etc.*). In this study, HEAs were prepared by combined centrifugal casting–metallothermic SHS and characterized by SEM and XRD. Combustion was performed at centrifugal accelerations *a* = 10–400 g. In this way, we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product structure more uniform. Thus synthesized HAEs exhibited a uniform distribution of the elements over the entire ingot. An increase in *x* (in **I**, **II**, **III**) was found to markedly change the microstructure (Fig. 1) and phase composition of HEAs.

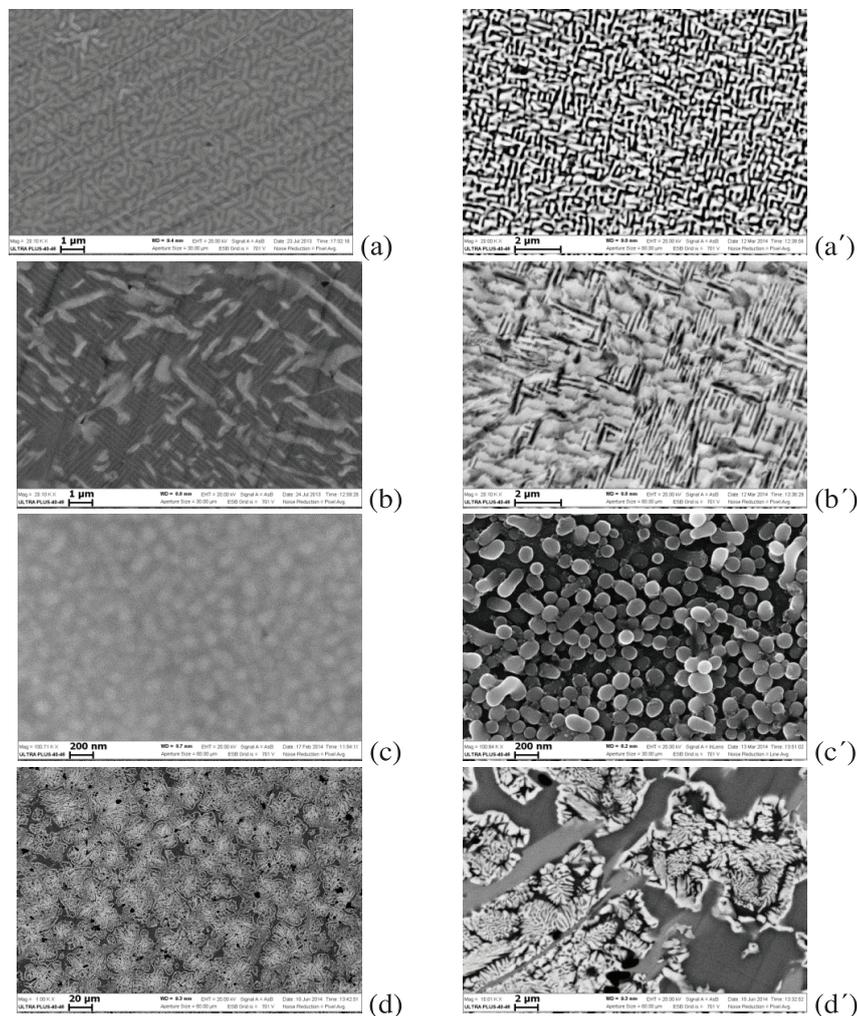


Fig. 1. SEM images of HEAs: polished (a, b, c, d) and after etching (a', b', c', d'); (a, a') NiCrCoFeAl, (b, b') NiCrCoFeAlCu, (c, c') NiCrCoFeMnAl_{1.6}, (d, d') NbTiMoZrCrAl_{0.5}Si_{1.0}

This work can be regarded as the first positive experience in SHS of cast HEAs. The present results can be expected to provide a technological background for a new cost-effective process for fabricating HEAs,

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Abstract: 1115

MICROSTRUCTURE AND PROPERTIES OF Al_2O_3/ZrO_2 EUTECTIC COMPOSITE BY COMBUSTION SYNTHESIS MELT-CASTING UNDER LOW PRESSURE

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Recently, Al_2O_3/ZrO_2 eutectic ceramics are attracting considerable interest because of their combination of high strength and toughness at elevated temperatures due to the special fiber or lamellar structure[1-3]. At present, several advanced techniques are employed to prepare Al_2O_3/ZrO_2 eutectic, including Bridgman[4], laser heated floating zone (LHFZ), edge-defined film-fed growth (EFG) and micro-pulling down (μ -PD) method[5]. However, large bulk Al_2O_3/ZrO_2 eutectic in centimeter scale with fine interphase spacing ($<1\mu m$) is difficult to fabricate by employing the above mentioned methods. Combustion synthesis, which is a novel preparation and processing technique for high-temperature ceramic and compound, has the advantages of high reaction temperature (3000-4000K) and large thermal gradient (10^3 - 10^6 K/cm) to prepare the large bulk eutectic ceramic[6,7]. Zhao *et al* reported the Al_2O_3/ZrO_2 eutectic with 30 cm diameter was fabricated by simultaneous thermit-combustion and gravity separation using CrO_3 , Al, ZrO_2 , Y_2O_3 and SiO_2 as raw materials [8], and Mei *et al* conducted a similar way to prepare Al_2O_3/ZrO_2 eutectic and studied the effect of gravity field on the microstructure of the products [9].

In previous work, the Microstructure of Al_2O_3/ZrO_2 eutectic coating prepared by combustion-assisted thermal explosion spraying was studied. The Al_2O_3/ZrO_2 coating can be divided into three regions according to the crystal structure along the growth direction. First region in contact with the Cu substrate was amorphous structure, and then was cellular crystal region, in which Al_2O_3 shows cystiform shape, and last dendrite Al_2O_3 crystal, the later-two of

which was embedded in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic matrix[10]. Moreover the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic ceramic composites were obtained by explosion synthesis[11], but it had the disadvantages that the pressure was higher than 30MPa and the size of products was smaller than $\Phi 20 \times 40 \text{mm}^3$. In this paper, $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic ceramics were fabricated by combustion synthesis under low pressure using Al and $\text{Zr}(\text{NO}_3)_4$ as raw materials. It had the advantages that the pressure was lower than 10MPa so that the safety of production could be ensured and large bulk products, which could reach $\Phi 60 \times 50 \text{mm}$, could be obtained.

The eutectic microstructure showed that rod-like ZrO_2 embedded in Al_2O_3 matrix with a spacing of 280 nm. Due to nanostructured eutectic, pull-out and bridge effects of rod-like ZrO_2 , as shown in Fig1., the bending strength and fracture toughness of the eutectic ceramic composites reached 1060MPa and $11.2 \text{MPa}\cdot\text{m}^{1/2}$, respectively.

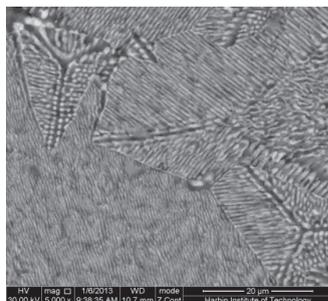


Fig.1 Backscattered electron image of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic

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Abstract: 1148

PRODUCTION OF NICKEL BASED SUPERALLOYS BY SHS PRODUCTION METHOD

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The earliest study about self-propagating high-temperature synthesis (SHS) technique which was a simple, low cost and low energy required process has been published by Merzhanov, Borovinskaya and Shkiro in 1967, described as the production of refractory inorganic materials from powder mixtures of a metal with nonmetal such as C, B or etc., by thermal explosion with combustion wave occurred during the exothermic reaction. During the last 50 years, all known structural ceramics, metal alloys, composite materials and intermetallic compounds were produced by SHS techniques both under normal atmospheric condition and under controlled atmosphere (inert, vacuum, high or low pressure, artificial gravity conditions). SHS production method is a mode of combustion process and first step of the process can be started with initiation of the powder mixtures by using different techniques (such as flux ignition, laser ignition, heated gas, heating coil, furnace, etc.) to produce a combustion wave. The synthesizing process begins when the combustion wave reaches heat release zone in nonequilibrium structure or the synthesis zone in the equilibrium structure [1-10].

In this study, Self-Propagating High-Temperature Synthesis (SHS) method was used for production of nickel based superalloys with a high energy efficient, fast and low-cost production technique. The effects of the initial mixtures and the reaction parameters on the reaction efficiencies, metallic recovery values and the compositions of SHS alloys were investigated mainly during the experimental studies. The raw materials used in the SHS experiments were high grade metal oxide powders and high purity metallic Al powders were supplied from Alfa Aesar®. The estimated alloy compositions in the final mixtures were calculated by thermodynamical investigations and the initial mixtures were prepared from mixing of dried metal oxide powders with Al powders calculated to produce the estimated alloy compositions. The powder mixtures were charged into a crucible and compacted after they were mixed thoroughly for 15 minutes in a turbula mixer. A copper crucible used in batch-type SHS reactions. A resistance wire was placed at the top of the crucible and the reaction realized by passing current through the wire. After initiation the resistance wire was taken out from the system and a highly exothermic reaction became self-sustaining and propagated throughout the SHS mixture. The obtained SHS products were discharged from the crucible after cooling. In the refinement studies, obtained SHS alloys with different compositions were used and remelted in an Edmund Buhler MAM-1 compact arc furnace. The remelting processes were carried out on an isolated chamber, and the arc was generated with W electrode on water-cooled copper plate. The remelting and cooling processes were realized rapidly, and after cooling the refined SHS alloys were characterized. The maximum total metal recovery value was measured as 80% without any Al₂O₃ addition. While the addition of 5 wt.% Al₂O₃ made increases in total metal recoveries, 10 wt.% addition decreased. The results of the chemical analysis showed that SHS alloys were produced within the composition limitations of the commercial superalloys compositions.

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Keynote VIII - Abstract: 1162

ONGOING DEVELOPMENT ACTIVITIES OF BORON LOADED PROPELLANT AT ROKETSAN

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Rockets and missiles, like most of the volume-limited propulsion system, primarily require high-energy density fuel ingredients for maximum flight range. Boron is considered to be a good fuel candidate as it has the highest volumetric combustion energy among all the elements [1]. However, due to its own negative traits such as high ignition temperature and hindered combustion due to liquid oxide layer on particles' surface, it is not easy to realize this potential with conventional rocket engines. Air breathing engines, on the other hand, can be regarded as a good solution for the extraction of energy stored in boron. These engines, as they do not carry the required oxidizer onboard, are much more efficient than conventional rocket engines.

ROKETSAN has been working on air breathing rockets for some time. In this paper, an overview of ongoing development activities of boron loaded propellant will be described.

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Abstract: 1140

SEMI-COMMERCIAL PRODUCTION OF TiB₂ BY SHS: SYNTHESIS, CHARACTERIZATION AND SINTERING BEHAVIOR

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Titanium diboride, TiB₂, is one of the technically most important metal borides revealing exceptional hardness, high melting point and outstanding thermal and electrical conductivity [1]. It is used as evaporation boats for aluminum smelting, armor, cutting tools and nuclear rods. TiB₂ is industrially accessible by carbothermal reduction in induction furnace in the range of 1500-1900° C [2,3]. The process is well-established, but due to high temperatures and long reaction times highly energy consuming. In the last 10 years different alternative synthesis techniques have been developed and discussed in favor of a more economic route among which the magnesiothermal SHS method came to the fore. More than 35 articles and studies are available on this topic, to date, the majority of them published quite recently.

The present talk is based on results of our study on SHS synthesized TiB₂ first started in 2012 in small quantities (50-100g, starting mixture) at Koç University. In this period, all preparation parameters (molar ratio of reactants, flux materials, etc.) hitherto known in the literature were tested and optimized. The acid leaching plays a crucial role in the purity of the final product. The optimum leaching time and temperature range were found to be 1h and 80-90° C, respectively. The SHS process was then scaled up first to 1kg and finally to a semi-commercial production level of 10 kg raw material/batch (» 2 kg pure TiB₂). Due to severe safety risks, the latter mentioned reactions were performed on the production site of Pavezyum Kimya-Istanbul. The details about the further upscale possibilities of the SHS-based TiB₂ synthesis, related risks and a feasibility study versus carbothermal process will be presented and discussed.

The characterization of the final product by PXRD, chemical analysis, SEM and DLS confirmed that the TiB₂ powder is quite pure (> 96.5wt. %) having an average particle size of ca. 560 nm. The results are well compatible with those reported for the other SHS-based TiB₂ materials. Compared to carbothermal-reduced commercial TiB₂ (TiB₂-CR), it is

an improvement both in purity (TiB₂-CR: ~95wt. %) and particle size (TiB₂-CR: ~4μm). The different morphology of the SHS-based TiB₂ powder is reflected also in the sintering behavior which was investigated by means of Sparkle Plasma Sintering (SPS) in the temperature range of 1400-1800° C. The results will be presented and discussed in context with the recently published SPS study on commercial TiB₂-CR powder [4].

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Abstract: 1002

COMBUSTION SYNTHESIS OF BORON NITRIDE VIA MAGNESIUM REDUCTION USING ADDITIVES

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This study is aimed at enhancing the product yield in combustion synthesis of h-BN using Mg reduction of B₂O₃ as the boron source under a low N₂ pressure by using additives. The reactant powders and the additives were placed in perforated aluminum containers without pressing. Due to a loose and highly porous structure of the powder stack, the surrounding N₂ can penetrate easily into it and the N₂ generated by NaN₃ or C₃H₆N₆ escapes easily, addition of these two additives only increases slightly the product yield in the low content region but decreases the product yield in the high content region due to decreasing temperature. Addition of inert particles (i.e., MgO or BN) increases the product yield only when the temperature is higher than the melting point of boron, under which coalescence of molten boron is suppressed due to capillary spreading of the molten boron on the particles. When the temperature is lower than the melting point of boron, addition of the inert particles decrease the product yield because of their cooling effect. NH₄X (X = Cl or Br) was found the most effective in enhancing the product yield because it creates an easier route for the nitridation of boron by first converting boron to BX_x, which then reacts with N₂ under the reduction of H₂. A product yield of 67% was achieved by simultaneous addition of NH₄Cl and BN under a N₂ pressure of 1.6 MPa.

Abstract: 1078

CENTRIFUGAL SHS HARDFACING WITH Mo₂NiB₂/Ni COMPOSITE

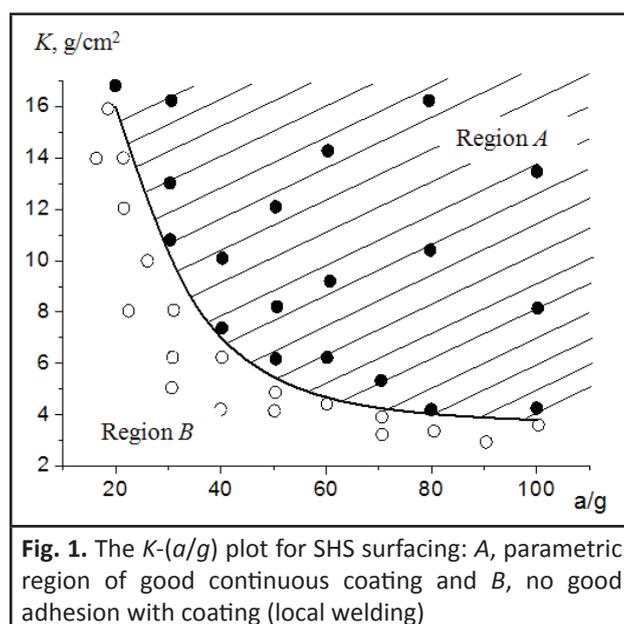
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The borides of transition metals are considered as one of the most promising candidates for production new tungsten free metal matrix composite (MMCs). But binary transition metal borides (Ti-B, Cr-B, Mo-B etc.) exhibit poor sinterability, high reactivity with matrix metals and as the result high brittleness of MMCs. Their application is restricted specific fields and has not wide use. Unlike binary borides, some complex transition metal borides (such as Mo₂NiB₂, Mo₂FeB₂, etc.) have been found most promising for designing new tungsten-free MMCs. Respective phase diagrams predict that ternary borides Mo₂NiB₂ and Mo₂FeB₂ may readily coexist with Ni and Fe, respectively. Recent studies proved that the Mo₂NiB₂-Ni, Mo₂FeB₂-Fe W₂NiB₂ - Ni metal matrix composites with excellent mechanical properties can be successfully produced via boronizing sintering [1]. These MMCs show a unique combination of properties such as high hardness, transverse rupture strength, good fracture toughness, low density, and excellent corrosion resistance.

In the present study, we made an attempt to synthesize cast Mo₂NiB₂-Ni metal-matrix composites and in-situ deposit such coatings onto a steel (and Ti alloy) substrate starting from relatively cheap materials (oxides) an energy- and cost-effective technique of centrifugal metallothermic SHS [2].

The quality of SHS surfacing depends on (a) green composition (T_c and U), (b) charge weight, (c) a/g ratio, and (d) type/weight of substrate. In this work, we fixed green composition and substrate weight (95 g) and varied parameter $K = m_{\text{mix}}/S$ which is the mass of green mixture m_{mix} per unit surface area S of substrate (between 3.5 and 1.5 g/cm²) and centrifugal acceleration a (within the range 1.0-200 g). These results can be used as reference data for deposition of coatings onto substrates of other configuration.

The coatings deposited at different values of K and a were then cross cut and the structure of a transition layer was thoroughly explored as for joint quality. The results are presented in Fig. 1 in the form of the K -(a/g) plot. Here region A corresponds to formation of a continuous coating strongly joined to the substrate while within region B no good joining was attained and deposited coating could be easily detached from the substrate even upon weak mechanical influence (impact).



Varying the values of K and a we can prepare MMC coatings with a thickness ranging between 2 and 8 mm. With increasing K , the coating thickness gradually grows from 3 to 8 mm. In order to deposit thick coatings, one has to use higher values of K ; whereas relatively

The coating has a clearly pronounced composite structure with Ni matrix with the Mo_2NiB_2 particles 3-10 μm in their size uniformly distributed over the volume of cast material. The XRD data confirm that the as-cast MMC coating is formed by orthorhombic Mo_2NiB_2 and intermetallic compound MoNi_4 with insignificant admixture of the MoNi phase. Transition zone (substrate/surfacing) clearly indicates the occurrence of chemical interaction between the two materials. Its small thickness (100-200 μm) can be associated with intense heat sink from melted reaction products into substrate. Transition zone thickness was found to increase with increasing K . Besides Ni, Mo, and B, the transition layer is seen to contain also Fe(Ti). For all coatings, their Fe (Ti) content decreased with increasing coating thickness H .

The Vickers hardness of thus deposited coatings was found to vary between 1000 and 1200 H_V . This makes such samples promising candidates for use in marine and aerospace propulsion engineering, power engineering, gas/oil transportation, as structural engineering materials, armoring materials, etc. This work can be regarded as the first positive experience of SHS surfacing with metal-matrix composites based on ternary borides Mo_2NiB_2 .

The work was supported by the Russian Foundation for Basic Research (joint Russia-Turkey project no. 14-08-91374).

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Abstract: 1008

FABRICATION OF MgB_2 BY COMBUSTION SYNTHESIS UNDER HIGH GAS PRESSURE

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The discovery of high-temperature superconductivity in MgB_2 [1], below T_c 39 K, has elevated considerable interest in the search for similarities and peculiarities in comparison to the high- T_c superconducting cuprates and fullerides [2]. The extreme interest to develop MgB_2 -based materials can be explained by intensive development of technologies that use liquid hydrogen. Although MgB_2 is a simple binary compound it is difficult to produce by conventional methods due to high vapor pressure of the elemental Mg during the elevated temperatures. Moreover, MgB_2 decomposes rather than melts and does not have any accessible liquid-solid transitions at ambient pressures. Thus, MgB_2 can be synthesized by a simple, alternate route: reaction of B with Mg vapor, generally at a temperature of about 900 °C for as little as a couple of hours. Preparation of the materials under high gas pressure can surpass the evaporation of Mg and allows getting a dense structure with superior mechanical properties [3].

Self-propagating high-temperature synthesis (SHS) under high gas pressure is promising approach for manufacturing of the polycrystalline MgB_2 materials. The previous study [4] demonstrated synthesis of bulk magnesium diboride by using SHS method in a flow of argon. In this paper we report the results for fabrication of MgB_2 under high argon pressure. To synthesis of magnesium diborides we used Mg (98%) and amorphous B powder (94%). The mixtures of Mg and B powders were prepared in the following proportions 55.3% Mg and 44.7% B. The two powders were carefully mixed in the high energy ball milling for 3 min and then a mixture was pressed into the specimens under 40 tons at 30 mm in diameter and 12 mm thick.

The tablets were placed into cylindrical preheating furnace of the high pressure reactor and then were heated to initiate SHS process. The pressure of Ar up to 10 atm. was created in the high pressure reactor. Self-sustaining synthesis was initiated at about 650°C (magnesium m.p.). The temperature of the powder bed increased to about 1100°C-1200°C. The reaction was completed after 2-5s. The temperature controller maintained the temperature inside the reactor, while the combustion temperature inside the samples were recorded by using micro thermocouples.

The microstructure and phase analyses of polycrystalline samples were conducted by X-ray analysis and scanning electron microscopy (SEM). XRD are shown that samples have 2 main phases: MgB_2 (72.3 wt.%) and MgO (23.4 wt.%). There are also some small impurities of Mg and SiO_2 . The XRD are identified that MgB_2 phase was increased up to 85 wt.% and MgO phase is decreased up to 12.6 wt.%, after leaching by solution 15%HCl (10ml) + NaCl (5g) + H_2O (10ml) at 80 °C during 60 min. According to SEM observation of MgB_2 bulk samples had the average grain size in the range from about 10 to 45 μm (Fig. 1).

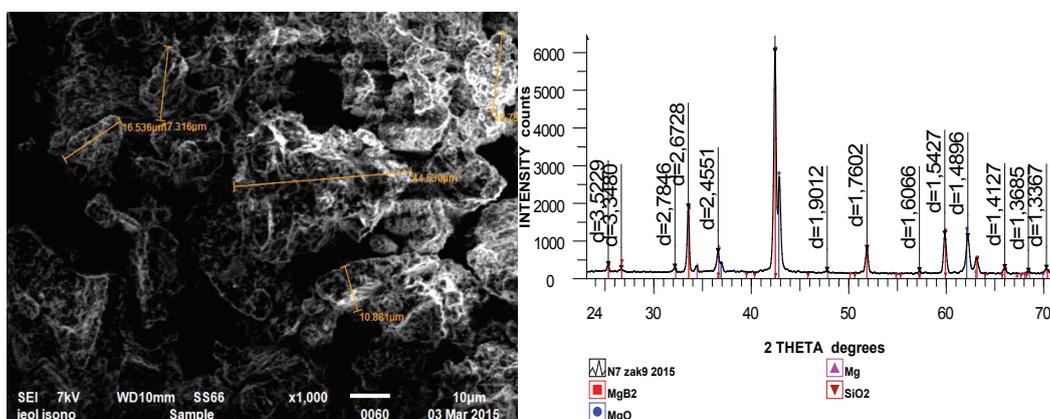


Fig. 1. SEM image of microstructure and XRD analysis of MgB_2

These preliminary results encourage continuing this study on the application of the SHS process under high pressure of inert gas for the fabrication of MgB_2 . Further efforts will have to be devoted to optimization of the final purity of the material. We can claim that synthesis of purity bulk magnesium diboride by SHS method under high pressure of Ar has well prospective to further investigation.

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Abstract: 1167

INVESTIGATION OF Mo-Ni-B TERNARY ALLOYS FOR PRODUCTION OF BORIDE-BASED CERMETS BY SHS METHOD

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Hard materials which are used as cutting tools and abrasion-resistant parts play an extreme important role in industrial applications. Tungsten base cemented carbides (WC-Co/Ni/Fe) are used frequently as well-known hard materials. Some investigations revealed that new hard alloys can be successfully applied to wear resistance applications such as injection molding machine parts. For example, borides which have high corrosion resistance and strength can replace cemented carbides for some specific applications. A new hard alloy alternative contains a metal matrix of nickel as a binder and Mo_2NiB_2 -type boride as a hard phase. Due to the poor sintering behavior of borides and the formation of brittle phases with metals during sintering, reaction boronizing sintering method was mostly used in previous studies which requires high power and consequently higher costs [1]. The Self-propagating High Temperature Synthesis (SHS) technique which is suitable for production of ceramic, intermetallic and metal matrix composites, is an efficient and low cost synthesis method. In metal matrix composites, due to the existence of diluent metal matrix, only high fraction and high energetic ceramic reinforcement is suitable for SHS processing. There are a few works reported about the in situ preparation of both reinforcement and matrix in composites by SHS method [2,3].

In this work, we investigated the production of Mo_2NiB_2 containing cermets by SHS method. Thermochemical evaluations were made to estimate the adiabatic temperatures and possible product compositions in the cast alloys by using FactSage 6.4 thermochemical software. The aluminothermic reduction process was performed in Cu copper crucibles under normal gravity and air environment by using oxides of metals (MoO_3 , NiO, B_2O_3) and Al as a metallic reductant. Alumina, (Al_2O_3) as a functional additive (diluent), were also added in order to reduce the adiabatic temperature of the reaction. Since the attained reaction temperatures for this system during the exothermic SHS process is so high (above 2700°C calculated by FactSage), the process is self-sustained and the melt consists of insoluble mixture of metallic compound and oxide phase which can be segregated under a gravity force. By changing the parameters such as reductant aluminum content and molar ratios of other initial components, we expected to change the yield of target product, mechanical properties, material loss and burning velocity. Different analysis methods (XRD, SEM, AAS, microhardness) were used during the experiments. The obtained SEM image and EDS data of a Mo-Ni-B cermet specimen showed that (Figure 1) nickel reacted with excess aluminum to produce Ni_3Al intermetallic which was formed in the matrix phase (1). The gray angular grains belong to Mo_2NiB_2 region (2) whereas the white ones are MoB (3). The hardness value of the specimen was found as 943 HV.

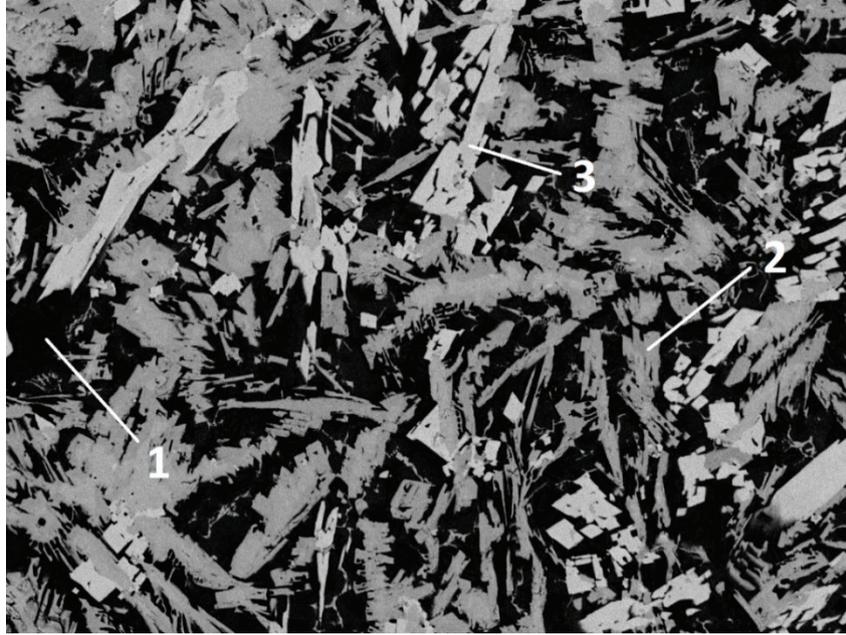


Figure 1. Back scattered electron microscopy image ($\times 500$) of hard alloy containing Mo_2NiB_2 produced by SHS method (1: Ni_3Al , 2: Mo_2NiB_2 , 3: MoB)

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HALL A - Thursday, October 15 / 2015

Keynote IX - Abstract:1142

ENERGETIC COMBUSTION AND SHS: COMPARATIVE ANALYSIS OF THE ACHIEVEMENTS AND UNSOLVED PROBLEMS

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We considered some common and different characteristics of energetic combustion (used for the generation of energy) and technological combustion (used for synthesis of compounds) and analyzed the effect of experimentally found and theoretically confirmed thermodynamic, kinetic, thermophysical and macrokinetic parameters on the combustion front propagation rate and the time of intermediate and final combustion product formation.

We provided explanation for some important differences in the patterns of the energetic combustion and gasless SHS on the basis of the comprehensive analysis of their high-temperature kinetic data. We also considered some achievements in the field of the modern theories of gasless SHS ("solid flame" and others) as well as discuss serious disagreements between these theories and experimental results. We showed that very close values of the liquid-phase diffusion in various melts ($D_l = 10^{-5} \text{ cm}^2/\text{s}$) can explain almost identical flame propagation rates for mixtures of components characterized by tremendously different values of the solid-phase diffusion which resolved one of the main paradoxes of the "solid flame" propagation theory. We confirmed this conclusion experimentally by measuring SHS rates in the range of several orders of magnitudes for Al foil-Ni powder samples.

After analysis of the effect of longitudinal and lateral heat transfer on the front propagation in energetic combustion and gasless SHS, we came to a conclusion about a qualitative difference between these two patterns. We also compared data on impact initiation of explosion in SHS systems and new data on kinetics of high-temperature SHS reactions under static conditions and came to a conclusion about a qualitative difference in their kinetics and about a leading role of mechanochemical interaction under high-speed impact. In this connection, we briefly discussed gasless detonation in SHS systems.

We analyzed gasification of impurities and melting in the preflame zone during SHS in detail for the first time as well as phase formation in the preflame and postflame zones. We considered qualitatively different features of superfast soot formation in classical industrial flames and very slow formation and growth of almost perfect single crystals of refractory compounds in the gasless SHS postflame zone. We showed that the final stage of SHS - phase formation, is responsible for practically important characteristics of SHS products including characterized by a perfect shape and phase composition (and quite often, by poor sinterability) refractory microcrystals synthesized in large SHS-reactors. Same processes and patterns are responsible for the excellent performance capabilities of large-scale SHS-composite items (press-dies, moulds, etc.) which, in accordance with the advanced one-stage SHS-compaction method, cool down slowly after the combustion, and for poor cutting capability of small cutting plates produced from SHS composites containing fast-cooling round grains of refractory carbides (the composition of these materials is close to that of hard alloy TN-20 used for the production of items using a traditional technology of slow sintering in a furnace).

We compared macrokinetic patterns of combustion and synthesis and phase formation of intermediate and final SHS products and came to a conclusion that for new technologies a number of new SHS-composites different from traditional ones produced in powder and ceramics industries should be developed. Such new materials can be manufactured by classical and new SHS-technologies characterized by process temperatures much higher than those of traditional furnace production methods.

Abstract:1048

INFLUENCE OF PHASE TRANSFORMATIONS ON THE SPIN COMBUSTION

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We consider combustion of a cylindrical finite-size sample formed from a mixture of solid reactants and inert low-melting metal. Ignition is carried out on the bottom surface of the cylinder for a finite period of time. The initial reactants and the reaction products are considered to be solid and melting of inert metal is not accompanied by a liquid phase. The surface of the sample is considered to be thermally insulated (adiabatic combustion). A dimensionless mathematical model describing the propagation of three-dimensional non-stationary combustion wave in the sample is presented in [1]. The influence of phase transition on the process of heat transfer is taken into account by introducing an effective heat capacity function $c(\theta) = 1 + Ph\delta(\theta - \theta_L)$. A similar method was used to describe the effect of melting of the inert component on the propagation of one-dimensional combustion wave [2]. Here, Ph is the relative heat of melting; $\delta(\theta)$ is the delta-function; θ_L is the dimensionless melting temperature. The mathematical model of combustion is investigated numerically by the finite-difference method. The sample radius R_0 and the phase transition parameters Ph и θ_L were selected as the governing parameters. The parameter R_0 indicates how much the radius of the cylinder is greater than the characteristic thickness of the reaction zone. The main purpose of the investigation is to study stationary spin combustion modes and the influence of the phase transition. Heat losses are compensated by the increase in thermal effect of the reaction, and the adiabatic combustion temperature remains constant. Stationary and periodic modes of solid flame combustion without melting are described in detail in [3]. The stationary single spin combustion mode that is the easiest one for describing the changes in the structure of the front is set on the samples of a small diameter $R_0 = 20 \div 40$ at a short distance in direction to the instability of the one-dimensional front. Fig. 1 shows the temperature distribution in the diametrical section passing through the front point on the axis of the cylinder with a conversion level equal to 0.5. The maximum temperature gradients are observed in the high-temperature region (combustion source). The temperature field rotates clockwise or anti-clockwise around the cylinder axis in the diametrical cross-section without changing the structure, and moves along the axis to the fresh mixture. The movement of the combustion source and accelerating the onset of the steady mode can be set by selecting the appropriate local disturbance of the temperature field at the initial moment of time. The combustion source provides a complete turn around a cylinder with a step along the generating line of the cylinder (pitch of a screw) approximately equal to the radius of the sample. High-temperature phase transition $\theta_L = -0.5$ leads to in the change in the structure of the combustion source: the area increases, the isothermal plateau appears near the melting point on the combustion surface, the temperature gradients decrease on the combustion surface. The low-temperature phase transition $\theta_L = -2.5$ has a little effect on the structure of the combustion wave compared to combustion of the sample at $Ph = 0$.

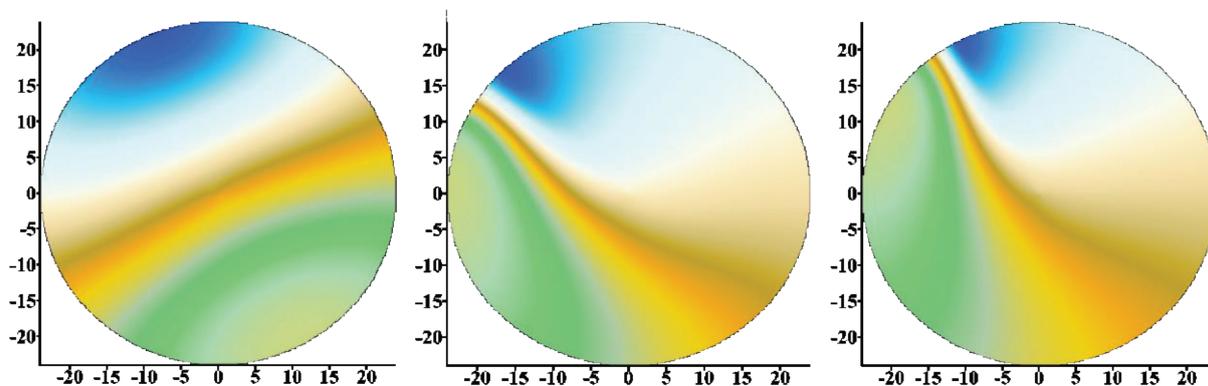


Fig.1 Temperature field: $\theta_L = -0.5$ (a), $\theta_L = -2.5$ (b), $Ph=0$

This work was supported by the Russian Ministry for Education and Science (project no. 10.1329.2014/K).

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Abstract:1139

IN-SITU TRANSMISSION ELECTRON MICROSCOPY AND ELECTRON DIFFRACTION INVESTIGATIONS OF SOLID-STATE REACTIONS IN $\text{Fe}_3\text{Si}(111)/\text{Si}(111)$ FILMS

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The formation of iron silicide phases in thin layers of iron on silicon and in Fe-Si thin layers are of great interest and have intensively been studied in the last decade because of their physical properties. According to the Fe-Si phase diagram a number of Fe_3Si , FeSi, and FeSi_2 modifications can be formed. Ferromagnetic properties in Fe_3Si have attracted attention because they have potential applications in spintronic devices. FeSi_2 exists in two phases, the metallic α phase and the semiconducting β phase. The phase $\beta\text{-FeSi}_2$ is a promising candidate for the use in optoelectronic light-emitting devices and infrared detectors.

It is well known that *in situ* transmission electron microscopy (TEM) allows the direct observation of a dynamic process through imaging and the selected area electron diffraction (SAED) is an ideal approach for the investigation of microstructure evolution. In this work we report the results of the *in situ* TEM and SAED investigation of the processes of solid-state reactions between an epitaxial $\text{Fe}_3\text{Si}(111)$ thin film and Si(111) substrate. In Fig.1 the cross-sectional high resolution transmission electron microscopy (HRTEM) image of the $\text{Fe}_3\text{Si}(111)/\text{Si}(111)$ structure at the initial state is shown. The epitaxial structure have prepared during the simultaneous evaporation from two iron and silicon sources on an atomically pure Si(111)7 \times 7 surface at the substrate temperature of 150°C. This structure has been identified as single crystal Fe_3Si silicide. The goals of the study are to determine the temperature of the initiation of the solid-state reaction and to study the structure and phase composition which is formed at the solid-state reaction.

In situ heating experiments were conducted with a JEOL JEM-2100 (LaB_6) transmission electron microscope at an accelerating voltage of 200 keV. For the heating experiments a Gatan 652 double tilt heating holder was used. The holder allows heating of a specimen from room temperature up to 1000°C with a controllable heating rate from 0.02 up

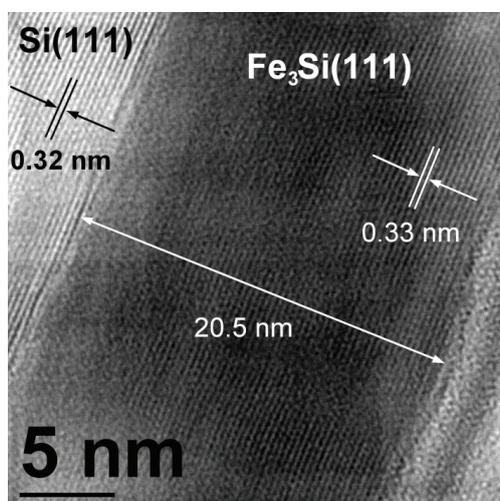


Fig.1 Cross-sectional HRTEM image of the $\text{Fe}_3\text{Si}/\text{Si}(111)$ structure.

to 20°C/s. The TEM is equipped by a Gatan UltraScan 1000 CCD Camera (4 Mpx) which allows acquiring high-resolution images, and, a Gatan ES500W Erlangshen CCD Camera (1.4Mpx) which allows acquiring up to 15 frames/s, so that the time resolution of the video recording is ≈ 0.06 s.

The annealing of $\text{Fe}_3\text{Si}(111)/\text{Si}(111)$ was conducted in the temperature range 200-550°C with the step of 50°C. It was found that the epitaxial $\text{Fe}_3\text{Si}(111)/\text{Si}(111)$ system was stable up to 400°C. The process of the solid-state reaction between the epitaxial $\text{Fe}_3\text{Si}(111)$ film and the monocrystalline $\text{Si}(111)$ substrate began with the formation of ϵFeSi and βFeSi_2 phases during annealing at 450°C. It was established that the growth of ϵFeSi and βFeSi_2 phases occurred with coherent orientation with respect to the initial phases - $\text{Fe}_3\text{Si}(111)$ and $\text{Si}(111)$.

The work was partly supported by the Russian Foundation for Basic Research (grants ## [13-02-01265a](#), 140300515a) and the Ministry of Education and Science of the Russian Federation (grant #2014/71/1763 in the framework of the state assignment for Siberian Federal University for 2014-2016).

Abstract:1158

PRODUCTION OF $\text{ZrB}_2\text{-B}_4\text{C-ZrC}$ COMPOSITE POWDER MIXTURES VIA SHS

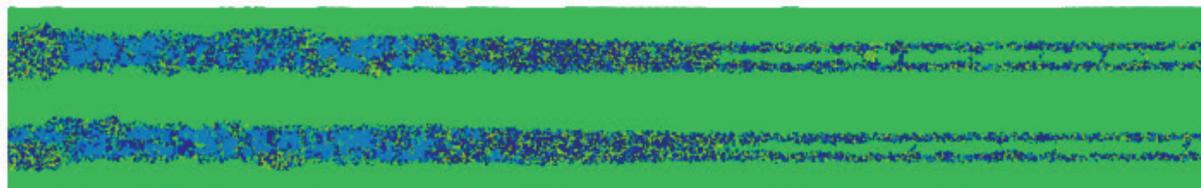
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SHS in nanofolds is of primary importance for their applications like, for instance, soldering and joining technologies. In these multilayers, a huge velocity of the reactive front and a low ignition temperature characterize the SHS process. The challenge is to understand the specificities of the propagating reaction that occur in layered nanometric systems.

We propose a full description of the reaction wave propagation from ignition to completion, by means of molecular dynamics (MD) simulations, using an embedded-atom method type potential. The system is composed of two alloyable constituents (Ni and Al) stacked over a few hundred nanometers. The self-sustaining reaction, initiated locally by increasing the temperature, propagates along the foil, without any further supply of heat, due to the exothermic interdiffusion of the two metals. Beyond the simulation of a large length scale thermal process by MD, this work demonstrates the relation between the dynamics of front propagation and the underlying microscopic processes. Some specific properties are revealed, while well-established experimental characteristics of front velocity are observed.

The figure below shows a snapshot of the arrested reactive front in a Ni/Al multilayered nanofoil. Metals layers are stacked perpendicular to the flame direction. The green areas correspond to atoms in fcc local configuration (Al or Ni). The blue grains show the formation of NiAl intermetallic during the SHS process while multicolor regions denote the presence of amorphous liquid alloy. The zone represented in the figure corresponds to the thickness of the thermal front of about 250 nm.



HALL B - Tuesday, October 13 / 2015

Keynote X - Abstract No : 1062

SHS PRESSING ALUMINUM-CERAMIC SKELETON COMPOSITES ON THE BASE OF Ti_2AlC MAX PHASE

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The aim of this study was to produce aluminum-ceramic skeleton composites (ACSC) based on MAX-phase of Ti_2AlC by the method of SHS pressing. The essence of the process consists in the following. A charge of exothermic mixture of powders Ti+C is placed in a die of a SHS press between two pellets pressed from a powder of aluminum. The SHS process is initiated in the charge and forms a porous skeleton of TiC as the refractory product of combustion. Aluminum pellets are melted due to the heat of combustion. Upon completion of combustion of the entire body of the charge, an excess pressure is applied to the die and aluminum melt penetrates the hot porous TiC skeleton.

SHS pressing was carried out in the die-reactor with the assembly of the pellets housed in a heat insulating sandy shell when the pressure of infiltration was 22, 28, and 35 MPa. The assembly of the pellets and the sandy shell were separated by a layer of carbon cloth. The SHS charge pellets had a diameter of 54 mm, a weight of 70 g and a porosity of 40%. The porosity of skeletons synthesized without compaction was determined by calculation-experimental method and was equal to 50.5%, that required for complete infiltration of the skeletons two aluminum pellets of 25 g each.

It was found that while obtaining the highly porous skeletons, the use of carbon-containing gasifying additives (colophony, carbamide, starch, sodium bicarbonate, sodium tetraborate) in the SHS charge suppresses the formation of the MAX-phases in the system Ti-C-Al during SHS. The best result was obtained when titanium hydride TiH_2 was used as a pore-forming additive. With the addition of 10% (mass) of titanium hydride to the system of $2Ti+C+25\% Al$, the combustion products do not contain impurity phases and consist only of the MAX-phase of Ti_2AlC . Accordingly, the SHS pressed ACSC was obtained by infiltration of synthesis products of $2Ti+C+22,5\% Al+10\% TiH_2$ system with aluminum melt. The results of XRD showed that the infiltration of the hot SHS skeleton with aluminum gave rise to new side phases: MAX-phase of Ti_3AlC_2 (7% by weight), titanium carbide TiC (5%) and titanium aluminide $TiAl_3$ (4%). The content of the basic MAX-phase remains high and the ceramic component of the composite consists of 76% of Ti_2AlC phase.

SHS pressed ACSC are characterized by the formation of an inhomogeneous distribution of aluminum in the sample volume. In the radial direction, two zones are formed with approximately constant different concentration of the aluminum: central and peripheral zones. In the central area, the aluminum content is less than in the peripheral zone. The distribution of the aluminum content over the height of the sample shows that the concentration of aluminum in the inner volume less than in the near-surface volumes. This inhomogeneity is due to different density of the infiltrated skeleton, caused by the nonuniform temperature field in the sample. In consequence of contact with the cold sandy shell, the temperature of the inner part of the sample is greater than the temperature of the subsurface part. Under the action of pressure of infiltration, the hot part is compacted more than the relatively "cold one" and the content of aluminum in the dense part is less than in loose part. With increasing the pressure of infiltration, the degree of compaction of the characteristic zones are aligned, and the inhomogeneity of the composition over volume of the sample decreases.

To assess the mechanical properties of SHS pressed ACSC, the Brinell hardness HB was used. The peripheral zone contains more aluminum and hardness of this zone is less than the hardness of the central zone. In the peripheral zone, the average hardness is only slightly dependent on the pressure of infiltration and is $HB = 128...132 \text{ kgf/mm}^2$. The hardness of the central zone increases with increasing the pressure of infiltration from 140 HB at $q = 22 \text{ MPa}$ to (150...152) HB at $q = 28$ and 35 MPa. In general, the level of hardness of the SHS pressed ACSC corresponds to industrial high-strength aluminum alloys of Al-Zn-Mg-Cu system having a hardness (150...160) HB. Hardening the aluminum alloys is done by heat treatment. However, hardening intermetallic phases have a low thermal stability, as a consequence the alloys have

a low high-temperature strength and are used up to temperatures of 100 to 120 °C. Hardening due to the skeleton of the refractory Ti_2AlC MAX-phase should provide higher high-temperature strength of the SHS pressed aluminum-ceramic skeleton composites compared with aluminum alloys.

The work was performed with financial support of RFBR (project № 14-08-97066).

Abstract No : 1007

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF MULTICOMPONENT CERAMICS BASED ON Zr-Si-Al-B. PECULIARITIES OF COMBUSTION AND STRUCTURE FORMATION

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Composite ceramic materials based on zirconium diboride ZrB_2 belongs to the class of high-temperature materials, which are widely used under the service conditions of ultra high temperatures over 1800 °C and aggressive environments [1]. It is primarily because ZrB_2 has an excellent combination of several properties such as high melting point (3245 °C), high strength, good thermal stability, corrosion and high temperature oxidation resistance [2]. It is known that the addition of Si and Al to boride matrix composites can improve some of the above mentioned properties like thermal stability and oxidation resistance [3]. Protective coatings deposited from ZrB_2 based matrix composites have a great potential for use as thermal protection structures for leading edge parts on hypersonic space vehicles. The use of multicomponent composite cathodes based on ZrB_2 with required concentration of Si and Al dopants for PVD (magnetron sputtering) of such coatings can be expected to markedly simplify a deposition process, to improve coatings homogeneity and process reproducibility, and to shorten a deposition time. Required multicomponent cathodes can be readily produced by combustion synthesis using the technique of so-called forced SHS- pressing.

This study is devoted to experimental investigations of the combustion process in Zr-Si-B-Al powder mixtures designed for the formation of zirconium diboride and silicide doped with Al in an amount of 10 %. We explored the kinetics and mechanisms of the combustion process, with special emphasis on the effect of dilution rate of the green reactionary mixture by final synthesis products. The dilution rate by the final product varied between 20 - 40 %.

The influence of the initial temperature (T_0) and the degree of dilution of the mixture by the final synthesis product on kinetics of the SHS process was studied. The increase in T_0 leads to a proportional growth of combustion temperature (T_c) and rate (U_c). Conversely the increase in the concentration of the final product (inert filler) in the green mixture composition leads to decrease of the T_c from 2400 to 1820 K and U_c from 3,0 to 0,7 cm/s. Furthermore, an increase in dilution rate reduced the values of the effective activation energy of the combustion process from 690 to 260 kJ/mol.

The staging of structural and phase transformations during synthesis were studied by the method of combustion front quenching in a copper wedge followed by SEM and EDS investigations of the sample characteristic areas. Also time resolved XRD analysis was used. An interesting fact is that upon dilution of the reactionary mixture by the final product in amounts of 30 and 40 % leads to primarily formation of zirconium silicides $ZrSi$, $ZrSi_2$ and complex aluminosilicide $ZrSiAl_2$ in the combustion wave. The formation of zirconium diboride ZrB_2 grains takes place in the aftercombustion zone. In the case of the reactionary mixtures without dilution or diluted by the powder of final synthesis products in amount of 20 % the primarily formation of ZrB_2 grains takes place in the combustion wave. The values of the effective activation energy of the combustion process for those mixtures are maximal.

Compact samples of ceramic materials and multicomponent cathodes for magnetron sputtering were obtained by the technology of force SHS- pressing. Their phase composition and structure were studied. It should be noted that the phase composition of the synthesized ceramic materials is slightly different from the calculated one.

Authors gratefully acknowledge the support from the Ministry of Education and Science of the Russian Federation in the framework of Federal Target Program on Priority Directions of R&D in Russia in 2014-2020 (agreement No. 14.575.21.0001, project identification No. RFMEFI57514X0001).

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Abstract No : 1149

PRODUCTION OF ZIRCONIUM DIBORIDE POWDER BY SHS

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In this study, production conditions of zirconium diboride powder, one of the advanced ceramics, by self propagating high temperature synthesis (SHS) method were investigated. Experiments were conducted in two stages including SHS synthesis and acidic leaching.

In the first stage of the experiment, the formation of ZrB_2 was tried to practice by SHS method using technical grade zirconium oxide (ZrO_2), boron oxide (B_2O_3) which was obtained from calcination of domestic product of boric acid (H_3BO_3) with the addition of reductive magnesium (Mg) powder, and obtained powder mixture containing ZrB_2 , MgO, $Mg_3B_2O_6$ and $Mg_2B_2O_5$ was leached with HCl to remove MgO, $Mg_3B_2O_6$ and $Mg_2B_2O_5$.

The effects of the initial molar ratios of Mg and B_2O_3 on the SHS experiments and the effects of temperature, duration, solid / liquid ratio and acid concentration on leaching experiments was investigated, respectively.

SHS experiments were realized in a metallothermic crucible in argon atmosphere. Sponge like sintered black product was obtained at the end of experiments. Increasing in the quantity of magnesium resulted in the evaporation of magnesium due to overheat that was generated by the increase in specific heat value of reduction reaction. The increasing in the addition of boron oxide resulted in the increase in magnesium boride formations.

X-ray diffraction analysis showed that SHS products contained ZrB_2 and MgO as main phases together with ZrO_2 , (Zr, Mg) O_2 , Zr_3O , $Mg_3B_2O_6$ and $Mg_2B_2O_5$.

The experiment with the 1/3/6 ($ZrO_2/B_2O_3/Mg$) of initial molar ratio was determined as the optimum SHS condition. The SHS products obtained by this condition were utilized in the leaching experiments. The powder mixture without including any phases (zirconium oxide, zirconium magnesium oxide) that unleached by acid solution, were used in the leaching experiments by using HCl acid solution to remove the impurities like MgO, $Mg_3B_2O_6$ and $Mg_2B_2O_5$. The temperature of the leaching solution was increased after the addition of SHS powders due to the exothermic reaction. There wasn't any changing in the color of powder was observed after the removal of impurities. In the experiments with 1/10 of solid/liquid ratio, the filtration process wasn't accomplished due to the gel formation of $MgCl_2(H_2O)_6$ phase.

The dissolution rates of Zr, Mg and B increased with the increase of the acid concentration. After the chemical analysis, performed on solutions that were obtained in the experimental stage, Mg content was measured as 2,70-3,05 g/L, B content was measured as 0,90-1,05 g/L and Zr content was measured as 0,5-0,9 g/L.

Consequently, the production of zirconium boride powder has been successfully carried out by self-propagating high-temperature synthesis (SHS) followed by HCl leaching.

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Abstract No : 1130

SYNTHESIS, KINETICS AND MECHANICAL PROPERTIES OF $M_{n+1}AX_n$ BY SHS AND SHS/PHIP

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The members of nano-layered ternary $M_{n+1}AX_n$ ceramics (where $n=1,2,3$, M is an early transition metal, A is a III A or IV

A element and X is C or N) have been attracted increasing interest due to the unique combination of the properties of both metals and ceramics: readily machinable, thermal and electrical conductive, thermal shock and high-temperature oxidation resistant, damage tolerant, lightweight, and elastically stiff. Ti_3AlC_2 , Ti_2AlC , Cr_2AlC , Ta_2AlC and their composites were investigated by self-propagating high-temperature synthesis (SHS) or/and pseudo-hot isostatic pressing (SHS/PHIP). Processing and kinetics of the $M_{n+1}AX_n$ ceramics were concluded. The adiabatic combustion temperature, flame-front propagating velocity, combustion characterization and numerical simulation of the synthesis of $M_{n+1}AX_n$ ceramics were presented. Typical mechanical properties including hardness, flexural strength and fracture toughness were determined. It was found that fine $M_{n+1}AX_n$ crystals could be synthesized by SHS and SHS/PHIP, and the $M_{n+1}AX_n$ matrix composites are identified to be a strategy for improving the mechanical properties of monolithic $M_{n+1}AX_n$ ceramic by SHS/PHIP.

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Abstract: 1165

PROCESSING OF MAX PHASES WITH USE OF SHS TECHNIQUES - ACHIEVEMENTS, PROBLEMS AND PROSPECTS

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The Self-propagating High-temperature Synthesis (SHS) has been used in authors works for preparation of MAX phases having nanolaminate structures, namely single phase and composite materials in the systems of Ti-Si-C-N and Ti-Al-C-N. The review of the possibilities of obtaining near single-phase SHS products, processing of them into sinterable powders and densification of the powders by pressureless sintering and hot-pressing are discussed. Finally, polycrystalline nanolaminate materials with controlled phase composition and microstructure have been obtained. The materials had been investigated as structure and functional materials by testing their mechanical as well as electrical, thermal and magnetic properties. The possibility of using of prepared powders to obtain ceramic polycrystals, composites and FGM, as well as their potential application are discussed. The achievements, problems and prospects in SHS processing of MAXs is discussed in compare to others materials technologies.

Keynote XI - Abstract No : 1067

AUTOWAVE CHEMICAL CONVERSION IN MULTICOMPONENT MIXTURES THERMITE TYPE WITH ACTIVE METALS

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SHS metallurgy has potential for synthesis of new refractory inorganic materials: ceramics, alloys and composite materials. One of the important problem of SHS metallurgy is chemical conversion control, which proceeds in combustion waves of high exothermic thermite mixtures of oxides, active metals and nonmetals. Results of the problem investigation are presented in the report on example of cast refractory materials based on Ti-Al and Nb-Si.

Basic mixtures (Ti/Al/CaO₂ and Nb₂O₅/Al/Si), allowing to obtain cast Ti-Al and Nb-Si by SHS metallurgy in centrifuges, were developed on thermodynamic calculation. In the experiments, regularities of mixtures combustion and formation of chemical and phase composition products were studied. The burning, melting and gravity separation limits have been detected. Great attention was paid to the composite structure formation by introduction of alloying elements (Hf, Nb, Cr and others) in the initial mixtures.

For example, the integral chemical composition of the metal and oxide products of Ti/Al/CaO₂/Nb₂O₅/Cr₂O₃ mixture is shown in Table 1.

Table 1 - Integral composition of combustion products

| The elemental composition of the combustion products, wt % | C/E | Ti | Al | Nb | Cr | Ca | O |
|--|-----|------|------|-----|-----|------|------|
| Metal layer | C | 60,1 | 32,4 | 4,8 | 2,7 | - | - |
| | E | 57,7 | 34,8 | 4,7 | 2,8 | - | - |
| Oxide layer | C | - | 22,8 | - | - | 40,8 | 36,4 |
| | E | 2,4 | 20,9 | - | - | 40,5 | 36,2 |

C - calculated composition, E - experimental composition

The table shows that the completeness of Ti transition from the original mixture in the target product (metal layer) is significantly less than 100 % and the content of reducing agent (Al) in the cast alloy is significantly higher than the calculated one. In the composition of the oxide product is titanium oxide, which indicates the competition of Ti and Al in the reduction of the original oxides. Similar results were obtained with the introduction of alloying elements (Hf, Ti and Cr) in the Nb-Si. Therefore, to obtain the composite material with a given composition, the original mixture must be corrected.

From the analysis of the microstructure at higher magnification, it follows that in the cast alloy has a composite structure in which the matrix of the Nb-Cr-Al distributed grains of Ti-Al. The oxide layer is a solid solution of Al_2O_3 -CaO- TiO_2 , in which there are individual metal particles.

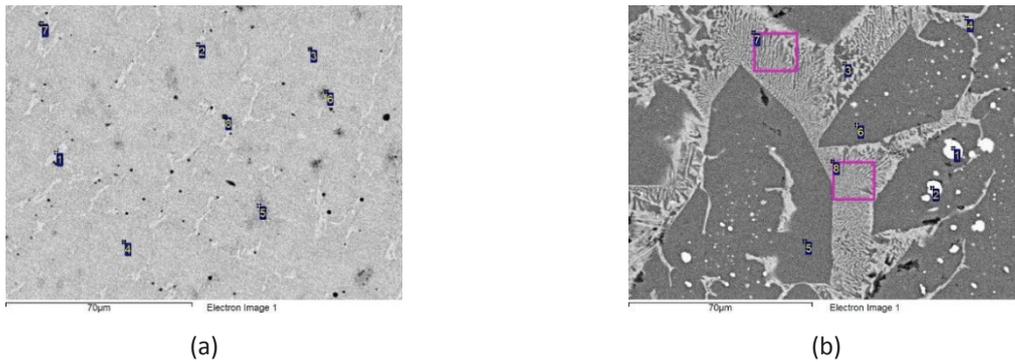


Fig. 1. The microstructure of the metal (a) oxide and (b) layers. The initial mixture Ti/Al/CaO₂/Nb₂O₅/Cr₂O₃. Overloading a = 250g

The competition of active elements in the chemical reduction processes, the interaction of chemical stages in the combustion waves have considered in the section devoted to the modeling of chemical transformations in multicomponent mixtures thermite type.

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Abstract No : 1155

A COMPARATIVE STUDY ABOUT PRODUCTION OF CHROMIUM CONTAINING IRON BASED ALLOYS FOR 3 DIFFERENT CONDITIONS BY METALLOTHERMIC PROCESS

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In this study, it was aimed to produce chromium containing iron based alloys via metallothermic process. In Turkey, Eti Krom A.Ş. is producing high carbon ferrochromium by consuming 2700 kWh/t energy. In the case of the low carbon ferrochromium production in Antalya, the energy consumption can be increased up to 8200 kWh/t. Instead of the electrical energy, aluminum scrap and powder are used for reduction and smelting on low carbon FeCr as the concept of the energy efficiency. Thus, energy consumption and pollution are decreased.

Mill scale is a layer of iron oxide which forms on the surface of ferrous materials during cooling after being processed in hot rolling or continuous casting plants. Mill scale contains iron (II) and iron (III) oxides, which result in a 70% total iron content in oxide form [3]. In this study, Mill Scale and Hematite (Fe₂O₃) are used as an Iron source, Chromite concentrate, Chromic acid (CrO₃) and Chromium Oxide (Cr₂O₃) used as an Cr source and finally Al used as a reductant. Table I, shows properties of raw materials.

Table I. Purity and Grain Size of Raw Materials

| Raw Materials | Purity, % | Grain Size |
|--------------------------------|-----------|--------------|
| Al | > 96.0 | < 150 micron |
| Cr ₂ O ₃ | > 99.0 | < 150 micron |
| NiO | > 99.0 | < 150 micron |
| Fe | > 98.0 | < 150 micron |
| Mill Scale | >70.95* | < 150 micron |

*iron oxide content

This study proposed Metallothermic process to produce iron based low-C FeCr alloys using a mixture of mill scale, NiO, Cr₂O₃, MoO₃. Al used as a main reductant, Mg and Si added for better Cr recovery.

In the first set of experimental studies, low carbon ferrochromium production from chromite was aimed and Eti Krom A.Ş. concentrate has been given in Table II. 98% purity Al powder was used as a reductant and minimum 99.7% CrO₃ containing chromic acid was added into the charge. Table II presents initial conditions of first experimental set.

In the second set of metallothermic experiments, a mixture of Mill scale, NiO, Cr₂O₃, MoO₃ and Al powders were used in order to produce metallic Fe, Fe-Ni, Fe-Ni-Cr, and Fe-Ni-Cr-Mo alloys. The metal oxide powders have over 96% purity and 150 µm average grain sizes. The advanced thermochemical simulations of the reactions were investigated in detail including different ratios of initial mixtures in order to reduce the number of experiments. Table IV shows results and initial conditions of second experimental set.

In the last series of experiments were carried out sequentially. The formation of Fe-Ni-Cr-Mo was conducted using the raw materials (Fe₂O₃, NiO, Cr₂O₃, MoO₃, Al) were provided taking account of purity and grain size.

For all experiments set, initial molar composition ratios for each mixture were calculated and the mixtures were mixed throughly 15 minutes in turbula mixer, dried in drying-oven and poured into copper crucible. W wire was placed at the top of the copper crucible and the reaction started by passing current through the wire.

Table II. Experimental datas for mixture compound

| Experiment No | Chromite-CrO ₃ | Chromite | CrO ₃ | Al(%) |
|---------------|---------------------------|----------|------------------|-------|
| 1 | %50 - %50 | 50 | 50 | 100 |
| 2 | %55 - %45 | 55 | 45 | 100 |
| 3 | %60 - %40 | 60 | 40 | 100 |
| 4 | %65 - %35 | 65 | 35 | 100 |
| 5 | %70 - %30 | 70 | 30 | 100 |
| 6 | %65 - %35 | 195 | 105 | 100 |
| 7 | %65 - %35 | 65 | 35 | 90 |
| 8 | %65 - %35 | 65 | 35 | 110 |
| 9 | %65 - %35 | 65 | 35 | 120 |

Table VI. Weight of the Initial Mixtures and Final Products (Stainless Steel "S.S.").

| Experiment Parameters | Initial Mixture, (g) | | | | Final Products | | Total Metal Recovery, % | Scattered Ratio, % |
|-----------------------|----------------------|------|------|--------------------------------|----------------|------|-------------------------|--------------------|
| | Mill Scale | Al | NiO | Cr ₂ O ₃ | Alloy | Slag | | |
| Fe Ni | 100 | 37,7 | 25,4 | x | 73,2 | 68,8 | 78 | 10,9 |
| 304 S.S. | 83,6 | 34,1 | 10,5 | 21,7 | 65,2 | 81,4 | 79 | 6,7 |
| 304 S.S. | 100 | 40,8 | 12,5 | 25,9 | 88 | 86,6 | 89 | 3,0 |
| 305 S.S. | 100 | 41,8 | 15,4 | 26,6 | 89,7 | 80,1 | 88 | 1,7 |
| 305 S.S. | 50 | 20,9 | 8 | 13,3 | 46,4 | 43,3 | 91 | 1,8 |
| 201 S.S. | 100 | 38 | 5,7 | 22,5 | 80,2 | 85 | 88 | 6,8 |
| 201 S.S. | 50 | 19 | 2,9 | 11,3 | 44,9 | 21,1 | 98 | 3,5 |
| 301 S.S. | 100 | 38,8 | 8,3 | 23,2 | 81,5 | 88,7 | 87 | 2,4 |
| 316 S.S. | 100 | 42,2 | 14,2 | 25,2 | 88,5 | 82,3 | 87 | 2,8 |
| 317 S.S. | 100 | 44,7 | 16,6 | 28,6 | 94 | 86,5 | 87 | 4,2 |

In the Chromic acid based experiment set, the highest yield occurs in additional %110 Al and 65-35 concentrate - CrO₃. It is calculated approximately % 66,46. In our future study, additional Al and charge amount optimization will be attempted. In the mill scale based experimental set the highest Cr recovery is calculated 72 % and in the hematite based set the highest Cr yield is detected 52 %

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Abstract No :1070

CENTRIFUGAL SHS METALLURGY OF CAST TiAl BASED ALLOYS AND APPROACHES TO IMPROVE STRUCTURE AND CHEMICAL COMPOSITION

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The combination of high specific strength (higher than most steels) and corrosion resistance determines the main area of application of titanium alloys as an aerospace technology. Titanium alloys are used in aircraft and rocket construction to operate in the temperature range from 250 to 600 °C, where aluminum and magnesium alloys can't be used. In order to impart titanium alloys the desired structure and operating characteristics are carried alloying with various elements, which can improve the heat resistance, ductility, to expand the region of existence or α and β -Ti, etc. The presence of gas impurities (oxygen, nitrogen, hydrogen, and carbon) leads to formation of interstitial solid solutions in both of titanium modifications, these harmful impurities, they reduce the ductility of titanium and its alloys, so their limited content allowable concentrations of 0.005 - 0.15 wt %.

Traditional methods (furnace metallurgy) to produce titanium alloys and titanium aluminides have a number of difficulties are caused by the high reactivity of the starting components at elevated temperatures, the temperature difference of the melting elements, evaporation, and the density of the initial components, it all has to use high-temperature vacuum equipment (vacuum arc, electron beam remelting), increased demands on the manufacturing of molds, etc. The existing technology of production is very complex and multistage [1].

In recent years, studies have been conducted on the development of new alternative methods for producing of intermetallic compounds including titanium aluminides and materials based on them. There are the smelting of titanium aluminide ingots using a plasma-arc and induction heating, electroslag remelting method under the "active" calcium fluxes. One of the most power-efficient and manufacturable method of producing titanium aluminide and materials based on them is Self-propagating High-temperature Synthesis (SHS) method [2].

The present study aims at the synthesis of cast titanium aluminide alloy doped with Nb and Cr by centrifugal SHS metallurgy. It should be noted that, SHS of TiAl composition from pure elements (Ti+Al) system requires preheating the initial mixture because the heat effect of the chemical interaction is not sufficient to implement combustion mode. In our work we used mixture of oxides (TiO_2 , Al, Nb_2O_5 , Cr_2O_3). To realize condition for self-sustaining combustion mode and to produce the final composition in the molten state the energy admixture (EA) was used. The EA was performed of calcium peroxide with aluminum. Besides, for promotion of homogeneous structure formation and reducing gas impurities functional additives (FA) were used. It was been found that mutual concentration of target mixture (TM) and EA as 90/10 wt % get just ability to combustion mode. At concentration of EA from 10 to 20 wt % SHS in the system leads to combustion but the final products are non-fusion. At concentration of EA ≥ 30 wt % the cast target products were formed as cast and completeness of gravity separation and oxide phase (Al_2O_3) and target alloy had maximum value of 95 % (from calculate value).

In the study the concentration of Al in target mixture was varied. It was been revealed that content of Al in the experimental target mixture from 24 to 35 wt % has not sufficient effect on SHS mode but varied chemical composition of alloy and the content of gaseous impurities. With increasing concentration of Al the oxygen content in the metallic phase decreased. It has been showed that effect of FA in amount about 3 wt % reduce concentration of gaseous impurities in final composition of the metal product.

The experimental studies showed strong influence of the initial synthesis parameters (centrifugal overloading, the mass of the mixture etc.), aluminum content in initial mixture, EA concentration on synthesis characteristics (burning rate, yield of target products into ingot, etc.) and formation of structure and composition of final products. It's shown the content of impurity gases (oxygen, nitrogen) doesn't significantly change with increasing of the initial weight of green mixture within range of 0.1 - 1 kg.

Authors gratefully acknowledge the support from the Ministry of Education and Science of the Russian Federation in the framework of Federal Target Program on Priority Directions of R&D in 2014-2020 (agreement 14.578.21.0040, project RFMEFI57814X0040).

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Abstract No :1166

THERMOCHEMICAL CALCULATIONS OF SHS-PRODUCED NiTi SMA'S BY FACTSAGE

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NiTi is one of the most acknowledged shape memory alloys. It can be used as actuator in electro-magnetic applications, biomaterials in dental applications and human bones due to the natural super-elastic behavior. It can be produced by using arc-melter, casting, reactive sintering or self-propagating high temperature synthesis (SHS) method [1]. The SHS method can be selected for obtaining porous NiTi structures. The amount and shape of the porosity structure of the SHS produced-NiTi alloys have been investigated by many researchers. Ni-Ti powder mixture cannot be ignited at room temperature, as a result, above mentioned parameters are heavily based on the preheating temperature. The high preheating temperatures usually decrease the porosities as it enhances the amount of transient liquid which fills pores and creates anisotropy in the structure. So, it is bound up with a threshold value. If the preheating temperature passes over this threshold, the solid skeleton, which holds the structure together, is broken and structure loses its shape due to melted zones [2-5].

In the present work, the equilibrium module of Factsage 6.4 software, to which Gibbs energy minimization method has been implemented, was used for estimating the value of adiabatic temperatures, and the molar ratios of solid and liquid products. SGTE 2011 database was selected in order to detect intermetallic compounds and solid solutions in the product.

For example, in order to simulate the SHS reaction, 0.5 mole of Ni and 0.5 mole of Ti were equilibrated and the reaction of the process was assumed as adiabatic ($\Delta H=0$). The pre-heating reaction temperature was set from 100 to 825 °C. The solid and liquid amounts and the adiabatic temperature (T_{ad}) values corresponding to the pre-heating temperature are presented in Fig.1. The amounts of solid and liquid are shown in left y-axis, whereas T_{ad} values are plotted at right y-axis. The system is under 1 atm. The heat energy released from SHS reaction is assumed to be consumed for the transformation from solid to liquid. As the pre-heating temperature is increased, T_{ad} increases until the temperature reaches the melting point of NiTi. Then, T_{ad} stays steady while the molar ratio of liquid/solid keeps on increasing. The complete melting of NiTi occurs when the pre-heating temperature is selected around 625 °C. This value is very close to that of experimental studies in the literature [2, 3]. Li et al. found the preheating temperature as 750 °C assuming the compound is not a solid solution [2]. Zhang et. al worked on the adiabatic temperature and kinetic conditions for NiTi alloys and they found similar results [3].

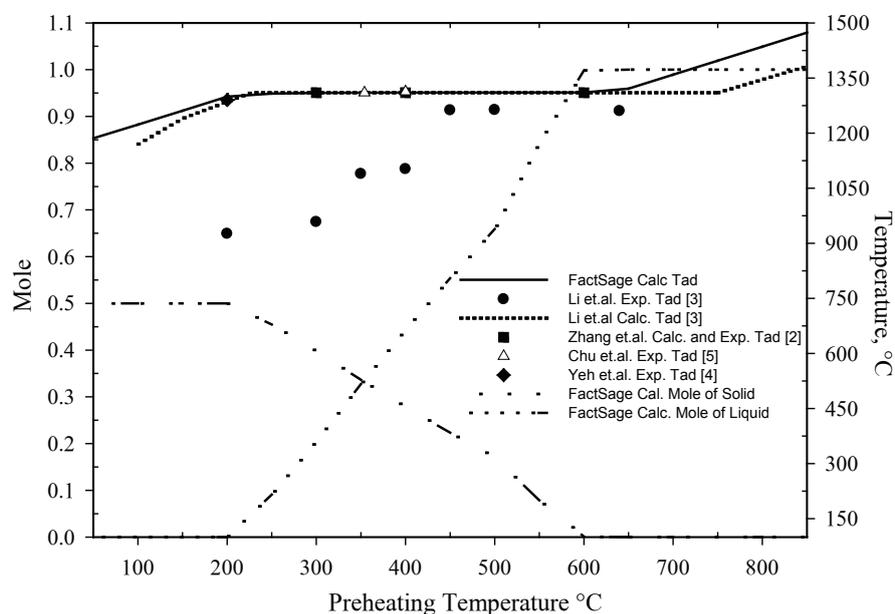


Figure 1 : The solid and liquid amounts in NiTi and the adiabatic temperature (Tad) values corresponding to the pre-heating temperature

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Abstract No :1120

THERMODYNAMIC ANALYSIS FOR COMBUSTION SYNTHESIS OF Al_2O_3/ZrO_2 EUTECTIC MELT UNDER HIGH PRESSURE AND CRYSTALLIZATION MORPHOLOGY IN RAPID SOLIDIFICATION

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Al_2O_3 - ZrO_2 eutectic has good combination of physical, thermal and mechanical properties, such as ultra-high hardness, excellent oxidation resistance and strength retention at elevated temperatures^[1-3]. These excellent properties made Al_2O_3 - ZrO_2 eutectic for a wide range of potential applications. Generally, eutectic ceramics was mostly prepared by Bridgman method^[3], laser heated floating zone method^[4], micro pulling down method^[5,6], combustion synthesis method^[8-10], thermal explosion spraying^[11] and so on. In addition, the mechanical properties of the Al_2O_3 - ZrO_2 eutectic are decided strongly by its microstructure which was influenced significantly by the cooling rate of the melt .

In this paper, Al_2O_3 - ZrO_2 eutectic coating was prepared by combustion-assisted thermal explosion spraying. Using the exothermal reaction between Al and $Zr(NO_3)_4$, the Al_2O_3 and ZrO_2 phases in reaction system were heated up to above the melting point, and then the Al_2O_3/ZrO_2 eutectic ceramics were formed through quick cooling, solidification and crystallization on the Cu substrate. The phases and morphology of the product were studied by XRD and SEM at the same time.

The relationship between adiabatic temperature, reaction pressure and the content of reagent was studied by thermodynamic calculations of Al-Zr(NO₃)₄-Al₂O₃-ZrO₂ systems in high pressure. The stability of the reaction products in the system was studied by calculations of the Helmholtz free energy. Through the XRD analysis of reaction products of different experimental conditions, we found that the stability variation of the reaction products, such as ZrN and Al₃Zr, was consistent with the thermodynamic analysis results, indicating that the thermodynamic analysis method is feasible. Rapid solidification of Al₂O₃/ZrO₂ melt of super high temperature was studied by a novel method, in this case the melt was prepared by explosion reaction using Al and Zr(NO₃)₄ as raw materials and sprayed to Cu-plate. With increase of the distance to the surface of Cu-plate, the melt solidified under lower cooling rate and the coating could be divided into four areas: monophasic, fine eutectic and coarse eutectic.

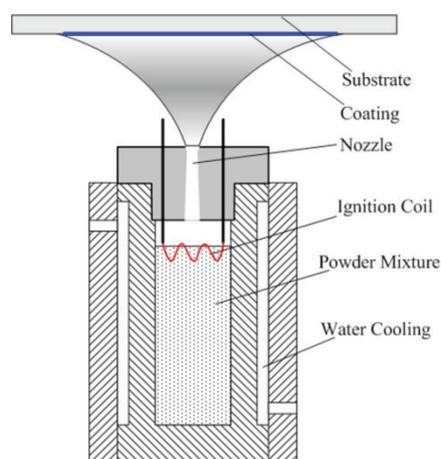


Fig.1. The device to prepare the Al₂O₃/ZrO₂ eutectic coating by combustion-assisted thermal explosion spraying

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Abstract No :1061

FABRICATION OF COMPOSITE POWDERS BASED ON TITANIUM CARBIDE AND IRON BY SHS WITH REDUCING STAGE

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A method is known to obtain composite powder of TiC-Fe from elemental powders of Fe, Ti and C by the reaction of self-propagating high temperature synthesis (SHS) $Ti+C+xFe \rightarrow TiC+xFe$ [1]. This version of SHS is the most obvious, but not the cheapest. To reduce costs to obtain such composite powder, the authors of this article proposed to use the SHS with the reducing stage [2]. In this case, iron oxide Fe_2O_3 is injected in the composition of the initial mixture instead of iron powder. Aluminum is typically used as a reducing agent of iron in so-called thermite reaction. However, the authors of this work tested also using carbon as a reducing agent.

1. Obtaining composite powder using a reduction reaction of iron with aluminum. Source components for holding SHS process are powders of Ti, C, Fe_2O_3 , Al. Pellets of the two compositions: Fe_2O_3+Al (thermite mixture) and Ti+C (SHS mixture) are separately prepared from these powders. The pellets are blended and burnt in a SHS-reactor. Liquid products of the combustion reaction of the thermite mixture infiltrate a porous skeleton formed of titanium carbide in combustion of the SHS mixture. Thus, voids remain in place of the pellets of the thermite mixture, and granules of the composite are formed from pellets of the Ti+C composition. The final product is easy-to-separated sintered granules of the composition of $FeAl-TiC-Al_2O_3$. The composition of the final product was investigated using X-ray diffraction analysis. The assumption that the granules of titanium carbide are infiltrated with liquid products of the thermite reaction is confirmed by microstructural analysis, which showed that spherical grains of TiC are distributed in the matrix of $FeAl-Al_2O_3$.

The obtained granules of the composite material based on iron and titanium carbide are comminuted to prepare powder. Comminution in the laboratory is conducted in 2 stages: 1) preliminary size reduction in a cone crusher; 2) grinding in a ball mill for 2 hours. The resulting powder is screened in the laboratory sieves for selection of the desired fractions.

The advantage of the described method of producing powder is the formation of the composite material immediately in the form of granules, which facilitates further grinding.

2. Obtaining composite powder using a reduction reaction of iron with carbon. In this case, the original components are powders of Ti, C, Fe_2O_3 . Loading into the SHS reactor and the combustion of the mixture of these substances is also performed in the form of powders. The course of the exothermic formation of titanium carbide in the SHS mode provides the necessary temperature conditions for the reduction of iron from its oxide by an excess of carbon. Thus, the amount of carbon in the initial mixture should be sufficient for the formation of titanium carbide and iron reduction. The SHS process produces a cake from individual granules of powder, which is easily amenable to grinding. Conducted microstructural and elemental analyses showed the presence of the elements of Ti, C, Fe and the absence of O in the grains of the powder. Thus, the conclusion can be drawn that the reduction of iron is really happening with the help of carbon, not titanium, since in the latter case, titanium oxide would be formed, and oxygen would be found in the composition of the grains of the powder.

A clear advantage of this method is the production of the composite material of Fe-TiC immediately in the form of powder, as well as the absence of aluminum in the composition of the initial mixture and correspondingly the absence of aluminum oxide in the final product. However, there are certain restrictions on the content of iron in the composite, because its reduction from Fe_2O_3 goes at the cost of the energy of the SHS reaction of formation of titanium carbide. At excess of Fe_2O_3 in the initial mixture of powders, burning becomes unstable, or generally, the charge mixture can not be ignited.

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Abstract No :1153

ETI ELEKTROMETALURJI LOW CARBON FERROCHROME PRODUCING PROCESS

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Eti Electrometallurgy Inc. was established in 1958 as a Turkish-French joint venture in Turkey. In 1970, the company had been acquired completely by the Turkish company Eti Holding. In 2004, the company was privatized and it was taken over by the Aksu Mining - Sarp Construction consortium that consists of the leading companies in their business sectors. Headquarters of our company is in the premises of the plant, which was spread on a 338.260 m² of total area. It is located on the edge of Antalya-Burdur highway about 8 km away from the Antalya city.

Eti Electrometallurgy Inc. is low carbon ferrochrome ,ferrosilicochrome and calcium carbide producer. Our company ranks within the biggest 1000 industrial establishments of Turkey even in the first 500 of the biggest 1000 exporters in Turkey.

Abstract No:1039

PRODUCTION OF ULTRA-HIGH TEMPERATURE CARBIDE (Ta,Zr)C BY SHS OF MECHANICALLY ACTIVATED MIXTURES

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Carbides TaC and ZrC are characterized by high melting point, hardness, resistance to corrosion and ablation (radiation-induced evaporation). They have been used to produce ultra-high-temperature composite materials for air- and spacecraft industries As one can see in the state diagram of TaC-ZrC, zirconium and tantalum carbides form a continuous series of solid solutions; the melting points of binary (Ta,Zr)C carbides are about 3800 K. The high melting temperature and corrosion stability of tantalum and zirconium carbides impose certain problems during production of materials and items made of them. The single-phase product with desired composition usually cannot be obtained by conventional powder metallurgy technology based on reduction reactions because of differences in chemical activity of metal oxides and diffusion coefficients of carbon in the carbide lattice.

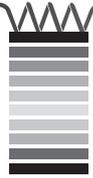
SHS can be used as an alternative method to produce tantalum-zirconium carbide with the highest melting point. The adiabatic combustion temperature for elemental synthesis of considered composition Ta-Zr-C is about 2914 K. This value is higher than the melting point of zirconium (2125 K) but significantly lower than those of zirconium and tantalum carbides and much lower than the melting point of tantalum-zirconium carbide. Carbide phase in the combustion wave can be formed by crystallization from the oversaturated zirconium melt. However, powder mixture Ta-Zr-C has a kinetic hindrance because of oxide films forms on the surface of Zr particle, so combustion synthesis under normal conditions is impossible. One of the real mean to overcome the kinetic hindrance is to mix the Ta-Zr-C ternary system under conditions when oxide films are mechanically destroyed, either completely or partially.

Aim of this work was to investigate the effect of the mechanical activation on the structure and phase composition as the initial powder mixtures and SHS products in the system Ta-Zr-C.

Zirconium (PTsrK-1 grade), tantalum (TaPM grade), and soot (P804T) powders were used as initial reagents. The mixtures were mechanically activated (MA) in an AIR-0.015 ball mill. The thermal effect of carbides formation was determined by high-speed calorimeter BCS-4. The influence of initial temperature T_0 on the combustion temperature T_c was detected using a W-Re thermocouple. The burning velocity U_c was detected with video record. The stages of phase transitions in the combustion wave were studied by dynamic X-ray diffraction analysis. To analyze the microstructure of the synthesized samples used scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) of the characteristic SCF areas using a NORAN energy-dispersive X-ray spectrometer. The technological parameters of force SHS-pressing were optimized to produce dense ceramic samples.

The combustion temperatures and rates of MA mixtures Ta-Zr-C depending on the initial temperature T_0 were determined. The self-heating phenomenon is observed even in argon atmosphere at $T_0 > 380$ K due to partial oxidation of the surface of zirconium particles by adsorbed oxygen. Zirconium oxide is formed in the combustion zone at the initial stage of chemical interaction; it is subsequently transformed into zirconium carbide. In addition, tantalum carbide is formed in the combustion zone, while the binary tantalum -zirconium carbide (Ta,Zr)C is formed closer to the post-combustion zone. In order to maintain the layer by layer stationary combustion mode of SHS, the initial temperature T_0 needs to be 298 K, while the duration of mechanical activation needs to be less than 5 min. After longer mechanical activation, the mixtures are prone to bulk combustion even at low initial temperatures. Single carbide phase (Ta,Zr)C with the lattice parameter of 0.4479 nm was obtained by forced SHS- pressing technology.

This work was carried out with partial financial support from the Ministry of Education and Science of the Russian Federation in the framework of state assignment No. 11.233.2014/K in the part of mechanism of combustion and structure formation and in the framework of Increase Competitiveness Program of NUST «MISiS» (No. K2-2014-012) in the part of dense product obtaining using force SHS-pressing technology.



HALL B - Wednesday, October 14 / 2015

Abstract:1004

SHOCK WAVE ASSISTED SHS PROCESS AND CONSOLIDATION OF Ta-Al -B₄C PRECURSORS

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The main purpose of presented work is to combine Hot explosive consolidation technology (HEC) and Self propagated High Temperature syntheses processes (SHS) and to obtain Ta-Al – B₄C cylindrical billets with low porosity and improved physical and mechanical properties.

The first stage investigation were carried out for explosive consolidation of powders at room temperatures to obtain billets with increased density without cracks and activated surfaces of consolidated particles. The second stage investigation were carried out for same billets but consolidation were conducted in hot conditions above and under of combustion reaction temperatures. The intensity of loading was equal to 10 GPA. The time of heating billets before loading was under 30 minute.

The investigation showed that the initiation of CS process and the full SHS reaction in Ta-Al-B₄C powder composites starts from 940⁰C. In order to fabricate billets near to theoretical density with perfect structure and correct geometry it's necessary to load billets before 940⁰C . During the HEC the dissolution of B₄C phase behind of shock wave front and formation of TaB and AlCTa₂ phases together with TaAl₃ were observed. The type of obtained intermetallic compounds depends from percentage of separate phases in starting composition.

The above mentioned and other features of structure-property relationship of consolidated Ta-Al –B₄C composites depending on loading condition and set up of HEC device will be presented and discussed.

Abstract:1012

CONVERSION OF MILL SCALE WASTE INTO VALUABLE IRON-CHROMIUM ALLOY USING ALUMINO-THERMIC AND ALUMINO-SILICO-THERMIC PROCESSES

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In steel production and steel processing, a large amount of waste materials (slag, dust and mill scale) are produced. Mill scale is one of these waste materials produced as a result of hot rolling of steel in all steel companies and its specific production is about 35-40 kg/ ton of hot rolled product [1]. On the other hand, mill scale is considered a rich iron source (> 67% Fe) with minimum impurities.

The recycling and utilization of iron-bearing by-products has been promoted in iron and steelmaking industry due to its several benefits [2]. Laboratory scale trials were conducted for reduction of composite pellets produced from mill scale using anthracite coal [3]. The trial results showed the possibility of using mill scale as raw material in blast furnace as well as in direct reduction plants producing sponge iron characterized by 84% total iron, 82% metallic iron and metallization degree of more than 97%. Mill scale formed in a continuous casting plant was direct reduced in pelletized form at different temperatures with either anthracite or metallurgical coke as solid reductants for obtaining iron pellets with high metallization degrees [4 and 5]. A study was made to recycling of mill scale to high purity iron by smelting in submerged arc furnace using two carbonaceous reducing agents (graphite or coke) [6]. By adjusting the smelting condition, the high purity iron was successfully produced by the smelting process which is suitable to be used in producing ductile cast iron and steelmaking processes. In a recent study[7], iron based alloys (FeMo, FeCrNi, etc.) were produced by using alumino-thermic methods starting from mill scales.

In the present study, Al-thermic and Al-Si-thermic processes have been used to convert a mixture of mill scale and low grade chromite ore into valuable iron-chromium alloy. The raw materials used in these experiments are mill scale (-0.5mm), low grade chromites ore (-0.5mm), Al-powder (-0.5mm) and Al-Si powder (-0.5 mm) as reducing agents and lime as a fluxing material. The raw materials were analyzed. In each experimental heat, the components of the charged chromite ore, mill scale, energizer, together with the investigated Al or Al-Si powder amounts, with or without fluxing material were manually well mixed together and the whole charge was charged into the metallic mould which was preheated to 200°C. The charge was heated up to 400°C while being in the metallic mould. The ignition mixture, composed of mill scale, magnesium metal, Al- powder and Na- nitrate was added to initiate the reaction. Once the reaction started it proceeds spontaneously. The reaction duration was about 90 seconds in each heat. The metal covered by slag was left to cool and then detached, weight and samples from it was taken for the determination of its chemical composition.

Low-C, high-Cr alloy steel containing 14-17%Cr is successfully obtained by adding Al or Al-Si amount in the charge equals or higher than the stoichiometric ratio. Comparison of the results of both alumino-thermic and alumino-silico-thermic processes, reveals higher metal yield and higher recovery when using alumino-silico-thermic process at lower stoichiometric ratio. On the other hand, at higher stoichiometric ratio, using alumino-thermic process results in higher metal yield and higher recovery of alloying elements. However, using Al-Si as reducing agent results in higher Si and Al contents in the produced alloy.

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Abstract:1164

COMPOSITES IN THE ALUMINUM OXYNITRIDE - MeN (Me=Ti, Ta, Nb, Cr) SYSTEM PREPARED FROM SHS-DERIVED POWDERS

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Aluminium oxynitride, gamma-alon, is a spinel-type structure solid solution of Al_2O_3 and AlN. Due to its good mechanical and chemical properties gamma-alon has a great potential application in high-performance structural ceramics [1]. Much attention has been focused on developing alon-based composites to improve its properties and performance. Additions of different types of hard ceramic phases such as Al_2O_3 , AlN, SiC, ZrN, TiN and TiC have been investigated. Formation of such composites enhanced aluminum oxynitride hardness, flexural strength, toughness and especially wear resistance. The aim of the present work is to present a new idea of producing CMC composed of aluminium oxynitride matrix and tantalum nitrides nitride particle reinforcement. The precursor powders were formed in a single step process using the SHS synthesis [2].

Starting powder mixtures were composed of aluminium oxide, aluminium and titanium, tantalum or chromium, respectively. Alumina and Al powders remained a ratio of 4:1 when adding other metals powder. The powder mixture were subjected to self-sustain high-temperature synthesis (SHS) in nitrogen atmosphere under a pressure of 3 MPa. The SHS-derived powders were ground and hot-pressed at 1750-1850°C for 1h under 25 MPa. The dense samples were composed of gamma-alon, small amount of aluminium nitride and respective nitrides: MeN and Me_2N . Increase of the nitrides content in the composites improved significantly their mechanical properties. The samples prepared from the powder containing formally 30 mol% of the metals show Vicker's hardness over 16 GPa, fracture toughness about 7 MPam^{0.5} and wear resistance three order of magnitude better than dense corundum material.

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Abstract:1144

SYNTHESIS OF TUNGSTEN NANOPOWDERS: COMPARISON OF MILLING, SHS, MASHS AND MECHANO-CHEMICAL PROCESSES

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The ITER project, being the most important international project on energy, aims at satisfying the ever increasing demand on energy, through the use of thermonuclear fusion of hydrogen isotopes to helium. In the presently considered configuration of the reactor, the lower part, called the divertor, will be made of tungsten and is aimed at receiving the

high energy particles resulting from the reaction, and from this interaction will result sputtering which will yield the creation of tungsten nanoparticles.

Due to a potential risk e.g. if a Loss Of Vacuum Accident (LOVA) occurs, due to a water leak from the cooling system or an air leak from the surroundings of the reactor chamber, periodical cleanings are scheduled, during which the tungsten nanoparticles will be removed. To prevent contamination to the environment and/or to people supervising the cleaning operations, High Efficiency Particulate Air (HEPA) filters will be used, but these filters always have a smaller retention capability for particles in the 100-200 nm range. Because these particles are the ones to which operational staff will be exposed, they are the most potentially dangerous ones. Our aim is to synthesize such ITER-relevant particles through other means, and to study their behavior in order to know how to deal with them.

Pure SHS e.g. thermitic reactions using WO_3 and Mg, NaN_3 , $NaBH_4$ [1, 2] or Zn, together with a preheating of the reacting mixture [2] have been used to previously to synthesize nanometric W powders. Mechanically induced thermitic reaction of WO_3 with Mg [3] or Li3N [4] have also been studied.

We are here aimed at studying the influence of parameters which have not been studied previously, especially the use of Mechanically Activated Self-propagating High-temperature Synthesis (MASHS) [5], i.e. to use as starting reactants powders which have been subjected to a short-time preliminary co-milling. Synthesis of tungsten nanopowders was studied using milling of micrometric tungsten, then using the WO_3 -Mg thermitic reaction, using SHS (Self-propagating High-temperature Synthesis), mechano-chemistry, and MASHS (Mechanically Activated SHS). Reactions are studied by measuring temperature and pressure inside the milling jar (mechano-chemistry), or by analyzing the temperature profile along the sample during the reaction propagation by infrared thermography (SHS, MASHS). After reaction, samples were analyzed by AFM or SEM, by XRD, and BET. Finally, some results on the behavior of different kinds of tungsten particles towards 3H [6], and in presence of hydrogen plasma [7] will be presented.

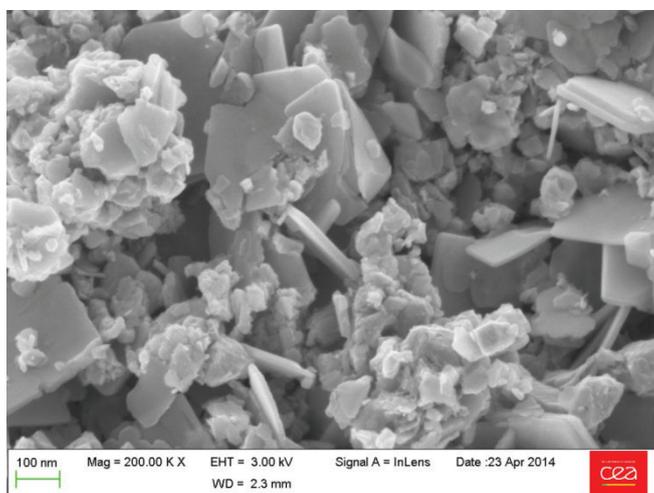


Fig. 1. SEM observation of a powder synthesized by mechano-chemistry

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Abstract:1035

COMBUSTION SYNTHESIS OF NANO-SIZED AMORPHOUS BORON POWDERS

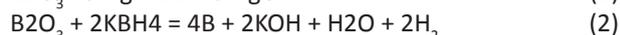
*Weimin Wang*¹

Wuhan university of Technology State Key Lab Wuhan-China¹

Amorphous boron powders have a higher heat of combustion than the traditional fuels like magnesium, aluminum, carbon and hydrocarbon. It also reveals a high specific surface, convenient to carry, high heat output and less contamination, interesting electrical and optical properties. These unique properties make amorphous boron powders an attractive prospect for practical applications in many fields such as nuclear reactor control, thermoelectric energy conversion, high-temperature devices, refractory materials and semiconductors. In recent years, various synthetic methods have been employed to prepare amorphous boron powders, such as diborane pyrolysis, laser ablation, molten-salt electrolysis, magnesiothermic reduction. In these methods, the magnesiothermic reduction also belongs to Self Propagating High Temperature Synthesis (SHS), which is a novel technology of synthesis of all kinds of materials. Once the reaction starts, it will continue with the help of the energy provided by itself, rather than from outside system. The amorphous boron powders prepared through this method present a small particle size and high activity, which is appropriate for the popularization and application. However, it is hard to control the SHS reaction process due to high exothermic effect in a few seconds. Excessive temperature will cause kinds of impurities, such as $MgxB_2O(x+1)$ ($x=2, 3$), MgB_x ($x=2, 4, 6$), B_xO , and lead to low purity (≤ 88 wt.%) as well as large particle size (about $0.5-5\mu m$). Generally, two dilution methods were used to adjust the SHS reaction process, excess B_2O_3 or Mg, and inert diluents (NaCl, KCl, $MgCl_2$ and MgO). Nevertheless, these control methods were demonstrated limited effect and consumptive of reactants or inert reagents. Moreover, additional three leaching and purifying processes were needed in order to obtain higher purity (≥ 90 wt.%) products.

The present work introduces a new way so-called active dilution method to synthesize nano-sized amorphous boron powders. Higher purity products could be prepared after only one leaching and purifying processes. The exothermic reaction could be effectively controlled through changing the endothermic reaction rate, which promotes the preparation of amorphous boron powders and inhibits the formation of by-products.

In this study, The raw materials magnesium (Mg), boron oxide (B_2O_3) and potassium borohydride (KBH_4) were of analytical pure grade and about 150-300 mesh ($50-100\mu m$) powders. The chemical reaction equations of the SHS reaction system $B_2O_3/Mg/KBH_4$ are presented as following:



The standard molar enthalpies of Eq. (1) and (2) were calculated as -24.57 kJ/(gram B) and $+14.73$ kJ/(gram B). The reaction system B_2O_3/Mg is extremely exothermic while the other reaction system B_2O_3/KBH_4 is highly endothermic. The SHS reaction process could be effectively controlled through properly changing the rate of the dilution agent KBH_4 .

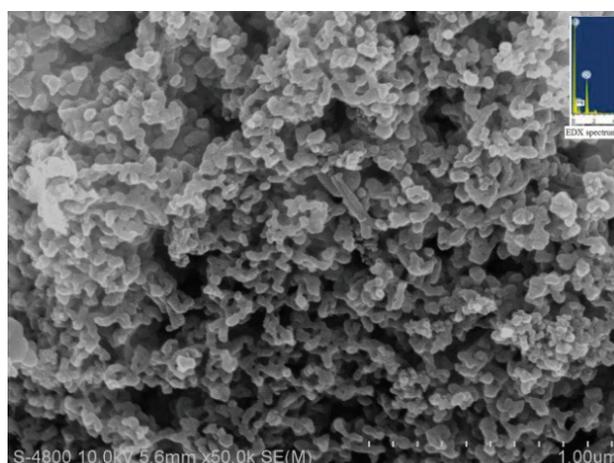


Fig 1 Morphology and EDX spectrums of nano-sized amorphous boron powder

The XRD patterns and FTIR spectrum of boron powders made by the active dilution SHS method reveal a broad peak ascribed to amorphous structure. As shown in the FTIR spectrum of the nano-sized amorphous boron powders, the characteristic peaks (2843 cm⁻¹ and 2917 cm⁻¹) of crystalline boron couldn't be observed. However, the characteristic absorption peaks ascribed to boric acid (712cm⁻¹, 812cm⁻¹, 902cm⁻¹, 1108cm⁻¹, 1380cm⁻¹ and 1640cm⁻¹) could be demonstrated, due to surface oxidation and hydrolysis. Therefore, the prepared boron powders were amorphous. The morphology of nano-sized amorphous boron powder was showed in Fig.1. It can be found that the boron powders was amorphous rod-liked structure with an average diameter of 20 nm and length of 80 nm. The corresponding EDX spectrums demonstrate the signal of boron. The oxygen peak may be ascribed to impurity and the surface oxidation. And the Mg peak can be resulted from impurity. In addition, quantitative analysis indicates the contents of boron is 93.69 wt.%.

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Abstract:1141

PARAMETRIC STUDIES ON TITANIUM-STAINLESS STEEL EXPLOSIVE CLADDING SUBJECTED TO UNLOADING RATIO

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1. INTRODUCTION

Explosive cladding is a solid state process, wherein controlled explosion impinges two or more metals to fuse together to form a clad. The energy emanating from a chemical explosive accelerates the flyer plate, across a predetermined distance onto the base plate, to be pressed together to form a metallurgical strong weld [1]. This study reveals the relationship between the interfacial undulations (amplitude and wavelength), and the properties of titanium-Stainless Steel 304L explosive clad is limited and is attempted herein. Ram tensile tests were carried out and the results are presented.

2. Microstructural Characterization

The microstructural observation of the titanium Gr-1 with stainless steel (SS304L) explosive clad composites show wavy morphologies (Fig.1) as reported by previous researchers [2]. The undulating interfaces are characteristics of explosive cladding process, is designed by the system parameters viz., nature of explosive, standoff distance and preset angle.

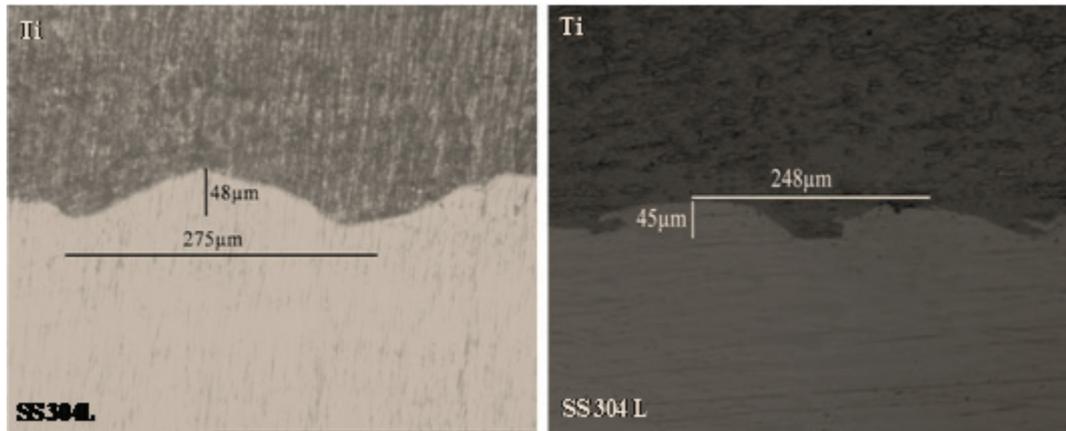


Fig.2. Microstructure of Ti-SS304L explosive clad

The Ti-SS304L explosive clad with smaller waves exhibited the highest tensile strength while the waves with higher amplitude exhibited the least value, though higher than the weaker metal titanium. The formation of hump, indication for perfect interlocking is observed as a consequence of the complete block of reentrant jet which is consistent with Manikandan et al. [3]. For a constant loading ratio, the amplitude and wavelength of the interfacial wave changes indicating the collision front is being influenced by other factors viz., standoff distance, quality of surface finish, density ratio and preset angle.

3. Ram tensile test

The Ram tensile strength of Ti-SS 304L explosive clad varies from 243 MPa to 275 MPa. It is observed that, the highest value of tensile strength is 275 MPa for a 3.5 mm thick flyer plate while it is 264 MPa for 6 mm thick flyer plates which are closer to tensile strength of stainless steel (293 MPa). The interface exhibiting smaller waves possess higher strength for all experimental conditions.

4. Weldability Window

In this study, an attempt was made to develop a weldability window based on empirical relations reported by earlier researchers [4] for varied flyer thickness Ti Gr-1- SS 304L with welding velocity ' V_w ' and collision angle ' γ ' as its ordinates. When the flyer plate thickness increases from 3.5 mm to 6 mm weldability window becomes narrow.

5. Conclusion

1. The explosive clad with smaller amplitude and wavelength exhibit higher strength due to increased contact area.
2. Ram tensile strength of the clad is higher than titanium indicating the bond is stronger than weaker metal.

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Abstract:1010

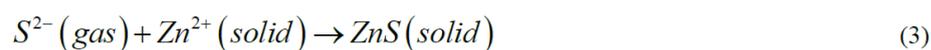
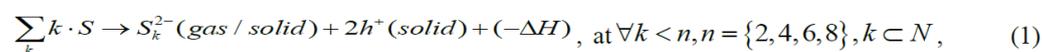
MULTI TEMPERATURE MODELING OF ELECTRICAL FIELD GENERATION DURING COMBUSTION SYNTHESIS OF ZnS

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Recent experimental and theoretical investigations revealed that the Combustion Synthesis of Sulfides (CSS) generates the transient electrical voltage up to 4 V [1] and the gravity affects to the value of voltage generation [2]. The mechanism governing the evolution of the extensive charge formation during the CSS has not yet been developed. In this report, we present the Two-Temperature (2T) model in which the temperature of gas phase and solid phase in CSS are not identical. Our model is based on kinetics as follows



We consider the multi temperature model to describe precisely the thermal front behavior in CSS before the steady combustion mode has been developed and/or interphase thermal equilibrium has been achieved by the reacting system. The results allow us to predict characteristic features of CSS in wide range of similarity parameters. The numerical results shown in Figure 1 revealed that the significantly higher amplitudes of the electric field in the radial component occur than in the axial one.

In accordance with this fact it is concluded that separation of the alternative charge carriers during CSS occurs much more effectively in the sample radial direction than in the axial one. In the axial direction the relative displacement of the negative carriers appears to be negligibly small with respect to that of the positive carriers. Therefore, the field of the negative carriers is almost completely compensated by the field of the positive carriers and a negligibly small axial electric field component is formed as the result. This effect can be explained also as a result of dispersion of flow of light electrons by the matrix of heavy sulfur neutral clusters. Obviously, that the flow radial dispersion would then prevail over its axial dispersion. While the flow cross-sectional area would be an increasing function of the axial coordinate in this case. It has been determined the range of CSS combustion front velocity with a negligible radiation heat transfer relative to that of heat diffusion.

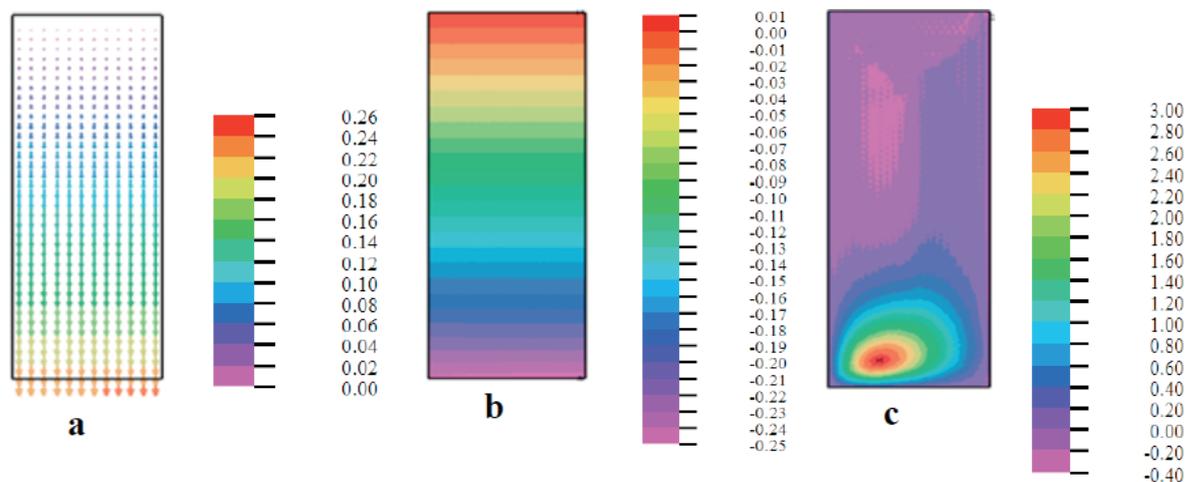


Figure 1. The 2T model of (a) - the electric field intensity vector; (b) - axial component of electric intensity vector; and (c) - radial component of electric intensity vector at $t=0.24$.

Combustion of green mixtures with the excess of sulfur appears to be applicable and providing such a mode of preferable thermal conductivity under the surrounding with the room temperature. By using the novel experimental cell to measure non-contact temperature distribution and electrical potential we have measured the voltage generated by the ascending and descending combustion waves during synthesis of sulfides (CSS) within the accuracy of less than 5 %. The results of simulation are in a good agreement with the experimental data.

Acknowledgement:

We acknowledge the financial support of this work in the frames of program #24 of the Presidium of the Russian Academy of Science (coordinators: academicians V.A. Levin and Yu.M. Mikhailov).

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Abstract:1027

SOLUTION COMBUSTION SYNTHESIS OF La- AND Cr- DOPED SrTiO₃ PHOTOCATALYSTS FOR SUSTAINABLE AIR POLLUTANT REMOVAL

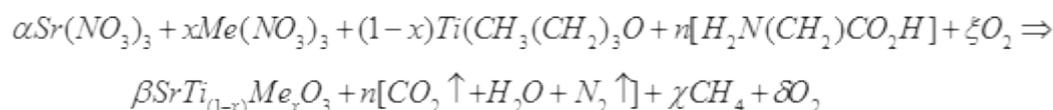
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Interest to development of efficient heterogeneous photocatalytic processes continuously increases, which is caused by the following reasons. It is revealed that many organic reactions occur quickly by photocatalysts at room temperature under solar radiation. Then, photocatalytic oxidation is able to erode almost all organic compounds into inorganic products, as in solutions and in gaseous phases, which may be used for effective cleaning of environment. This will allow utilizing solar energy for directing efficient ecological processes. The most part of heterogeneous photocatalysts are presented by nanostructured titanium dioxide (anatase), which is connected with the amorphous phase characterized by a large amount of surface defects, the existence of which facilitates an effective separation of charge carriers and the increase of their lifetime. It was shown recently that chromium and lanthanum doped SrTiO₃ perovskites exhibit high photocatalytic activity [1].

The goal of this work was to synthesize nanostructured La- and Cr- doped strontium perovskites SrTi_(1-x)La_xO₃ and SrTi_(1-x)Cr_xO₃ at (x=0.01-0.2) by using Solution Combustion Synthesis (SCS) approach [2] and examine their photocatalytic absorption properties. Doped perovskites with metal atoms contains more interstitial defects altering the cubic crystal lattice. Consequently, these materials experienced a shift in the absorption of incoming EM waves, causing the band gap to widen or become more narrow depending on the effects of the defects. Moreover, oxygen vacancies are fairly common in SrTiO₃ crystals that induce free electrons in the conduction band of the material, making it more electron/hole pairs by photo-excitation. These vacancies can be produced using SCS by altering reaction processes at the moderate temperatures. Perovskite nanostructured particles may decrease the concentration of NO_x pollutants and cigarette smoke in air, as well as volatile automobile emissions. When exposed to UV or visible light, these nanoparticles can oxidize organic pollutants into nontoxic substances, such as CO₂ and water, and can disinfect a variety of bacteria and viruses in secondary wastewater treatment. The synthesis of high purity nanocrystalline powders (<100 nm) is the key to improve the performance of perovskite-based ceramics for both electronic and catalytic applications [3].

The highly exothermic oxidation of glycine is the driving force in the solution (nitrate-glycine) combustion synthesis. The fine perovskite powder was formed by the overall reaction:



where *Me* are metals Cr or La and α , β , ξ , δ , x , and n are stoichiometric coefficients. The reactants mixture contained Sr- and La- nitrate precursors, butyl titanate $Ti(CH_3(CH_2)_3O$ and glycine. Figure 1 shows absorption wavelength UV-VIS spectra of $SrTiO_3$ and $SrTi_{0.9}La_{0.1}O_3$ produced by solution combustion synthesis. Although $SrTiO_3$ powders are white, all La doped strontium perovskite were light gray in color. The $SrTiO_3$ had an absorption maximum at approximately 395 nm that agrees with the value of 387 nm in the literature. The spectra of $SrTi_{0.9}La_{0.1}O_3$ exhibit absorption in visible light region with the maximum peak at 644 nm.

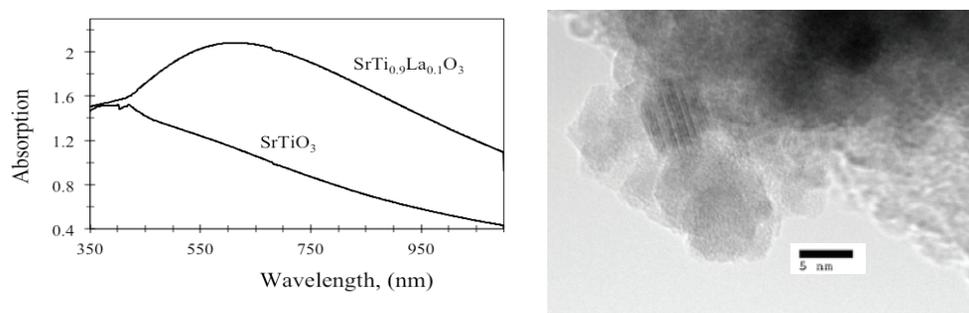


Figure 1. (left) The absorption wavelength spectra of $SrTiO_3$ and $SrTi_{0.9}La_{0.1}O_3$; (right) TEM image of $SrTi_{0.9}La_{0.1}O_3$ nanoparticles, (bar-scale is 5 nm).

The results of our work demonstrate that high efficient nanostructured photocatalysts particles of $SrTi_{(1-x)}La_xO_3$ and $SrTi_{(1-x)}Cr_xO_3$ can be synthesized by a solution combustion synthesis. The main parameter affecting the process, product particle size distribution and photocatalytic properties is the ratio of metal nitrates and glycine.

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Abstract:1005

SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS OF RARE-EARTH OXIDE NANOPOWDERS FOR TRANSPARENT CERAMICS

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Rare earth oxide (Y_2O_3 , Lu_2O_3 and Sc_2O_3) based ceramics are promising materials for laser host media. The key step of optical ceramic technology is the preparation of low agglomerated submicron powders with a narrow particle size distribution.

At the moment coprecipitation is a commonly used method for preparing powders with the desired properties. On the other hand one of the promising methods to prepare nanopowders for laser ceramics is a self-propagating high-temperature synthesis (SHS) also known as combustion synthesis. The advantage of this method is the absence of a number of conventional stages (filtering, washing, drying, etc.) which significantly simplifies the process and reduces the possibility of the powder contamination.

There are a number of papers devoted to SHS of RE_2O_3 powders using metal nitrates as oxidizer and organic compounds as a fuel. The most popular fuel is a glycine. At the same time starting materials that are readily available in a highly pure state are preferable to use because of the strict requirements for the purity of the powder. Such materials include volatile acetic acid (CH_3COOH) and acetylacetone ($C_5H_7O_2$). And their salts with lanthanide ions would serve as a fuel. Therefore, our work focused on developing of SHS fabrication technique of high-pure rare-earth oxide (RE_2O_3) nanopowders from different precursors.

For a preliminary assessment of these fuels utilization possibility thermodynamic study of reaction systems $RE(NO_3)_3$ - $RE(CH_3COO)_3$, $RE(NO_3)_3$ - $RE(C_5H_7O_2)_2$ and $RE(NO_3)_3$ - NH_2CH_2COOH was performed in the approximation of adiabatic conditions. It was found that the forms of the dependences of the adiabatic temperature, amount of matter and volume of gaseous synthesis products does not dependent on metal cation, but determined by the type of the fuel. The optimal conditions for SHS lies in a small excess of oxidant region, i.e. when the mole fraction of the metal nitrate is 65 - 70% in the case of acetate precursor, 85 - 90% and 40 - 50% for glycinate and acetylacetonate precursors respectively.

According to the data of scanning electron microscopy (SEM) and static light scattering methods the Y_2O_3 and Lu_2O_3 powders produced by the acetate-nitrate approach have a plate-like morphology; the particles are combined in "soft" agglomerates up to $\sim 50 \mu m$ in size. Under ultrasonification the agglomerates could be crushed down to individual particles less than 200 nm. According to BET-method the dispersity of the product is defined by the synthesis parameters and the average particle size does not exceed 100 nm. At the same time, low agglomerated scandia powder could not be prepared by this method because of scandium acetate hydrolysis.

To produce Sc_2O_3 the scandium acetylacetonate ($Sc(C_5H_7O_2)_3$) and glycine (NH_2CH_2COOH) were used as fuels. $Sc(C_5H_7O_2)_3$ was synthesized by the reaction of scandium carbonate with acetylacetone in isopropyl alcohol media. SEM reveals similar morphology for these two powders. But according to light scattering method only the powder prepared using glycine has a low agglomeration degree.

The synthesized RE_2O_3 nanopowders were used for transparent ceramics sintering. The powders were uniaxially pressed into disks with diameter of 15 mm and thickness of ~ 2 mm. The compacts were sintered at $1800^\circ C$ for 2 hrs under vacuum of 10^{-3} Pa.

It was found that undoped RE_2O_3 could be sintered to the full density but transmittance of the samples does not exceed 10%. To improve the optical properties of the ceramics, different sintering aids were introduced into the host oxide on the powder preparation step. At the present time highly transparent ceramics of La_2O_3 -doped Y_2O_3 and Y_2O_3 - or ZrO_2 -doped Sc_2O_3 ceramics were prepared. Y_2O_3 powders were also doped with 5 mol% of ytterbium oxide as the active component. The sample of $Y_{1.7}La_{0.2}Yb_{0.1}O_3$ composition with the highest optical quality was used in lasing experiments. An effective free-running lasing was observed with clear spectrum peak at 1030 nm. Exploratory research of the Y_2O_3 and ZrO_2 sintering additives effect on the transparency of lutetium oxide ceramics is also considered with presentation of the results.

The reported study was supported by RFBR, research project No. 14-03-3194014 *mol_a*

Abstract:1013

RARE EARTH IRON NANOSTRUCTURED GARNETS: COMBUSTION SYNTHESIS AND MAGNETOELECTRIC PROPERTIES

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The rare earth garnet ferrites exhibit remarkable physical and chemical properties that are sensitive to the crystallite size and method of preparation [1]. There is a major challenge to produce these materials in nanoscale due to particles conglomeration during the ferrite nucleation and synthesis. High resistivity of garnet ferrites makes them suitable for high frequency and low loss applications. Rare earth elements include Lanthanides as well as Yttrium and Scandium.

In this paper we report Solution Combustion Synthesis (SCS) [2] of nanostructured particles of yttrium ($Y_3Fe_5O_{12}$) and samarium ($Sm_3Fe_5O_{12}$) garnet ferrites and compare their magnetic and electrical properties. Thermodynamic calculations of the $Y(NO_3)_3-2Fe(NO_3)_3-nC_2H_5NO_2$ system producing $Y_3Fe_5O_{12}$ predicted an adiabatic temperature of 2250 K with generating carbon dioxide, nitrogen and water vapor. The considerable gas evolution helps to produce the synthesized powders friable and loosely agglomerated. The adjusting the glycine/metal nitrates ratio can selectively control the crystallite size and magneto dielectric properties of the ferrites.

Various analytical tools including X-ray Diffraction (XRD), Transmission Electron Microscope (TEM), Vibrating Sample Magnetometer (VSM) with cryogenic system (PPMS, Quantum Design, USA) were used to evaluate ferrites structure and electromagnetic properties. The yttrium, samarium and iron nitrates were used as metal precursors and glycine as a fuel. Increasing the glycine content increased the reaction temperature during the SCS and consequently the particle size. The particles morphology of as-synthesized yttrium ferrite prepared with 3 wt. % concentration of glycine is shown in Figure 1, a-b. Higher magnification of the products shows that the agglomerates contained ~20 nm particles with smooth surfaces. SCS caused considerable gas evolution generating many pores so that the as-synthesized powders became homogeneously agglomerated. All combustion products were friable, and had a spongy porous structure with porosity of up to 80 %. Concentration of residual carbon was lower than 1 wt. %.

The study of the magnetic properties of produced materials was performed by measuring dependencies of magnetization (M) on magnetic field strength (H) under 5 - 300 K presented in Figure 1, c. Results of the analysis show that magnetization curves for the $Y_3Fe_5O_{12}$ and $Sm_3Fe_5O_{12}$ samples at temperatures of 5 K and 300 K are distinctly different. The hysteresis plot for $Y_3Fe_5O_{12}$ exhibits magnetization moment (M) ~ 3 times larger than $Sm_3Fe_5O_{12}$.

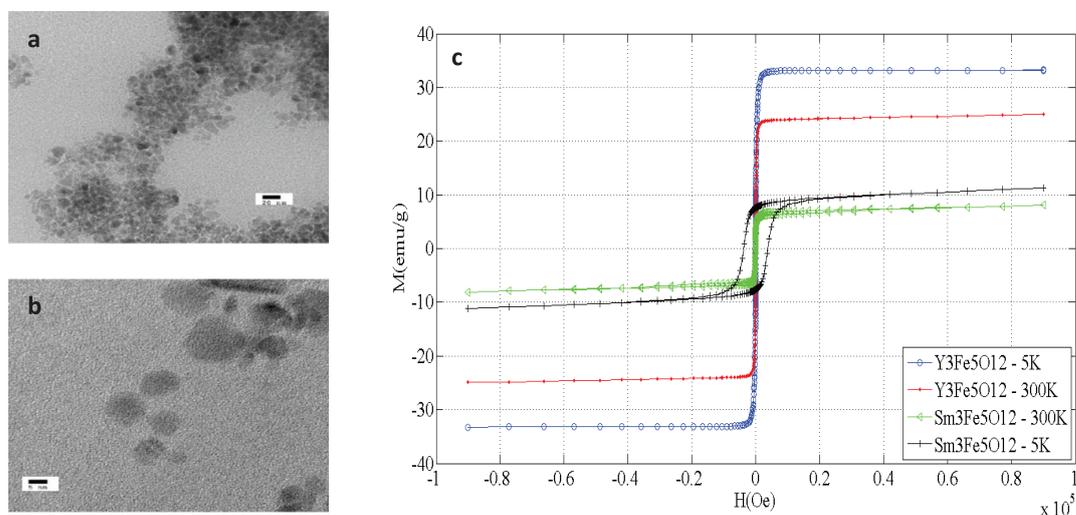


Figure 1. TEM images of yttrium ferrites produced at 3 wt. % glycine: the bar scale (a) - 20 nm; and (b) - 5 nm; (c)

Magnetic hysteresis loop of yttrium and samarium garnets at 5 K and 300 K.

Magnetization of zero-field-cooled (ZFC) and field-cooled (FC) measurements at the temperature range of 1.9-300 K shows different patterns when the fraction of glycine is increased. The analysis of ZFC and FC magnetization curves of annealed samples confirmed that nanoparticles exhibit superparamagnetic behavior. The increasing concentration of glycine leads to escalation of blocking temperature. Reduction of dielectric permittivity (ϵ_r) towards frequency indicates the relaxation processes in the composites, and the values of ϵ_r are shifted upward along the operating temperature.

Acknowledgement

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Abstract:1022

COMBUSTION SYNTHESIS OF NANO STRUCTURED CATALYTIC ACTIVATORS FOR REDUCTION OF SOOT ACTIVATION ENERGY

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Modifications of the conventional air-blown and atmospheric-pressure pulverized-coal combustion furnaces are being under development to enhance energy efficiency, reduce greenhouse gases and toxic emissions, and reduce the size and cost of future coal based power plants. Coal combustion by using nano-activators is promising approach that ensures energy-efficient and environmentally friendly burning of the solid fuels. The main contribution to world electricity production is provided by coal (40 %), gas (19 %), nuclear and hydropower delivers about 16 % of each. Thus, the future growth of power generation capacity will still be maintained by the coal combustion. The coal combustion efficiency shall increase with reducing carbon ignition temperature.

The goal of the present study is to identify nanostructured complex oxides catalysts that can be used for reduction of carbon ignition temperature actually to decrease combustion activation energy. An extensive set of complex oxides such as LaCrO_3 , PrCrO_3 , $\text{La}_{0.8}\text{Cr}_{1-x}\text{Li}_x\text{O}_3$, CeCrO_3 , $\text{Ce}(\text{Li})\text{CrO}_3$ and $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ where $x=0.1-0.7$ were synthesized and tested as potential catalyst for soot combustion. These candidate catalysts were selected due to their high oxygen exchange and storage ability, high temperature stability, the ability to tune their properties by doping, and their low price relative to that of noble metals. We synthesized powders of various complex oxides by two methods (i) Carbon Combustion Synthesis of Oxides (CCSO), which was developed and patented recently [1] that enables a rapid and easy synthesis; and (ii) Solution (metal nitrates-glycine) combustion synthesis (SCS) [2]. The aqueous phase rapidly started boiling and the reactants mixture then ignited and the oxides synthesis *in situ* occurred.

Figure 1 (left) shows XRD patterns of the as-synthesized products. The patterns indicate that the synthesized powder were pure perovskites phase. XRD analysis revealed that all the synthesized catalysts samples were single phase and highly crystalline. The catalytic activity of the as-synthesized powders was tested in a temperature-programmed combustion (TPC) apparatus. It consists of quartz fixed bed inserted in a reactor. The fixed bed was packed with a mixture of 0.1 g of amorphous carbon (45 nm), 1 g of the powdered catalyst and 10 g of silica pellets (0.3-0.7 mm in size). The catalyst/carbon/ SiO_2 mixture was confined between two layers of quartz wool. A computer-regulated furnace heated the sample up to 700 °C at a heating rate of 5 °C/min. The effluent gas compositions were determined by a mass spectrometer. Figure 1 (right) shows the TPC profile for soot oxidation under gas flow rate of 100 cc/min.

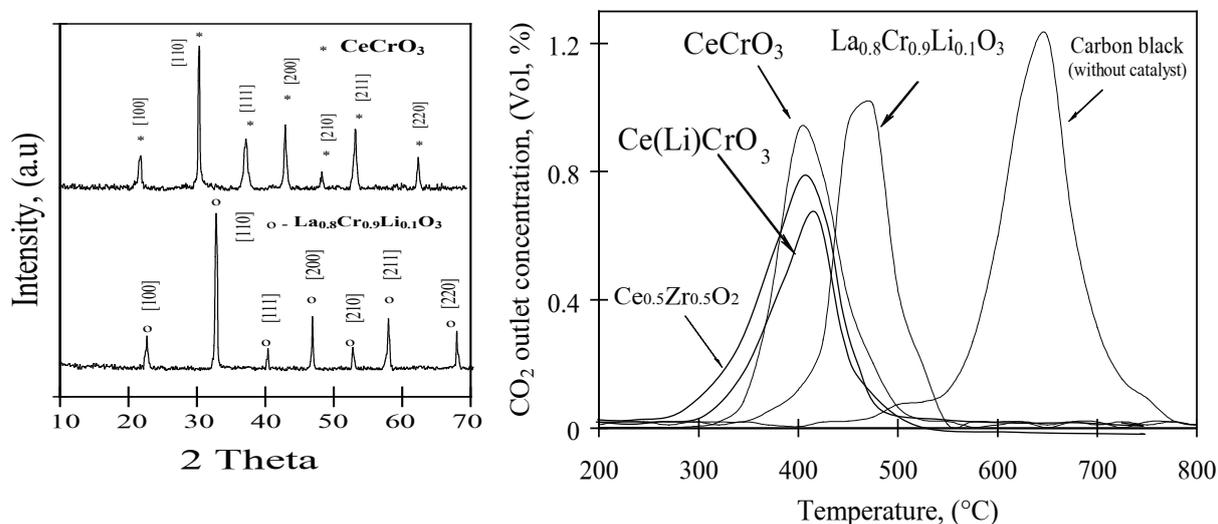


Figure 1. (left) X-ray diffraction patterns of as-synthesized CeCrO_3 and $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$ produce by CCSO; (right) TPC runs of the catalytic carbon combustion over CeCrO_3 , Li-doped CeCrO_3 , $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$ and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalysts powder. Non-catalytic combustion of soot reported as a reference.

The lower the temperature at which the effluent CO_2 has peak the higher is the catalytic activity and the lower is the ignition temperature. The $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst produced by CCSO shows the substantial performance with peak temperature of 390 °C as opposed to the 670 °C of non-catalytic combustion. However, the preliminary experiments showed that the activity of the oxides synthesized by SCS was somewhat higher than those synthesized by CCSO. Thus, after initial screening of the oxides made by CCSO, we synthesized the most promising ones by the more lengthy SCS methods.

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Abstract No : 1021

PLASTIC DEFORMATION AS MECHANISM FOR RAPID SINTERING OF NANO CERAMICS WITHOUT GRAIN GROWTH BASED SHS REACTION

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Densification of nano-grain ceramics is important, because smaller grain size results in the enhanced mechanical and functional properties. However, preparing fully-dense fine-grained ceramics is difficult by traditional sintering procedures, while the high temperature required for sintering results in excessive grain growth. For the purpose of preparing dense nano-grain ceramics while limiting grain growth, many efforts were paid for exploring new techniques of sintering. Chen proposed a two-step sintering method, in which fully dense Y_2O_3 was prepared by a quick first-step heating at 1250-1350°C to achieve an intermediate density (75~80%) and then cooled down to a final-step holding at 1150°C for 20h. The suppression of the final-stage grain growth is achieved and the finest grain size of fully dense ceramics is 60nm, which is about 4~6 times the starting powder size due to the coarsening in the first-stage heating(1). Kang reported the sintering of 5 mol. % TiO_2 -excess BaTiO_3 at relatively low temperature with a very long soaking time up to 100 h, and

got pellets with relative density of 95 % with limited grain growth(2). Anselmi-Tamburini and Munir made attempts to obtain nanometric cubic zirconia in an SPS apparatus with a special die which could apply pressure up to 1000MPa. The temperature required to achieve the 95% relative density decreases with the applied pressure, which results in the grain size decreases from 200nm to 15nm(3). Preparing dense nano-grain ceramics without grain growth is still a challenge. A new method based on Self-propagating High-temperature Synthesis plus quick pressing (SHS/QP) for producing dense nano-grain ceramics was suggested and developed(4). The heat generated by SHS reaction is applied to act as a heating source, which supplies a heating rate of 1300-1600°C/min to the sample. The densification can be performed within a few minutes. Dense nano-grain ceramics were obtained under pressure of 100-120MPa in several minutes. The process has higher heating rate and shorter densification duration than traditional sintering processes, which leads to no or limited grains coarsening. The densification process is likely different from traditional sintering techniques. It is suggested that the plastic deformation mechanism may play an important role and is dominating in the densification. The method is promising in the fabrication of nano- or ultrafine grain ceramics.

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POSTER SESSIONS

1.Theory of SHS: combustion, structure formation, methods of modeling.

Abstract No : 1003

GASLESS COMBUSTION OF THERMALLY COUPLED LAYERS

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Formation of the sample in the form of thermally coupled layers of gasless reagents allows us to conduct synthesis in the systems incapable of self-propagating combustion. For completeness of the synthesis there is a need for the reagents in adjacent layers to be controlled, alternating the donor layers ((DL), heat sources) and acceptor layers ((AL), heat consumers) [1]. The subject of the work is gasless combustion of a multilayer system consisting of high-energy layers (DL) and inert or low-energy inner layers (AL) in the presence of external heat extraction. The main objective is to find the characteristic modes of combustion and synthesis of products depending on the parameters of the layered compositions. We consider gasless combustion of a flat multilayer system with a rectangular cross section. Layers are interchanged and the donor layer joins the acceptor layer, forming a layered pair of AL-DL. The parameters and composition of such layered pairs (in total N pairs) are transferred through the entire thickness of the sample (Fig. 1). Heat exchange with the environment is realized through the external layer by the Newton's law. Combustion is carried out when all layers of the sample simultaneously contact with a hot surface in the plane perpendicular to the symmetry plane of the sample. The surface of the sample is insulated from the opposite plane of combustion.

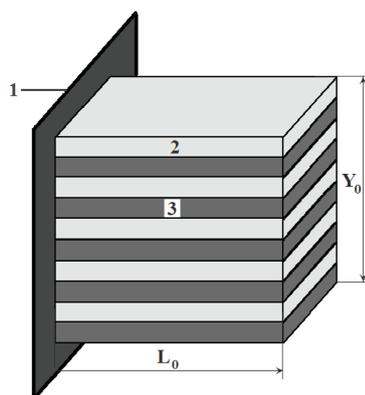


Fig.1 Scheme of the sample.

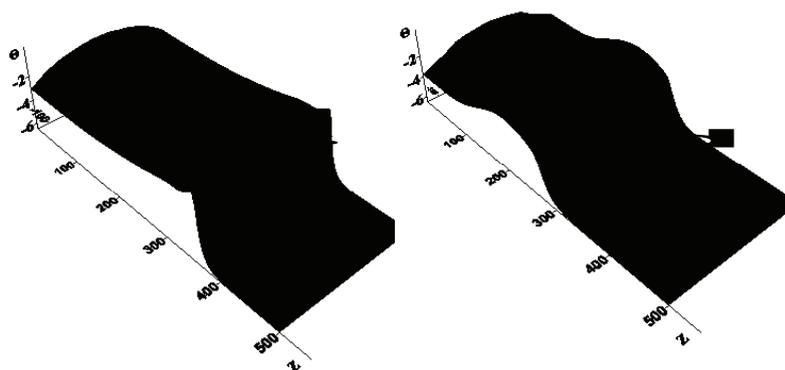


Fig.2 Temperature field: N=1 (a), N=2 (b).

We consider two layered compositions: inert or reactive layer-donors (AL). Addition of combustion products to a reactive green mixture is, on the one hand, one of the most effective ways to reduce the combustion temperature, on the other hand, leads to destabilization of the combustion front. In such conditions, AL should be considered to be heterogeneous, which prevent propagation of the combustion wave. The heterogeneity scale was equal to the thickness of AL. The regions of stationary and non-stationary combustion modes were found. It has been shown that the increase in number of layers can lead to the transition from one stationary combustion mode to another one through the intermediate non-stationary mode. The critical content of inert material (product of combustion) was found to be about 30% for multilayer composites when there is no combustion in the system. The combustion characteristics are shown to be dependent on the amount and composition of the weakly exothermal mixture and the number of layers for the systems with reactive layers. After increasing the number of layers at a constant total thickness of the sample, it takes place «homogenization» of the system. The combustion fronts in all layers form a united front (Fig. 2). It has been shown that there is an optimum ratio between the volumes (mass) of layers, when the synthesis is completely conducted in internal layers in the presence of external heat losses.

This work was supported by the Russian Ministry for Education and Science (project no. 10.1329.2014/K).

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Abstract No : 1033

SPECIALTY PRESS-MOLD PROVIDING CONTROL OF COOLING AND CRYSTALLIZATION OF SHS PRODUCT: DESIGN AND CAPABILITIES

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Self-propagating high-temperature synthesis is a modern highly efficient method for the production of a number of useful powders, composite materials and items. SHS processes have an advantage over traditional (furnace) technologies of the powder metallurgy since a number of valuable products can be manufactured in a one-stage SHS-based method.

Today the improvement and optimization of the existing SHS technology that would result in the production of resultant items characterized by a uniform, homogeneous crystal structure seems to be the most promising. In this sense, the synthesis of microcrystals of a required geometry is the most important task. For example, at a one-stage SHS-compaction production of cutting plates (used in manufacturing of cutting inserts, drill bits, etc.) the shape of the microcrystals of synthesized borides, carbides, etc. must be as close to that of the corresponding single crystals as possible. This goal can be attained by controlling the cooling of the combustion product thus influencing the formation of its crystal structure.

In this case, the most important challenge is to slow down the cooling of SHS product to ensure a sufficient time for the formation of desired microcrystals (which is normally much longer than the time of the reaction occurring in the combustion wave). In other words, it is necessary to perform a quasi-static crystallization of the combustion product in the volume (vs. the dynamic incomplete crystallization taking place in the vicinity of the combustion front).

The slowing-down of the cooling can be performed by controlling the temperature gradient and cooling rate of the still hot synthesized item [1], which can be attained by Joule heating of the volume of the SHS product [2].

Design of the developed vacuum press-mold used for this purpose is presented in Fig. 1. In this press-mold still hot SHS product can be electrically heated for a long time that was not possible to perform in the previously used one [3]. In contrast to traditional for powder metallurgy methods and instruments for electrothermal processing of items, this press-mold provides a uniformly distributed heat evolution over the item volume provided there is no direct contact with the electrodes. This minimizes heat losses and excludes potential problems due to welding of the electrodes on the item end surface. In this way, both the quality of the synthesized product and service life of the electrodes significantly increase. Moving disk electrodes which come into contact with the item can also be used in this press-mold.

To ensure a reliable and symmetrically distributed electrical contact between the electrodes and the end surfaces of the item special pyrolytic graphite grids were used.

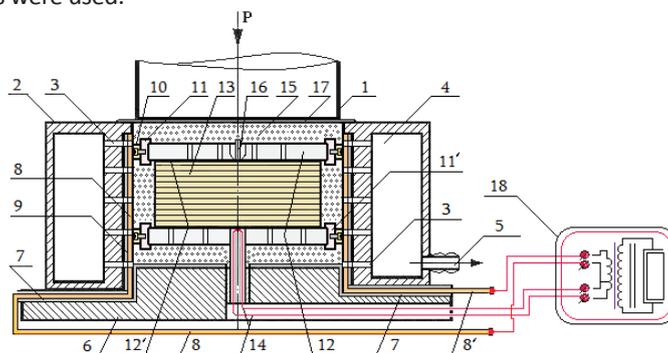


Fig.1. Design of the new press-mold for the electro-forced SHS compaction.

1. Puncheon; 2. Matrix; 3. Channel for vacuum-pumping; 4. Vacuum pump chamber; 5. Vacuum connector; 6. Tray; 7. Thermo-dielectric liner; 8(8'). Contact conducting section; 9. Thermo-dielectric matrix liner; 10. Sliding contact; 11(11'). Segment-end current collector; 12. Perforated graphite plate with pyrolytic graphite grid (12'); 13. Blank for SHS-compaction; 14. Initiating spiral; 15. Quartz sand; 16. Dielectric liner - current collector fixture 88'; 17. Sealing flexible polyethylene plate; 18. Current-carrying unit.

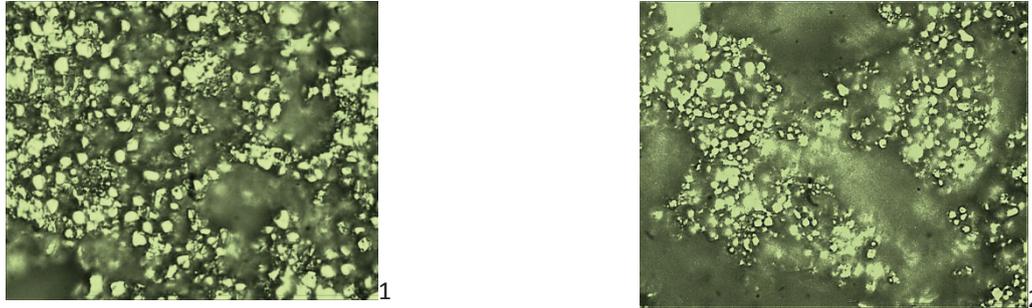


Fig. 2. Metallographic study of the surface of synthesized hard SHS alloys of the TH-20 type (x 1000): 1. Without electro-thermal heating; 2. With electro-thermal heating ($U = 3-3.5$ V, $J = 550-600$ A, heating time - 30 min).

Two photos for metallographic study of the hard alloy samples (Ti 80 % + C 20%) obtained in the absence of additional heating (i.e. according to a standard STIM technology [4]) and in the presence of additional Joule heating of the synthesized SHS-product.

In spite of a preliminary nature of this result, the effect of the Joule heating and thermostating of the synthesized material on its structure seems to be obvious.

This practical approach based on the theory of SHS is believed to be quite promising for the further development and optimization of SHS-compaction production method for manufacturing composite materials and items.

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Abstract No : 1060

STRUCTURE OF SHS PRODUCTS: NUMERICAL SIMULATION

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This work aimed at numerical modeling of structural features of SHS products. Previously we have synthesized Ti_3SiC_2 crystals by SHS method [1]. The crystals were found to have a two-dimensional structure (Fig. 1) arising due to preferable growth in direction a of the elementary cell (Fig. 2). Accumulation of differences between atomic positions in TiC and Ti_3SiC_2 lattices gradually destroys conformity between two structures and hinders crystal growth in directions b and c .

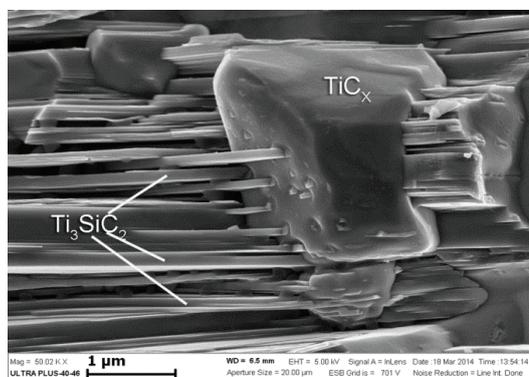


Fig.1. SHS-produced Ti_3SiC_2 crystal.

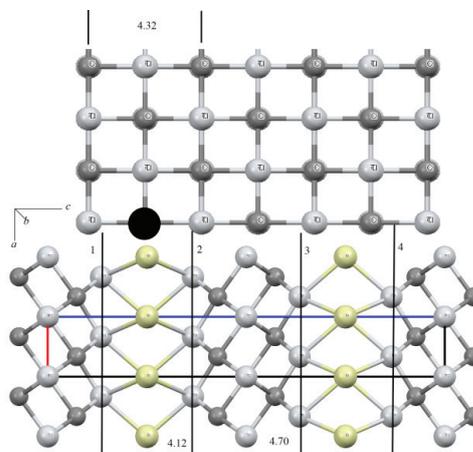


Fig.2. Relationship between TiC (top) and Ti_3SiC_2 (up) structures: ● stands for hole, distance in Å.

Our XRD patterns showed the presence of reflections that could hardly belong to hexagonal B_4C crystals, irrespective of their origin [2-4]. To explain the phenomenon, we theoretically modeled the insertion of atom C into one of icosahedra in boron carbide structure (Fig. 3). This gave rise to a change of position of the C atom in the icosahedron. The length of the B-C bond in the icosahedron decreased by 0.01 Å (5% volume decrease). Calculations showed the appearance of reflexes with 'prohibited' icosahedral indexes (Fig. 2). This effect is not due to the emergence of a new low-symmetric phase.

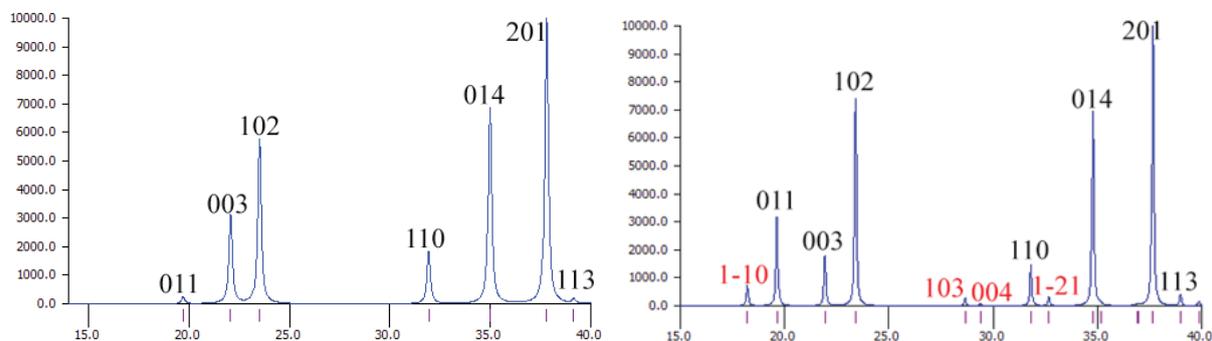


Fig. 2. Theoretical XRD patterns of B_4C crystal modeled without (left) and with (right) account of icosahedron distortion.

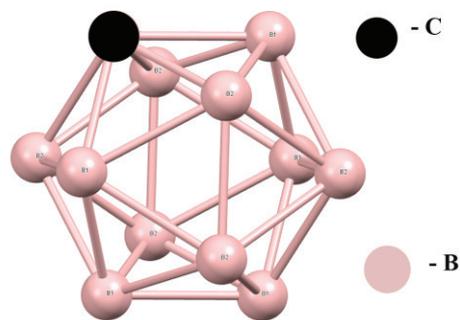


Fig.3. Icosahedral cell of boron carbide.

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Abstract No : 1088

MATHEMATICAL SIMULATION OF SOLID-PHASE PLUNGER EXTRUSION WITH DOUBLE COMPRESSION OF COMPOSITE MATERIALS

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One of the perspective and actively developing SHS methods is the SHS-extrusion method for receiving lengthy products from fragile and difficult deformable powders of refractory inorganic materials now. In this paper mathematical modeling of the SHS-extrusion to identify opportunities for two-stage compression of the material is carried out. The results of the study, presented below, have shown that such a process scheme may have important practical implications. Based on the proposed model of solid-phase extrusion with two-stage compression of the material we studied the influence of process parameters (the radius of the hole of the transition matrix, the height of the workpiece) and thermal conditions (criteria Bio) on the length and density of the resulting long samples.

The results of the study showed that such technological scheme may have important practical implications. For rods of large diameter (5mm) two-stage compression for the selected process parameters (same c single-stage compression) allows you to get the rods 97% of the maximum possible, and for single-stage compression with the same settings, only 72%.

However, this result is of a General nature: during the extrusion of small (1.5 mm) radius of the cross section of the outlet: extrusion in a single stage allows you to extrude a rod with a length of less than 18%, the use of two-stage compression allows only a slight increase up to 22%. The most part of material isn't squeezed out and there is an obstruction of an exhaust outlet of a matrix. Most of the material is not squeezed out and there is a blockage of the outlet of the matrix. An important application of two-stage compression is to choose the radius of the intermediate matrix. In some cases, you can identify the optimal transition radius, for receiving of qualitative ekstrudat. The dependence of the completeness of the extrusion from the degree of deformation through the intermediate matrix has a nonmonotonic character. This is due to a competitive interaction processes of the heat sink, compaction and extrusion. The increasing branch of this dependence corresponds to the positive effect of two-stage compression. Falling branch time of extrusion is increased, and therefore, the heat sink material does not have time to be squeezed out and the effect of two-stage compression becomes negative.

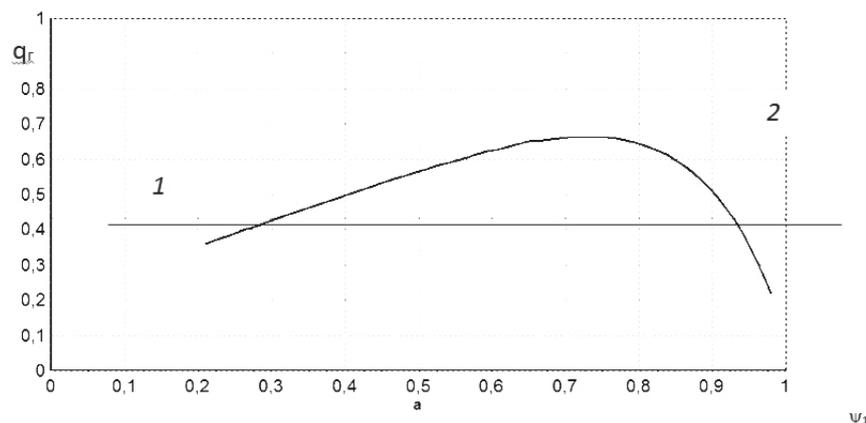


Fig. 1. Dependence of mass of the squeezed-out part of (q_g) on the degree of deformation ($\psi_1=1-S_2/S_0$): 1) one-stage sinking, 2) two-level sinkings. S_2, S_0 - the bottom area of the base of the mold and the holes of the transition matrix respectively

Obviously, there will need a combination of experimental and theoretical studies. Currently, it is still difficult to trace all the opportunities of multi-stage compression of the material at SHS-extrusion. One of the aspects of the practical application of this technological scheme is to achieve submicrocrystalline state of materials with the purpose of increasing their strength characteristics.

Abstract No : 1097

SYNTHESIS AND REACTION MECHANISM OF Ti_2SnC FROM Ti/Sn/C POWDER BY SELF-PROPAGATION HIGH-TEMPERATURE TECHNIQUE

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Harbin Normal University Department of chemistry Harbin-China¹

Ternary MAX phase Ti_2SnC was synthesized by self-propagation high-temperature synthesis(SHS) technique of sub-stoichiometric $2Ti:Sn:C$ and $2Ti:1.03Sn:C$. The density of $2Ti:Sn:C$ and $2Ti:1.03Sn:C$ are 4.120 and 3.7490, the porosity of them are 32.5204% and 40.2809% respectively, which are measured by hydrostatic weighing method. XRD, EDS, SEM and DTA were used to characterize Ti_2SnC powder. The a and c lattice parameters of Ti_2SnC are 3.186 Å and 13.630Å at room condition, respectively. The reaction mechanism was analyzed on the basis of the XRD, EDS, DTA results as well as SEM observation. In the Ti-Sn-C reaction system, Sn starts to melt into liquid at 232°C. With the increase of the temperature, the structure of Ti-C that C is coated by Ti was formed. Then, Ti reacts with Sn to form binary system Ti_xSn_y , such as Ti_6Sn_5 and Ti_5Sn_3 , and TiC is formed at about 800°C. The class disk of Ti_2SnC is fabricated with the reaction of TiC and Ti_xSn_y at 1100°C. But the reaction of TiC and Ti_xSn_y is incomplete, because the reaction rate of the self-propagating high temperature synthesis is faster, and the temperature of it is higher. Hence the products remain unreacted Ti_6Sn_5 , Ti_5Sn_3 and TiC phase. At the same time, it is found that Ti_2SnC decomposes to TiC and Sn at 1250°C.

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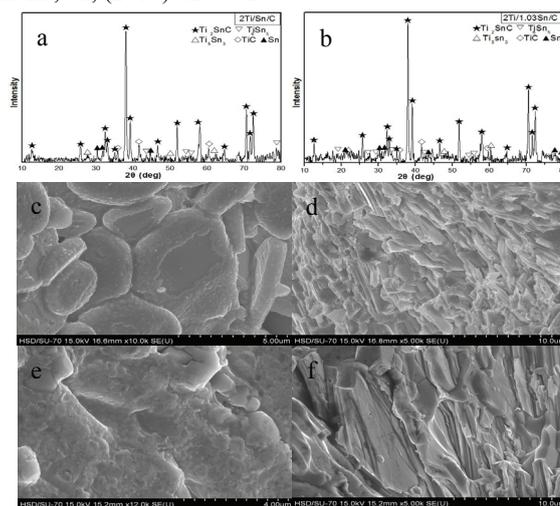


Fig. a and b XRD pattern of $2Ti:Sn:C$ and $2Ti:1.03Sn:C$ respectively, Typical SEM micrographs of Ti_2SnC samples obtained from (a,b) $2Ti:Sn:C$, (c,d) $2Ti:1.03Sn:C$.

Abstract No : 1117

COMBUSTION OF Ti - B MIXTURES UNDER QUASI-STATIC PRESSURE

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In this work, we explored the SHS reaction in Ti - B powder blends in conditions of quasi-static compression using a specially designed experimental setup. The experimental technique was based on measuring of combustion temperature in two points of the sample and a voltage difference between them.

Ti + B mixtures were prepared from the powders of titanium (PTM brand, mean particle size < 45 μm , >99.1% pure), black amorphous boron (mean particle size <1 μm , >99.5% pure). Cylindrical green pellets ($f = 12 \text{ mm}$, $l = 15 \text{ mm}$) with a relative density of 0.6 were obtained under a pressure of 200 kg/cm^2 .

Combustion temperature was measured using tungsten-rhenium thermocouples WR5/20 with a diameter of $d = 0.2 \text{ mm}$. A voltage difference arising during combustion in the sample was detected with two thermocouple electrodes WR5. The distance between electrodes was 15 mm.

Maximal burning velocity (210 mm/s) was attained during combustion of stoichiometric composition Ti-2B. Deviation from stoichiometry leads to a decrease in burning velocity. It was established, that the first and the second concentration limits are reached with ratio $[\text{B}/\text{Ti}] = 0.75$ и $[\text{B}/\text{Ti}] = 5.5$ respectively.

The amplitude and duration of combustion induced EMF pulses depend on ratio $[\text{B}/\text{Ti}]$. In case if $[\text{B}/\text{Ti}] \leq 1$ EMF is positive; $1.5 \leq [\text{B}/\text{Ti}] \leq 3$ is bipolar; $[\text{B}/\text{Ti}] \geq 3.5$ is negative.

Arising of EMF during combustion of mixture Ti - xB with low boron concentration is associated with changing of free electrons' density in a titanium conductor, and at high concentration - with appearing of p-conductivity in boron particles during heating in the combustion wave. Formation of bipolar electrical signal was associated with formation of EMF in the titanium conductor in the low-temperature part of the combustion wave and in boron's particles in the high-temperature part.

This work was supported by the Russian Foundation for Basic Research (project no. 14-03-31536).

Abstract No : 1156

A STUDY ABOUT THERMOCHEMICAL SIMULATION OF ZrB_2 - B_4C - ZrC SYSTEM

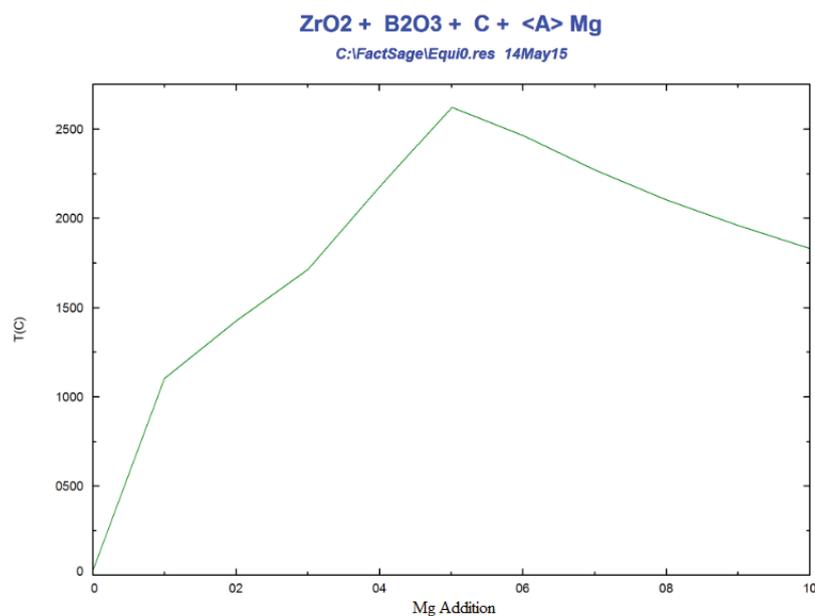
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Yalova University Chemical and Process Engineering Yalova-Turkey¹ İ.T.Ü. Metallurgy and Materials Engineer Istanbul-Turkey²

ZrB_2 , ZrC and B_4C are significant metal borides and carbides. They are being used in various industrial areas from space technology to nuclear industry owing to their physical properties such as high melting point, high thermal/electrical conductivity and low density. Present study was conducted to simulate self-propagating high-temperature synthesis (SHS) reactions. ZrO_2 , C , B_2O_3 were used as starting material and Mg was used as a reductant to produce ZrB_2 , ZrC and B_4C powders via SHS.[1]

The advanced thermochemical simulations of the reactions were investigated in detail including different ratios of initial mixtures, as well as different initial temperatures in order to reduce the number of experiments. In addition, the adiabatic temperatures were calculated for each system by using FactSage 6.2 Thermochemistry simulation software. Since the adiabatic combustion temperatures (T_{ad}) of the SHS reactions obtained by the high energetic precursor mixtures change between 2500 and 3500 K, the combustion products (alloy and oxide) will be in liquid-phase state. Thus, the melting temperature difference clearly will result in a very good separation of the multi-phase alloy and the slag phase. The systems having appropriate conditions were identified and the experiments were carried out.

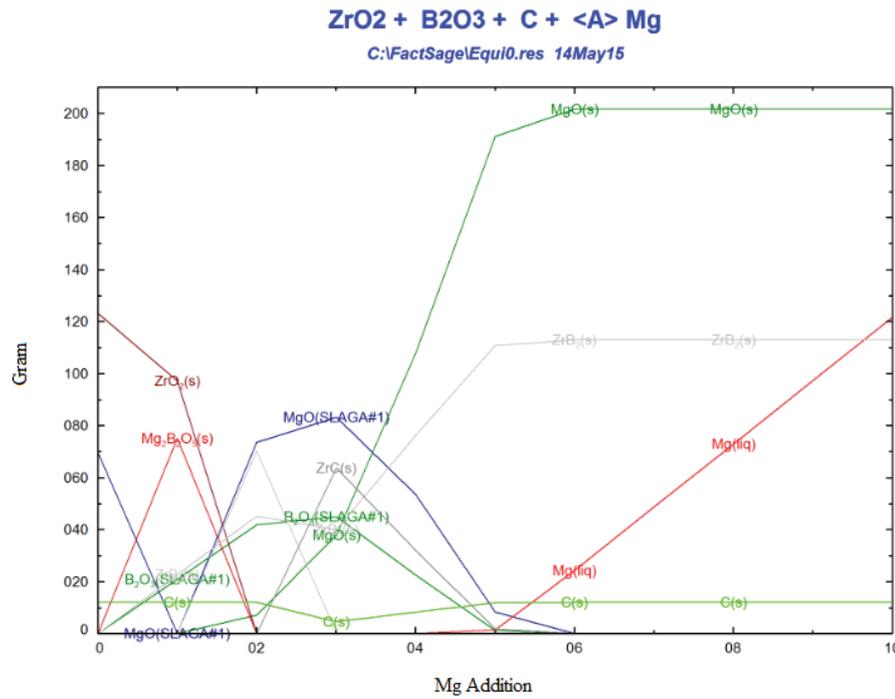
In this study, it was aimed to simulate ZrB_2 - B_4C - ZrC system to reduce amount of SHS experiment. Firstly ZrO_2 , B_2O_3 , C and Mg added to reaction and adiabatic temperature determined. Figure I. shows the changing of Adiabatic Temperature with Mg addition.

Figure I. Adiabatic Temperature of Zr-B-C system



Secondly, probable phases defined for the same conditions. In this simulation effect of reductant sthociometry was investigated and probable phases assigned. Figure II. Presents effect of Mg addition on the Zr-B-C system.

Figure II. Probable Phases of Zr-B-C System



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2. Mechanisms and kinetics of SHS processes.

Abstract No : 1014

IN SITU SYNCHROTRON INVESTIGATION IN THE Ti-C-Ni AND Ti-C-NiO-Al SYSTEMS

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Self-propagating high-temperature synthesis (SHS) has been performed in the Ti-C- Ni and Ti-C-NiO-Al systems in order to obtain TiC-Ni composites. The addition of Ni gives the synthesized composite TiC-Ni, some very interesting structural and mechanical properties thanks to the combination of metallic and ceramic properties [1, 2].

The purpose of this study was to investigate the phase's formation during SHS reaction when the nickel is part of reactive mixture in the first system and when it is a product of the reaction, in the second one. Time-resolved X-ray diffraction (TRXRD) experiments using an X-ray synchrotron beam (ID11, ESRF Grenoble) was carry out to monitor in situ the structural and thermal evolutions taking place during SHS.

The results show that while for the former case the reaction is initiated by the allotropic transformation of Ti from hexagonal to cubic, intermediate phases (Al-Ti intermetallics) precede this transition in the later case. In the final materials the presence of nanosized Ni particles was observed.

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Abstract No : 1025

COMBUSTION OF MARTIAN REGOLITH SIMULANTS WITH MAGNESIUM

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The University of Texas at El Paso Mechanical Engineering El Paso-United States¹

It has been shown recently that mixtures of JSC-1A lunar regolith simulant with magnesium are combustible [1-4]. Thermite-type reactions in these mixtures could be used for *in situ* production of construction materials on the Moon. Because of complex composition of lunar regolith, however, the mechanisms of these reactions are not well understood. Also, for Mars mission applications, it is important to explore the possibility of using Martian regolith in such mixtures.

In the present work, combustion of two Martian regolith simulants (JSC-Mars-1A and Mojave Mars) with magnesium was studied using thermodynamic calculations and combustion experiments. To understand the reaction mechanisms in these mixtures as well as in the mixtures of JSC-1A lunar regolith simulant with magnesium, thermoanalytical experiments were also conducted.

It has been shown that the Martian regolith simulants form combustible mixtures with magnesium. The measured combustion temperatures and identified product compositions are in reasonable agreement with thermodynamic predictions. For Mojave Mars, combustion is accompanied by oscillations in the front motion and by the formation of a layered structure of the product. This effect is more significant at lower concentrations of Mg. The mixtures of JSC-Mars-1A with magnesium at 20-30 wt% Mg burn more vigorously than mixtures based on Mojave Mars (Fig. 1), which is apparently associated with the higher content of iron oxide in JSC-Mars-1A.

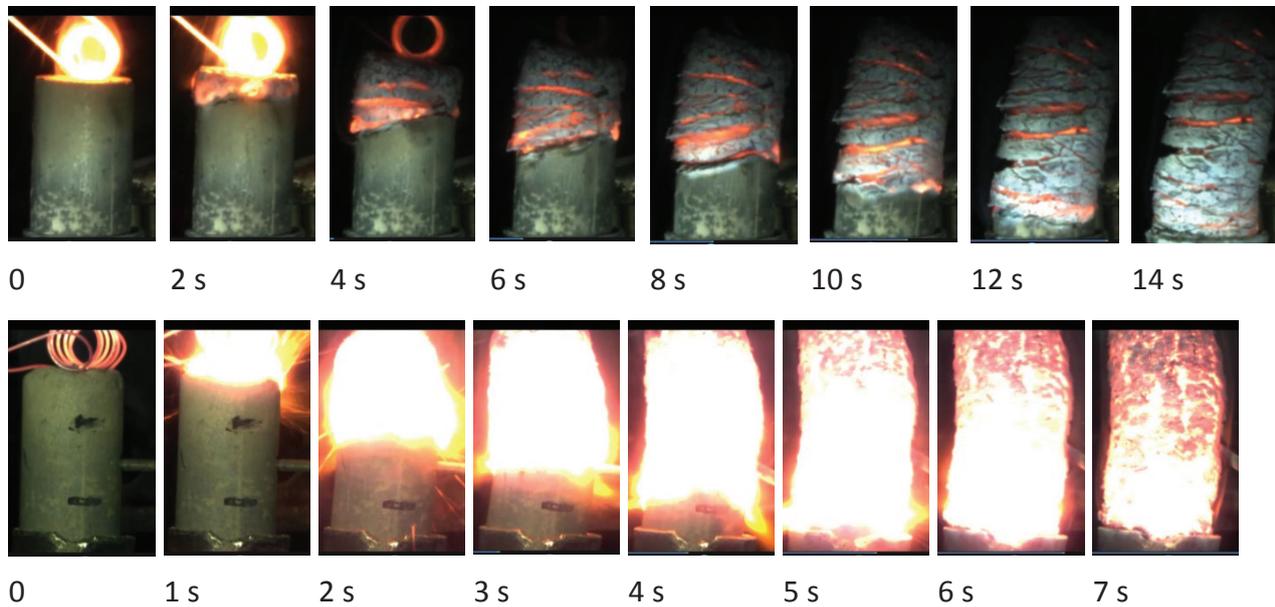


Fig. 1. Combustion propagation over compacted mixtures of (top) Mojave Mars and (bottom) JSC-Mars-1A regolith simulants with magnesium (20 wt% Mg). Time zero was selected arbitrarily.

Thermoanalytical studies have shown that iron oxide plays a dominant role in the combustion of JSC-Mars-1A simulant with magnesium. For Mojave Mars material and JSC-1A lunar regolith simulant, which include more silica and less iron oxide, silica exhibits a significant effect on the combustion, promoting reactions at lower temperatures.

This research was supported by the NASA Office of Education (Group 5 University Research Centers). AD was supported through a GAANN fellowship of the U.S. Office of Education, while SC was supported by the Campus Office of Undergraduate Research Initiatives (COURI) of the University of Texas at El Paso. The authors thank Dr. Bonnie Cooper for providing Mojave Mars simulant.

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Abstract No : 1034

UNSTABLE GAS-FREE COMBUSTION OF DISC-SHAPED SYSTEMS

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The most interesting phenomena (self-oscillating and spin combustion modes of condensed systems) occurring during unstable propagation of the exothermic reaction front are found and described in the studies of SHS processes [1 - 3]. Considering the spin mode, the combustion front is a center of a chemical reaction moving over a substance, which can propagate over the surface layers of the sample and through the inner layers of the sample.

We present here the results of experimental studies for gas-free combustion of the Ti + 2B planar system with the addition of disc-shaped copper. The experiments were carried out in a bomb at a constant pressure of inert gas of 6 atm. To watch the process of spin combustion, we conducted frame by frame filming (camera "Konvas"). In some cases the burning samples were subjected to rapid quenching in liquid argon. The final products of combustion were studied by metallographic (PMT - 3) and X-ray diffraction (DRON - 2) analyzes. Diagram of the process took the form of a "hat", the head part of which was an igniting tablet from a mixture of titanium and boron and was located in the center of the reaction sample. Ignition was initiated by a hot coil. After initiation of the reaction the tablet burned in the spin mode, "spin" also occurred in the sample.

Dynamics of the burning discs was as follows. After local initiation of the reaction in the red-hot head part of the "hat", the reaction center moved over the flat surface of the disk, describing a two-dimensional spiral trajectory. Moreover, the increase in diameter of the reaction sample leads to the fact that the chemical interactions become much more complicated. This assumption is indirectly confirmed by the results in [4], where numerical experiments have shown that the increase in radius of the cylindrical sample leads to complicated dynamics of the combustion center. For example, when the diameter of the sample is 10 mm there is one stable "spin", 2 - 3 - headed "spin" appears for the diameter of 25 mm. The further increase in diameter led to the increased number of "spins" (see Fig.).

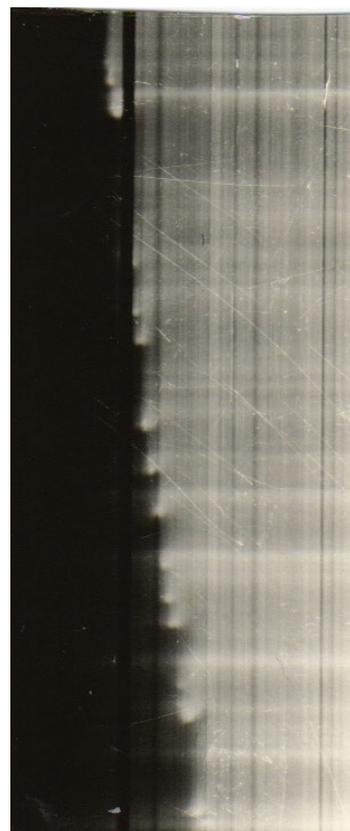


Fig. Many-headed «spin».

Spin propagation of the flame front considered in this paper can be explained by instability due to lateral disturbances of the one-dimensional self-oscillating mode. This phenomenon is physically caused by an excess of enthalpy in the combustion front, since for gas-free systems the region of the high temperature gradient is much smaller than the area where the chemical transformation is essential. In this case, the self-oscillating mode characterized by pulsations (subsequent interchange of bursts and depressions) is the result of two major factors: the presence of heat excess in the combustion front, and the heat flow from the reaction products to the conversion zone.

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Abstract No : 1051

STUDY OF FERROSILICOALUMINIUM NITRIDING

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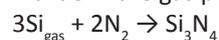
At present time, nitrides are the most demanded materials and are used in all branches of industry. As a rule, expensive superfine metal powders are used to produce nitrides and nitride-based materials. In this connection, there is a need in the search for low-cost raw material to produce nitrides. The use of commercial ferroalloy as cheaper reagents can significantly reduce the cost of nitrides and nitride-based materials. In [1,2] it was shown the possibility of using ferroalloys for producing nitrides in the processes of self-propagating high-temperature synthesis (SHS). The obtained materials were highly competitive with materials produced from pure reagents according to operational characteristics. This work is devoted to the study of the mechanism of ferrosilicoaluminium nitriding. The interest to this alloy lies in the fact that the alloy is complicated and contains two nitride-forming elements. It should be noted that the mechanism for nitriding of complex ferroalloys containing several nitride-forming elements have not been studied so far.

Ferrosilicoaluminium (FSA, FS65A15 grade) was used as a raw material. Initial FSA was a multiphase material consisting of silicon, high-temperature leboite (FeSi₂), and aluminum that was present in the form of solid solution in the FeSi₂ phase, according to the results of X-ray fluorescence analysis (XRF). The Fe, Al₂O₃, Al_{0.5}Fe_{0.5} phases were present as impurity phases. The results of chemical analysis showed that the content of silicon in the alloy was 60%, the content of aluminum was 13%, and the rest was iron. To study physical and chemical transformations occurring during the interaction of nitrogen with ferrosilicoaluminium in detail, the process of alloy nitriding was investigated in a tubular furnace at a specified temperature and also by differential scanning calorimetry (DSC).

The results of the nitride formation investigation under isothermal conditions have shown that nitriding of FSA begins with the formation of AlN in the temperature range of 800 - 900° C, and the formation silicon nitride at 1100° C, which correlates with the formation heat of nitrides of aluminum and silicon. The results of the complex thermal analysis show that that the process of FSA nitriding has three characteristic stages characterized by different speeds.

Mechanism for nitriding of ferroalloy containing two nitride-forming elements can be represented as follows:

1. T = 800 - 900°C. There is interaction of nitrogen with aluminum that is the part of leboite and aluminum in the phase Al_{0.5}Fe_{0.5}, which leads to the formation of aluminum nitride.
2. T = 900 - 1200°C. The phase transition of high-temperature α-leboite takes place with extraction of silicon (solid phase nitriding of silicon).
3. T = 1200 - 1350°C. The melts of silicide and silicon nitride are mainly formed by the mechanism of "liquid - gas".
4. T = 1350 - 1500°C. There is dissociation of iron silicide with extraction of silicon and extracted silicon interacts with nitrogen to form silicon nitride. In this temperature range, silicon evaporates from the eutectic melt and forms silicon nitride in the gas phase according to the reaction:



5. Dissociation of silicon nitride can take place in the high-temperature region. However, dissolving AlN in Si₃N₄ to form a solid solution based on Si₃N₄, as well as the formation of β-sialon with the Si₃Al₃O₃N₅ composition increases thermal stability of Si₃N₄.

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Abstract No : 1092

THERMOCHEMICAL CONVERSION OF IRON COMPOUNDS IN A WAVE OF FLAMELESS COMBUSTION

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Thermochemical conversion of compounds of transition metals with forming of highly porous composite material, comprising nanosized particles of these metals and derivatives thereof, can occur in the flameless combustion wave of energy-rich materials in ballasted polymeric systems [1]. The distinctive features of this process are the absence of a flame, the low maximum temperature (250^o-400^oC) and propagation velocity (0.05-1.0 mm/s) of the combustion wave and, also, incomplete chemical transformation of the energy component with releasing of chemical reactive gaseous products. In this paper the study of the process of phase formation in the combustion wave mixture of iron oxide (III) - hexogen in a nitrogen atmosphere is presented.

Time-resolved XRD method shown that the process of reduction of iron oxide (III) in the wave of flameless combustion occurs in stage by stage manner (fig.1). From the moment of ignition to the moment when combustion front reach the detection area, only diffraction peaks of components of initial mixture were found, which correspond to the materials in the crystal states - hematite and hexogen. When the combustion front reach the detection area the fading of lines of the initial components and the appearance of line of (200) FeO are observed. Lines of the phase FeO are recorded during 15 seconds and then disappear but at the diffraction field the nucleation and growth of the intensity of the Fe₃O₄ phase lines (220) (311) (400) is observed. This phase is the single crystalline phase in a final product of combustion of the mixture. Thus, the analysis of the diffraction pattern of the mixture in the combustion process reveals that the formation of the final product occurs through the intermediate phase FeO to the final Fe₃O₄ phase. The process occurs entirely in the solid phase, without amorphization of structure. Size of coherent phase scattering area of Fe₃O₄ was 5-7 nm, and the specific surface area is up to 80 m²/g. Thus, as a result of the flameless combustion of mixtures, containing the iron precursor, a highly porous polymer matrix filled with particles of nanosize-iron compounds is formed.

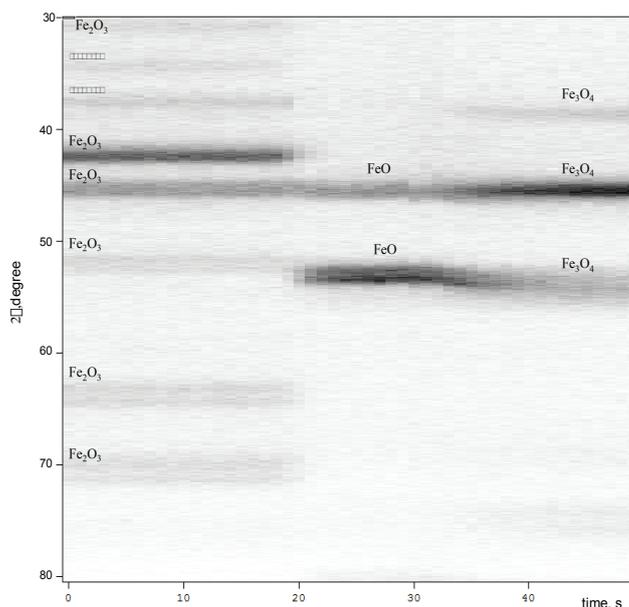


Fig. 1 The diffraction picture of the combustion process of mixture Fe_2O_3 - hexogen.

Work supported by the Presidium Foundation of Russian Academy of Sciences N.24, "Combustion and Detonation"

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Abstract No : 1093

GAS EVOLUTION DURING SHS OF TiC

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As is known, the evolution of impurity and adsorbed gases during SHS reactions may strongly affect (due to occurrence of gas-transport reactions) the combustion mechanism and hence the burning velocity. Moreover, gas evolution complicates subsequent processing of still hot combustion products (such as densification or extrusion).

Earlier, position of a gas evolution on the profile combustion wave was inferred indirectly: either from gas pressure profiles recorded during combustion [1] or from still frames of video records [2, 3]. In this work, we suggest a method for direct detecting a position on gas evolution sites that was tested on SHS of TiC in Ti + 0.65C mixtures (by weight). Experiments were carried out in the setup schematically presented in Fig. 1.

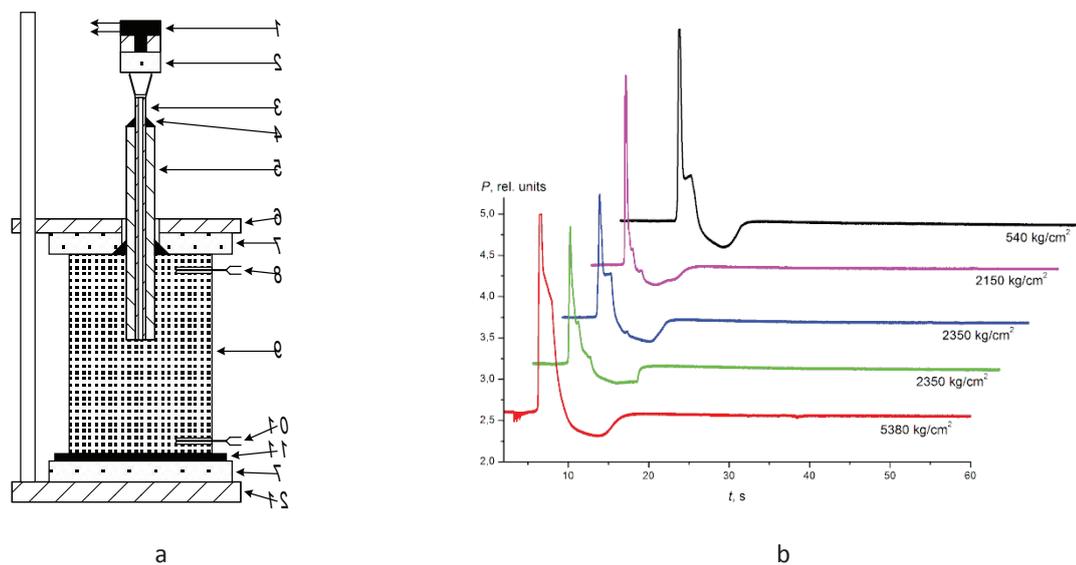


Fig. 1. (a) Experimental setup: 1, pressure gauge; 2, mineral wool; 3, syringe needle; 4, heat-resistant glue; 5, ceramic tube; 6, clamping plate; 7, BN plate; 8, thermocouple T2; 9, sample; 10, thermocouple T1; 11, initiating TiB strip; 12, bedding; and (b) typical pressure profiles recorded by gauge 1 (indicated are compacting pressures).



Fig. 2. Overall view of samples: (a) unburned, (b) burned, and (c) burned sample in cross section.

It has been found that gas evolution in the system under study gets started just behind the combustion wave.

This work was financially supported by the Russian Foundation for Basic Research (project no. [15-03-03531](#)).

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Abstract No : 1098

ACOUSTIC EMISSION METHOD APPLICATION FOR SHS PROCESSES STUDIES

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According to the standard definition [1], acoustic emission - class of phenomena whereby transient elastic waves are generated by the rapid release of energy from localized sources within a material. A particular case of the acoustic emission phenomenon deals with the acoustic wave generation caused by reconfiguration of the material internal structure [2,3]. This effect is observed in different physical and physical/chemical conversions, in particular in the self-propagating high-temperature synthesis (SHS) processes [3,4], and so such processes can be studied by means of recording and processing of acoustic signals.

It is known that in case of hydrogen interaction with metals, including in the SHS mode, acoustic signals appear, in particular, as a result of changing material density caused by hydrogenation, which is accompanied by cracking or dispersion of an initial compact sample to the powder [5]. In this work the aforementioned method was used, in order to

research kinetics of hydrogenation and dehydrogenation of metallic titanium samples, whose initial states were different (pieces of compact metal, powder). In the experiments highly pressurized hydrogen was supplied to the reaction chamber, where there was a metal sample pre-heated in vacuum for the sample surface transition into the chemically active state [6]. Titanium hydrogenation kinetics was studied by means of recording the pressure variation rate in the chamber, as well as acoustic emission signals accompanying chemical conversion. For example, fig.1 shows dependencies of the aforementioned parameters on the process duration that were obtained as a result of hydrogenation pieces of compact titanium.

Based on the pressure variation in the chamber it is obvious that the hydrogenation reaction occurs intensively even at the initial seconds of the experiment after hydrogen inlet into the reaction chamber. Besides, in case of compact titanium hydrogenation, the amplitude of the acoustic emission signal is growing for certain rather durable time period, and its maximum is substantially shifted in time relatively to the moment of the gas supply. Such acoustic signal signature reveals that the sample's morphological and phase restructuring, leading in the long run to the metal cracking during hydrogenation, occurs the most intensively upon reaching a certain degree of the metal saturation with hydrogen. The dependence of the said parameter on the initial state of the metal and experimental conditions was investigated by the authors.

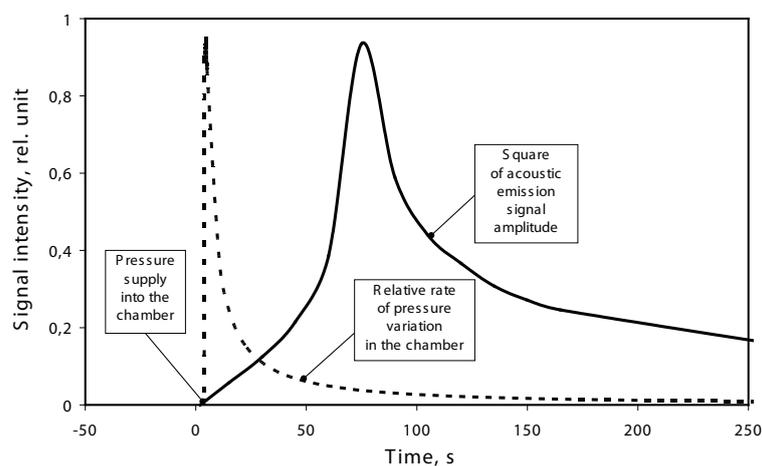


Fig.1 Dependencies of pressure variation rate in the chamber, and square of the acoustic emission signal amplitude on time of compact titanium hydrogenation

The results obtained demonstrate a good potential for the use of the acoustic emission method for looking both at the kinetics of heterogeneous chemical reactions, and structural transformations in the materials during physical and chemical conversions, which accompany the SHS processes.

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Abstract No : 1121

**INVESTIGATION OF PHASE FORMATION DURING SHS OF MATERIALS WITH FLUORINE
PHLOGOPITE MATRIX**

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Hydrothermal and pyrogenic methods with crystallization from melts are known for production of fluorine phlogopite [1]. SHS as alternative method allows its manufacturing in the combustion mode without melting equipment [2].

In this work we studied influence of a diluent (MgO) on the product phase composition. The sequence of phases forming directly in the combustion wave was monitored by time-resolved XRD method [3]. This method is based on recording of sequence of XRD patterns in a wide angular range during material synthesis with the determined time exposition (from 100 ms). The method allows to carry out *in situ* registration of changes of phase composition (from initial components up to final products throughout the intermediates) and to determine the sequence of phase transformations during combustion.

In experiments we used mixtures with different MgO content and established absence of principal differences in phase formation sequence. Thus during combustion of the mixture containing 8% wt of MgO (Fig. 1a), the front approaches the zone of XRD registration in 20 sec, intensity of diffraction lines corresponding to main initial phases SiO₂, Mg, Al and MgO drops up to background level and only weak diffraction lines of SiO₂ can be seen in Fig. 1a in the 21st sec of registration. A new MgAl₂O₄ phase appears while MgO line dies away, i.e. the diluent participates in the phase formation. Then (22–24 sec) a new line corresponding to Na(K)Mg₃(Si₃AlO₁₀)F₂ appears. After the front leaves the registration zone, we registered phases based on Mg_x(SiO₄)_yF₂.

XRD analysis of the final product after cooling proves presence of fluorine phlogopite Na(K)Mg₃(Si₃AlO₁₀)F₂ as well as Si, MgAl₂O₄, Mg₃(SiO₄)F₂, Mg₅(SiO₄)₂F₂ and Mg₇(SiO₄)₃F₂.

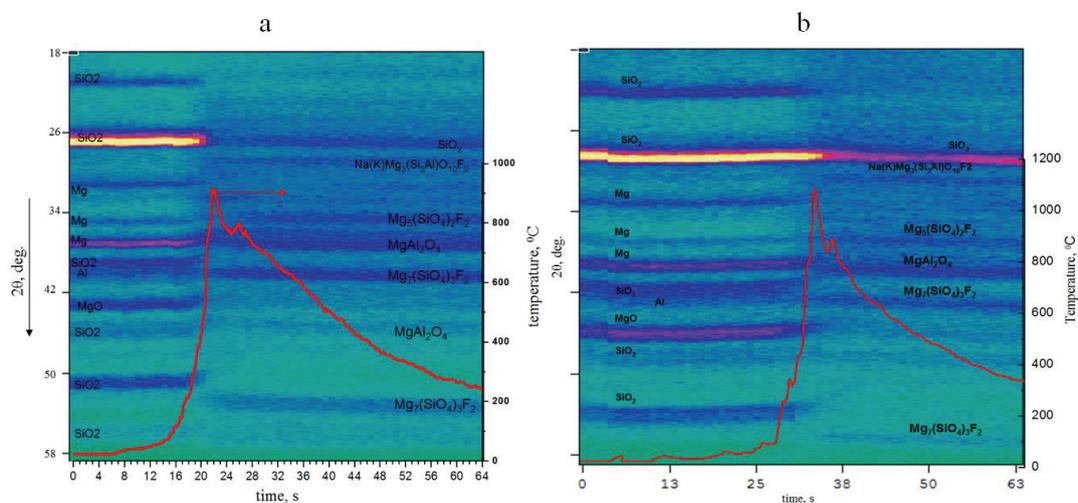


Figure 1. Diffraction pattern for mixture of 92% $(\text{SiO}_2\text{-Mg-Al-Na}_3\text{AlF}_6\text{-KClO}_4)$ +8%MgO (a) and 85% $(\text{SiO}_2\text{-Mg-Al-Na}_3\text{AlF}_6\text{-KClO}_4)$ +15%MgO (b).

In the case of mixture containing 15 wt% of MgO, MgAl_2O_4 phase appear instead of Mg, Al и MgO lines which can be caused by interaction of liquid Mg, Al and SiO_2 . After combustion front passing lines corresponding to $\text{Mg}_x(\text{SiO}_4)_y\text{F}_2$ appear at 31 sec of registration (Fig.1b). The line of fluorine phlogopite $\text{Na(K)Mg}_3(\text{Si}_3\text{AlO}_{10})\text{F}_2$ is registered at 33 sec of the process.

This work was financially supported by the Russian Foundation for Basic Research (project no. 13-03-12061 ofi_m).

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Abstract No : 1161

COMBUSTION SYNTHESIS OF METAL SULFIDE CERMETS: COMBUSTION CHARACTERISTICS, AND MECHANICAL PROPERTIES

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Self-propagating high-temperature synthesis (SHS) of a ceramic metal composite (cermet) consisting of chromium-chromium sulfide is developed. The thermochemical properties and phase diagram of the chromium-sulfur system are investigated using a comprehensive multi-phase, multi-component equilibrium database. Thermodynamic calculations show that some metals such as chromium, iron, and zinc can react with sulfur without the formation of gaseous products at normal pressure and yet demonstrate sufficiently high flame temperatures to support reactive wave propagation. In this study, the microstructure, mechanical properties, and combustion characteristics of chromium-chromium sulfide cermets are investigated. The chromium-chromium sulfide cermet was manufactured using self-propagating high-temperature synthesis, a process where the material is created under a self-sustaining combustion reaction between the chromium and sulfur. This type of synthesis allows the creation of near-net shape structures and offers the possibility of tuning material properties and material behavior by changing the composition of the reactant.

The quenching dimensions (thickness and diameter) are measured in different geometries, and an analysis of the quenched sample enables the chemical thickness of the reactive front to be estimated. The quenching dimension and chemical thickness are found to be on the order of a millimeter and exhibit little dependence on the Cr:S ratio when the reaction is Cr-rich. The velocity of the reactive front is also measured and again appears largely independent of the Cr:S ratio. Visualization of the front highlights the importance of differentiating propagation velocity and fundamental burning velocity.

Microstructural characterization was performed using optical microscopy, scanning electron microscopy, and energy dispersive spectroscopy (figure 1). The mechanical properties of the cermet (Young's modulus, fracture toughness, flexural strength and microhardness) have been measured and related to morphology and chemical composition of the samples. Results show that dense cermets (about 7% porosity) with specific structure have been obtained. Pure CrS has a significant hardness, but its toughness was insufficient for tool applications. However, we found that the density and fracture toughness of the cermets increase with the addition of Cr. The addition of Cr also improved the flexural strength and hardness of the cermet by 60% and almost 38%, respectively (table 1).

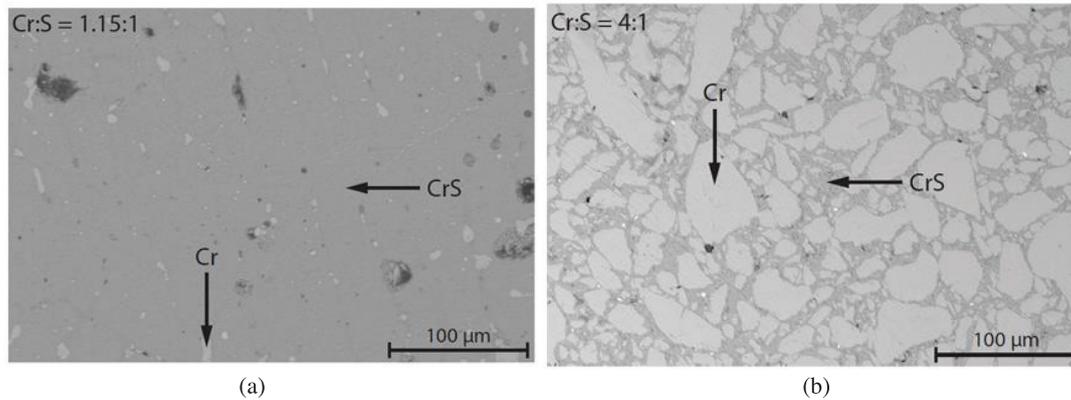


Figure 1: Micrographs of (a) Cr:S molar ratio 1.15:1 and (b) Cr:S molar ratio 4:1 cermets. The light gray phase is metallic chromium, while the darker matrix is chromium sulfide.

Table 1: Summary of material properties for chromium/chromium-sulfide cermet at varying molar ratios

| Property | Molar Ratio | | | |
|--|-------------|-----|-----|-----|
| | 1.15:1 | 2:1 | 3:1 | 4:1 |
| Density (g/cm ³) | 4.0 | 4.7 | 4.9 | 5.4 |
| Vickers Hardness (MPa) | 221 | 239 | 258 | 305 |
| Flexural Strength (MPa) | 445 | 558 | 630 | 713 |
| Young's Modulus (GPa) | 108 | 138 | 153 | 186 |
| Fracture Toughness (MPa·m ^{1/2}) | 2.4 | 3.2 | 3.5 | 4.1 |

Abstract No : 1016

THE EFFECT OF PRELIMINARY MECHANICAL ACTIVATION ON STRUCTURAL CHARACTERISTICS OF THE REACTION MIXTURE Ti + Ni

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Mechanical activation (MA) is an effective method for stimulating of chemical reactions, which allows increasing possibilities in the synthesis of inorganic materials [1 - 3].

For example, using mechanical activation can be synthesized low-energy compounds that no burn in a traditional organization synthesis virtually.

Now, the bulk of experimental studies are devoted to the study of combustion characteristics and phase composition in condensed systems with preliminary MA [4 - 9].

Much less work pays attention to the study of singularities that appear in the reaction mixture during MA.

In this paper we investigate the regularities of the dynamics of the agglomerate internal structure formed during the MA and its influence on subsequent synthesis Ti - Ni.

Experimental technique

We used: powders of titanium and nickel PTEM1 brand PNE1, the powder mixture composition Ti - Ni 55,06 wt.% (Stoichiometry of 1: 1), planetary mill M-3 (45 g), argon medium. The weight ratio of the balls to the powder was 5: 1. The MA time - from 1 up to 9 min. Structure and composition of the investigated activated powder mixtures and combustion products were examined by scanning electron microscopy (Philips SEM515) and optical metallography (Axiovert200M).

The values of layer thickness were calculated by examining the cross section of agglomerates by metallographic polished section. The number of measurements for calculating the average value of one point is from 200 to 950.

Results and discussion

The growth duration of MA time to 5 min leads first to gradual and then very rapid increase in the size of the agglomerates. Then, the agglomerates size is not substantially increased; there is even a certain decrease in the time interval from 5 min to 6.5 min of MA.

The thickness of the layers in the agglomerate as well as size has changes for all MA time: they flat out in the general trend, creating a more developed the interface.

An important aspect in experimental studies is the knowledge of effective kinetic constants which allows using the developed mathematical models to obtain preliminary prognostic evaluation.

The kinetic constants characterizing the dynamics of the growth of interfacial layers formed in the internal structure of the agglomerates was determined with using mathematical model describing the formation of the layered structure of the agglomerates in a binary mixture in a grinding mill power density [11].

The theoretical dependence of the size and thickness of the layers of the specific interfacial area in the agglomerate as function mechanical activation time were obtained.

It was found that with increasing MA time in the cycle of the mill "grinding - agglomeration" decreases the width of the layers of the layered structure of the agglomerates take place. The interfacial surface increases, becomes more developed. This will contribute to increase the rate of chemical interaction between the titanium and the nickel at the synthesis.

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Abstract No : 1046

THE INFLUENCE OF 'L - S' ENVIRONMENT SYSTEM ON PHASE FORMATION DURING COMBUSTION OF THE SHS SYSTEM 'W - TI - N'

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The paper presents investigation of the process of phase formation in the combustion wave of self propagation high temperature synthesis (SHS) for system W-Ti-N. The holistic approach, analysis of the fusibility curve of the "W-Ti" and diagram of the parameters of combustion were used. All graphs were represented as different kind dynamic structure [1, 2].

The SHS-processes were carried out in the reactor of constant pressure, in an environment of nitrogen gas at pressures 15-20-25 at. The initial mixture consisted of titanium powder and tungsten. Absorbed nitrogen was determined by the difference in weights before and after synthesis. The amount of absorbed nitrogen determined the completeness of the transformation in dimensionless form, formulations of titanium nitride and tungsten.

The process of phase formation takes place in the solid - liquid L-S environment, resulting in all physico-chemical properties of the environment play a crucial influence on the occurrence of compounds kind, crystallographic characteristics and gross formula of titanium nitride and tungsten, intermetallic compounds and solid solutions. Catalyst for reactions defines the following rule: a finite amount of titanium nitride $\sum T_i N_i$, as "the purpose of burning", is determined by the amount of absorbed nitrogen, which first was in connection with tungsten and formed intermediate disintegrating nitrides $\sum W_m N_n$.

The experimental data were processed holistically, as in the study of complex systems. Integrity was the fact that for any coordinate plane deposited all values of the parameter of combustion obtained by change many other options.

56 SHS acts were carried out in the work and 56 values of the investigated parameter burning were plotted. Values of the degree of conversion, the calculated number of nitrides of tungsten, etc. were used in our case. These values were combined in discrete trajectories in accordance with a constant value of the selected parameter - invariant. So many "points - status" constitutes something chaotic, but provides valuable information, if we analyze the shape that form curves, envelopes of this "cloud" data. These curves coincide with the lines of the liquidus - solidus when overlaid on the fusibility curve of system "W-Ti". The clear dissipative structures were obtained, which according to the laws of self-organization [3, 4] was supposed to represent discrete, periodic painting or attractor kind with trajectories towards the equilibrium point, or a series of parallel lines, or multiple closed curves, or other kinds. The kind depends on the selected invariant parameter, which is selected from a set of characteristics of the combustion system "Ti - W - N" - namely, the degree of conversion, the type of gross formula, type intermetallic compounds. It was found that 56 values are 14 trajectories, representing 14 direct restrictions curves solidus and the liquidus. Such lines are called "conoids". They mean that at a constant temperature in point of the intersection of conoid with solidus and liquidus curves formed intermetallic compounds (W_iTi_j) in the melt with the same formula as any change to the start content of titanium and tungsten. Analysis of conoids allows to calculate the number of intermetallic compounds

using the “lever rule” [5].

It was established experimentally that the values corresponding to the same formula of titanium nitride take up position long conoid.

This plotting and holistic analysis allows define a set combustion temperature, the completeness of the transformation, the gross formula of all possible nitrides and intermetallic compounds using measured amount of absorbed nitrogen and knowledge of the start composition.

The formation of 14 kinds of titanium nitride, according to 14 conoids is possible in the SHS system “W - Ti - N”,

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3.SHS of powder materials (micron, submicron- and nano scale)

Abstract No : 1037

COMBUSTION SYNTHESIS AND DIELECTRIC PROPERTIES OF THE DOPED BARIUM TITANATE

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Perovskite materials include a wide group of compounds that have a cubic structure with general formula of ABO_3 , where A is usually an alkaline-earth or a large lanthanide, and B is usually a transition metal. Perovskites used in great amount of electro devices applications such as electronic, electro-optical and electromechanical devices. Materials such as barium titanate and its derivatives play an important role in modern electronics industry. There are a large amount of publications devoted to the synthesis of barium titanate by various methods including combustion synthesis method (CS), but there are only a few papers devoted to the preparation of doped barium titanate ($Ba_{1-x}R_xTi_{1-y}R''_y$) by CS method. In the present work, we have tried to develop CS method in order to synthesize a variety of doped barium titanate ceramic nanomaterials with perovskite symmetry and general formula $Ba_{1-x}La_xTi_{1-y}R_yO_3$ (where R - Fe, Cu), while are free from by-products. $Ba(NO_3)_2$, $TiO(NiO_3)_2$, were used as starting components and $La(NO_3)_3$, $Fe(NO_3)_3$, $Cu(NO_3)_2$ as dopants. Glycine was chosen as the most suitable reducing agent [1].

The stoichiometric quantities of raw components were dissolved in distilled water. After solutions were mixed with a pre-synthesized solution of titanyl nitrate. The prepared solutions placed in quartz crucibles and put into a muffle furnace with temperature of 600°C. Exothermic inflammation of the components with a sharp increase of temperature started after water has completely evaporated. The synthesis duration was in the range of 6-10 minutes.

In order to investigate phase composition and microstructure of synthesized materials they were subjected to X-ray phase analysis and microscopic examination. Barium titanate was the main crystalline phase of obtained materials. Crystalline phase of barium ferrite, copper oxide and lanthanum oxide were detected in samples of studied ceramic materials. A number of studies showed that the formation of by-crystalline phases based on the dopants decreases with increasing content of the reducing agent, as well as the titanium component. In addition, samples were annealed at 800 °C during 60 minutes to enhance the uniformity of the phase of the synthesized material. The combination of these technological methods allowed to increase degree of substitution of regular crystal lattice ions of barium titanate by Fe^{3+} and Cu^{2+} ions. At the same time the intensity of lanthanum phase maxima changed slightly, which means that the introduction of lanthanum ions into the crystal lattice of barium titanate is difficult under these conditions.

The synthesized materials have a fine crystal structure that is characterized by a low density. The microstructure of synthesized materials contains some crystal elements aggregated in the form of thin plates, dendritic and filamentary formations.

Dielectric permittivity and dielectric loss factor were determined using disk shaped specimens (10 mm in diameter, 3 mm thick) with deposited silver contacts. The temperature dependence of dielectric permittivity shows, that all materials exhibit a wide temperature range of the ferroelectric-paraelectric phase transition, which can be related to a nanostructure of the materials under study. With decreasing grain size, the strain on the grain surface grows thus making the phase transition more difficult. This assumption is supported by the results of calorimetric analysis.

We have found the dielectric permittivity of materials based on barium titanate doped with lanthanum and copper ions reaches abnormally high values ($20 \cdot 10^4$). In case of lanthanum and iron doped materials maxima value of dielectric permittivity reaches $4 \cdot 10^4$. We consider that the achievement of abnormally high values of the dielectric constant in doped materials related to the formation of quasi-free electrons in the material structure. Additional negative charge, which is formed is compensated by changing of charge portion of titanium ions. In addition, copper and iron ions promote the formation a large number of microcapacitors.

The value of dielectric loss factor of studied materials reaches 0.05. We believe that this is due to the large amount of energy that is spent on polarization of barium titanate structure.

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Abstract No : 1056

PHASE EVOLUTION OF YAG POWDERS OBTAINED BY GEL COMBUSTION COMBINED WITH FIELD-ASSISTED RAPID SYNTHESIS TECHNIQUE

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Yttrium aluminum garnet (YAG) nanopowders were synthesized by a novel method combining gel combustion and field-assisted rapid synthesis technique. Based on the phase analysis, pure hexagonal YAlO_3 (YAH) firstly crystallizes between 800 °C and 820 °C from amorphous oxide. And then, the YAH phase transforms to YAG during 830-900°C. The grain size of YAG powder calcined at 925°C for 3min is about 60nm. And YAH powder is 20nm when calcined at 820°C. Phase formation in different atmosphere was also investigated. YAG is crystallized directly from amorphous precursors without any intermediate phase in a muffle furnace under flowing air. Phase formation in a tube furnace under argon atmosphere prefers a reaction route via a YAH-YAG route. Although it is the same as field rapid synthesis way, the formation of YAH is coincident with YAG phase. Furthermore, it is suggested to prepare fine-grained YAG ceramics at low temperature using transitional phase of YAH as raw materials. It is confirmed that the atmosphere during heat treatment is the key factor that leads phase transformation route toward different pathways. For powders calcined in the atmosphere lack of oxygen it follows a YAH-YAG route while a flowing air atmosphere drive YAG crystallization directly from the amorphous.

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Abstract No : 1058

DEVICE OF MOLTEN GRANULATION FOR OBTAINING THE POWDER MATERIALS FOR SHS

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In production of metal powders for SHS processes the most effective direction is dispersion (dispergating) of metal fusions through acting on them with a stream of gas or liquid [1-4]. High speed dispersion allows to receive powders which particles have the structure giving them the specific properties suitable for SHS. But there are also essential shortcomings: high energy consumption, potential of explosion, need of application of the inert atmosphere. At high speeds of dispersion the aerodynamic forces promoting formation of a significant amount of oxides are great. At low-speed dispersion rather large fraction, insufficiently active for SHS is formed. For different metals conditions of powders formation and activation are different; therefore data only on aluminum powders are provided in the report related to SHS and metalthermy.

For the purpose of increase of high-quality active metal powders obtaining efficiency, we created an experimental plant of hydro-vacuum absorption and granulation (dispersion) of fusions, which basis are E. Godetsky's (Ukraine) engineering developments [5]. In this installation a working body is water, which moves in the closed channels on the closed contour, creates vacuum, granulates fusion and carries away a granulation product from a working zone to a place of its warehousing. The plant excludes contact of the fusion drops with the atmosphere that prevents their oxidation. The plant and technology are environmentally friendly as dust, gases, noise, light, heat, water are not discharged in the working zone and environment. The schematic hydraulic diagram of the plant is provided on fig.1.

The plant is produced and tested at then Rustavi metallurgy factory, which is "RustaviSteel" LTD now. Aluminum powders, aluminum-magnesium alloys, bronze and cast iron are made. Microphotographs of the obtained powders are given on fig.2

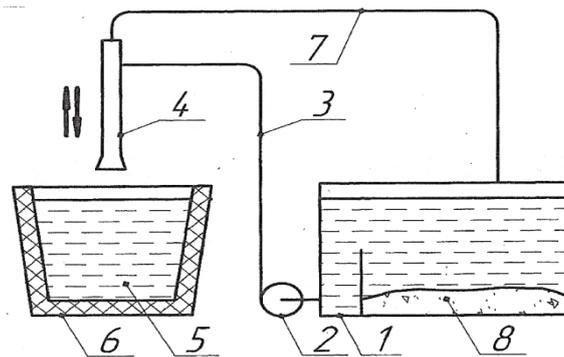


Fig.1. Device of molten granulation for obtaining the powder materials for SHS

1 - Tank sump; 2 - Water pump; 3 - Blasting pipeline; 4 - Sucking head; 5 - Fused metal; 6 - Scoop; 7 - Discharging pipeline; 8 - Granulated material (powder).

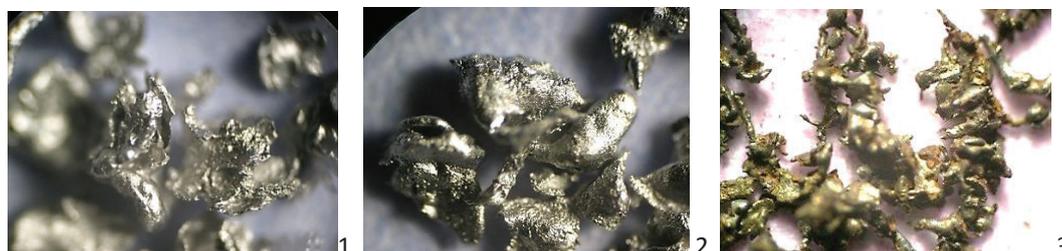


Fig.2. Microphotographs of the obtained powders, x100. 1-Al; 2-Al+Mg; 3-Fe;

As the tests showed, process of the aluminum dispersion is efficient enough, providing the following technical performances of the produced powder, complying to the appropriate requirements [6]: a) Aluminum contents with oxidation extent within temperature interval 20-1000°C over 90%; b) Active aluminum contents 94-95 mas.%; c) Aluminum oxide contents maximum 5-6 mas.%; d) Absorbability less than 3,0-3,5%; e) Absorbed moisture within interval 5,1-5,5%.

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Abstract No : 1059

SOLUTION COMBUSTION SYNTHESIS OF LUMINESCENT PIGMENTS ON THE BASES OF Co-Al-Mg-Ba-O, Co-Al-B-O, Co-Ba-B-O FOR INK APPLICATIONS

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In this study, inorganic luminescent pigments of Co were produced by Solution Combustion Synthesis and their photoluminescence and coloring properties were investigated. Cobalt pigments on the base of nanosize oxides and spinels were synthesized by the combustion of aqueous solution containing stoichiometric and non-stoichiometric amounts of metal nitrates in the following three systems:

1. $\text{Al}(\text{NO}_3)_3$, $\text{Mg}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and urea as a fuel/reducer,
2. $\text{Co}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, H_3BO_3 and urea,
3. $\text{Co}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, H_3BO_3 and urea.

The aqueous solution containing the redox mixture in a Pyrex glass when introduced in a muffle furnace preheated to 600 °C, boils, foams combustion to produce the corresponding oxides and spinels. The produced pigments with $\text{Co}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Mg}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and urea as a reducer the in the (aq.) initial batch gave blue color depending on

the percentage of the reactance in the mixture.

The produced pigments with $\text{Co}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, H_3BO_3 and urea as reducers the in the (aq.) initial batch gave a violet color (fig. 7) while the produced pigments with $\text{Co}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and urea and H_3BO_3 as reducers the in the (aq.) initial batch gave dusty-violet color (fig 8).

For the first system (EB3 and CB1 to CB4 samples) XRD analysis and Colour Characterization were used in order to correlate the structure characteristics of the Co pigments to the pigment colour that is produced.

XRD analysis (fig.1) shows that in Al-Mg-Ba-Co-O system were received blue luminescent pigments of cobalt aluminate (CoAl_2O_4) and Colour Characterization (fig) according the cobalt concentration becomes more pronounced the blue color. The initial batch EB3 synthesized without $\text{Co}(\text{NO}_3)_2$ at the first experiments, to find the proper concentration of urea for the effective combustion reaction.

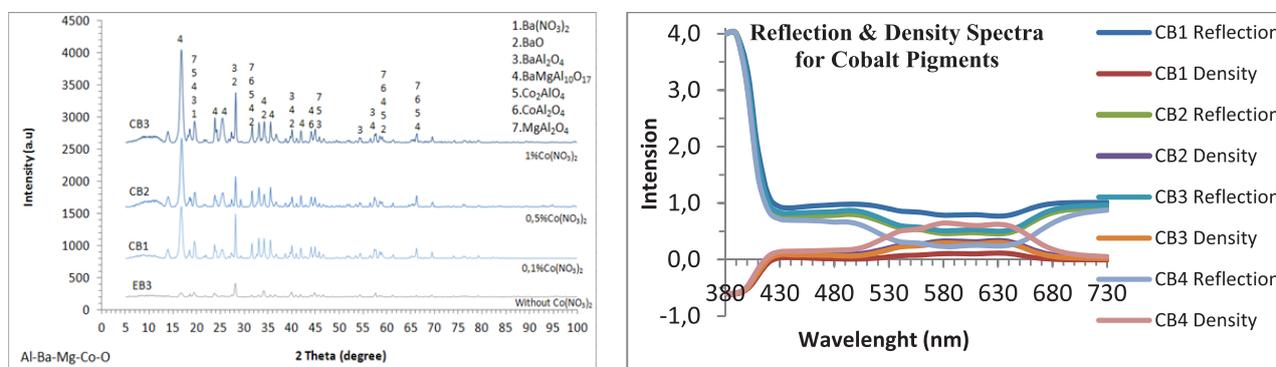


Fig. 1. XRD patterns of the samples:EB3 (Al-Ba-Mg-O),CB1 (Al-Ba-Mg-0,1%Co-O),CB2 (Al-Ba-Mg-0,5%Co-O), CB3 (Al-Ba-Mg-1,0%Co-O) synthesized through the solution combustion synthesis by heating at 600°C with the use of urea.

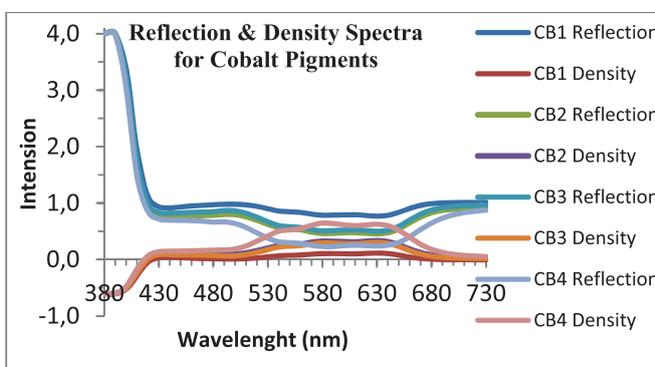


Fig. 2. Reflection and Density Spectra for Al-Ba-Mg-Co iluminascent pigments. CB1 sample precursor contains 0,1% Co,CB2 sample precursor contains 0,5% Co, CB3 sample precursor contains 1,0% Co and ,CB4 sample precursor contains 2,0% Co.

In the fig. 2 a large pick is observed in the area of 380-410nm that indicates the strong luminescence properties of the produced pigments. It is also obvious that colour properties are increasing (figs 3-6) by the raise of cobalt concentration that was used in the initial precursor mixture.

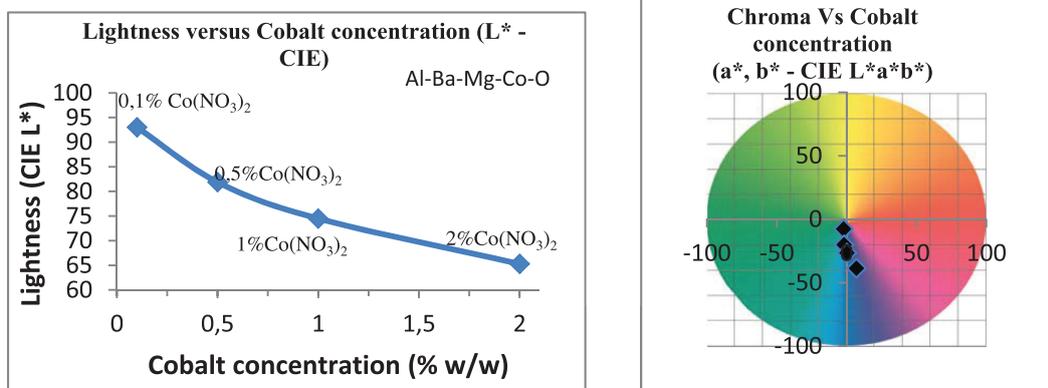


Fig.3. Lightness for Al-Ba-Mg-Co iluminascent pigments. CB1 sample precursor contains 0,1% Co, CB2 sample precursor contains 0,5% Co, CB3 sample precursor contains 1,0% Co and CB4 sample precursor contains 2,0% Co.

Fig. 4. Colour changes and saturation increase as the Co concentration of the precursor mixture raises from 0,1 to 2,0%.

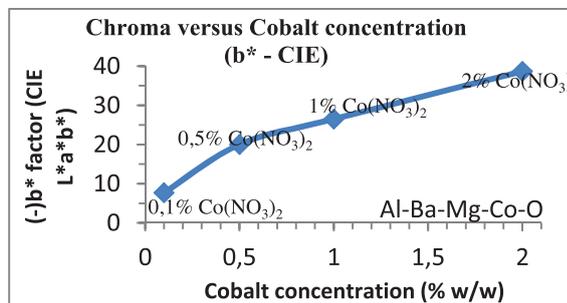
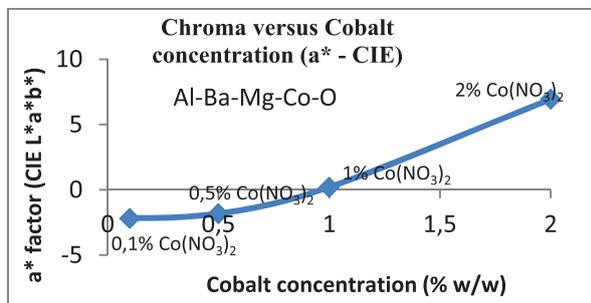


Fig. 5 a* factor - Red colour (CIE L*a*b*) increases as the concentration of the Co increases in the precursor mixture from 0,1 to 2,0%

Fig. 6. (-)b* factor - Blue colour (CIE L*a*b*) increases as the concentration of the Co increases in the precursor mixture from 0,1 to 2,0%

In the figures 3, 5, 6 colour properties of the produced pigments are correlated by the increase of the initial cobalt concentration of the precursor mixture. Lightness is decreasing while a* and (-) b* parameters are strongly increasing as cobalt concentration in the initial mixture is increasing. Saturation increase is depicted in the CIE L*a*b* diagramme of the fig.4 and Reflection and Density Spectra for Al-Co-B-O and Ba-Co-B-O pigments are presented in figs 7 & 8.

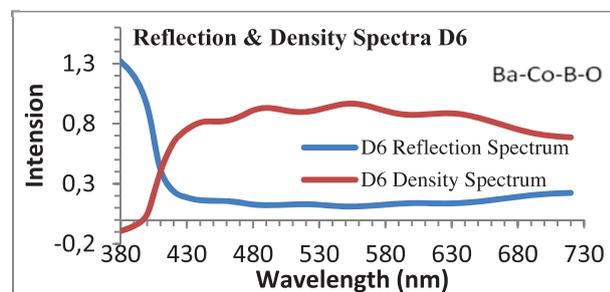
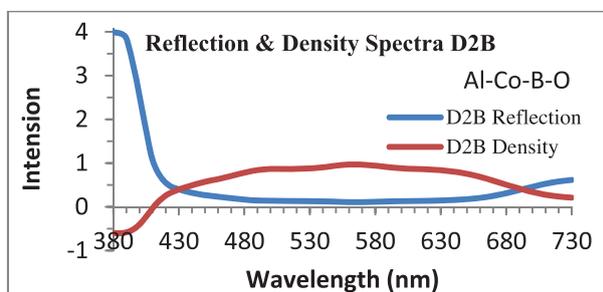


Fig.7 Reflection and Density Spectra for Al-Co-B-O pigments

Fig.8 Reflection and Density Spectra for Ba-Co-B-O pigments

Abstract No : 1063

HYDROTHERMAL SYNTHESIS OF ONE DIMENSIONAL TiO₂ POWDERS

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One dimensional (1D) TiO₂ nanofibers were synthesized via hydrothermal method using basic aqua solutions and using P25 commercial powder (Degussa) as Ti-precursor at temperatures of 130 °C for 12, 24, 36 h. The hydrothermal system was isolated from the environment and hydrothermal reactions were allowed to execute at autogeneous pressure and at a stirring rate of 250 rpm. After hydrothermal synthesis powders were acid treated to obtain fibers in a corn-cob-like structure. Then, resultant powders were calcined at 450 °C for 1 h. Powders synthesized were characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), X-Ray diffractometer (XRD), and Brunauer-Emmett-Teller (BET) surface area analyzer. Results revealed that discontinuous corn-cob-like fiber morphology was obtained. Diameter of fibers was changed between 30- 50 nm while length was several micrometers. Crystal structure of the powders was anatase after calcination. The surface area of fibers were changed in the range of 50-60 cm²/gr.

Abstract No : 1071

Ni-Al INTERMETALLICS DISPERSION-STRENGTHENED WITH CR₂O₃: SYNTHESIS AND CHARACTERIZATION

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As is known, Ni-Al intermetallics are being widely used in different branches of modern industry, including aerospace and power engineering. Their service parameters can be improved by dispersion strengthening upon doping intermetallics with finely dispersed particles of hard and heat resistant compounds. A promising candidate for the role of strengthening agent seems to be Cr₂O₃ which is being used in a wide range of high-temperature applications.

In this communication, we report some our results on SHS fabrication and characterization of Ni-Al intermetallics dispersion-strengthened with Cr₂O₃. The material was porous and the Cr₂O₃-NiAl interface exhibited numerous spherical drops and cracks.

SHS reaction in Ni + Al + Cr₂O₃ mixtures were performed with yield around 10, 20 and 30 wt % Cr₂O₃. During combustion, added Cr₂O₃ acts as diluents and thus decreases the combustion temperature, porosity and grain size.

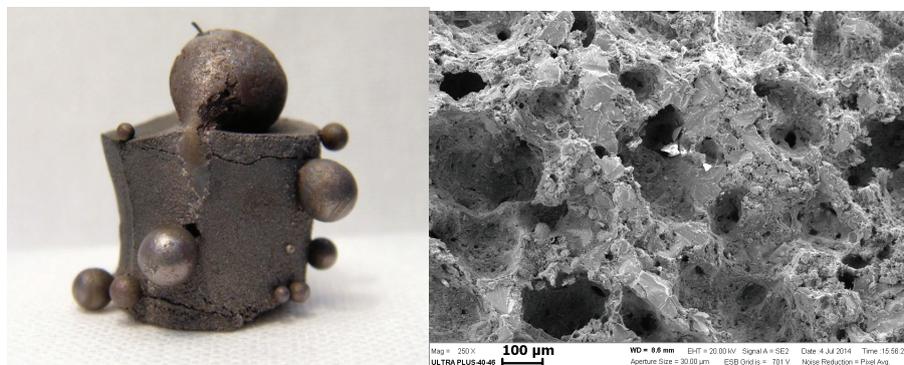


Fig.1. Burnt sample and microstructure of the product derived from Ni-Al mix containing 10% Cr₂O₃.

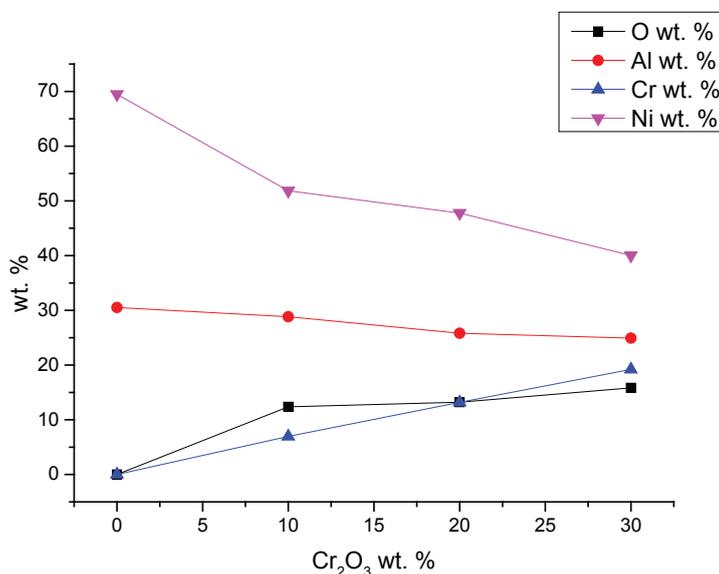


Fig.2. Chemical composition of the burnt Cr₂O₃-NiAl samples vs. Cr₂O₃ % content.

According to our XRD data, the products derived from Ni-Al mixtures containing 10, 20, 30 % Cr₂O₃ contained solid solution of Cr in NiAl and trace amounts of Cr and Al₂O₃. The reaction between the embedded Cr₂O₃ particles and NiAl melt in combustion-synthesized NiAl-Cr₂O₃ composites can be expected to improve the service parameters of thus synthesized composite material.

Abstract No : 1081

PHYSICO-CHEMICAL PROPERTIES OF COMBUSTION SYNTHESIS CATALYSTS AND THEIR ACTIVITY IN LIQUID PHASE HYDROGENATION

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Combustion synthesis (both SHS and Solution Combustion, SCS) is characterised by very high heating and cooling rates which results in catalytic materials with very high activity since their distorted structure results in a plethora of catalytically active centres. In addition, studies have also shown that SHS catalysts display increased selectivity and their activity can be enhanced by increasing their specific surface area [e.g. 1, 2]. Recently, a lot of work devoted to SCS catalysts has appeared, due to the very high surface area (of the order of 100-250m²/g) of the nano-structured materials produced [3-4].

Liquid phase hydrogenation is one of the most important chemical processes and it utilises a large fraction of the total amount of catalysts used by industry. From the non-noble metal catalysts, nickel-based catalysts are the most active. For example, nickel - molybdenum catalysts are used extensively in oil reforming [5]. In catalytic hydrogenation, hydrogen and an unsaturated compound are, as a rule, activated on the surface of the catalyst. The degree of activation of the components depends on the potential of the catalyst, on its nature and on the structure of the unsaturated compound. In the case of electrohydrogenation, the charge of the surface and hence the chemical composition of the catalyst will, above all, change during the reaction. At hydrogenation in solutions, the rate of reaction frequently depends on the solubility of hydrogen while during electrohydrogenation such dependence does not occur. Hence the difference does not only appear in the mechanism of the elementary process, but also in the macroscopic stages. Joint catalytic and electrocatalytic hydrogenation allows optimization of the process by using conditions at which one or the other will be more emphasized.

This research project has been designed to study and enable the clarification of the mechanisms and the kinetics of reaction that take place during hydrogenation of unsaturated compounds with various structures, using Combustion Synthesis catalysts based on nickel.

Nickel-based catalysts have been produced by SHS as well as SCS. The SHS catalysts were synthesised using initial batches based on the systems: Al/Ni, Al/NiO, Al/Ni/Mo, Al/NiO/Al₂O₃ and Al/NiO/MoO₃/Al₂O₃ with varying concentrations of components. The SCS catalysts were synthesised using solutions based on the systems: Ni, Al-Ni, Ni-Cu, Ni-Mo, Ni-Fe and Ni-Mn again with varying concentrations of components.

The catalysts synthesised were characterised by a range of tests and measurements including XRD, SEM, BET, FT-IR, TEM, and EPR which allowed the determination of the atomic structure and the properties of the catalysts.

The catalysts produced, were used for a series of catalytic studies for liquid phase hydrogenation. The reactive substances selected have different structures (aliphatic, aromatic), degree of saturation (double and triple bonds) and class of liquid to be hydrogenated (hydrocarbon, alcohol, acid, aldehyde). Butin-2-ol, phenyl acetylene, benzene, acetone and maleic acid are the unsaturated compounds that are used as model substances for determination of catalysts activity in hydrogenation process with different diluters (water and ethanol).

All the liquid phase hydrogenation experiments are carried out at temperatures between 40°C and 80°C and the saturation of the powdered catalysts is carried out over 1 hour. After this, the reactive substance is added in appropriate quantity for reaction with 50ml of hydrogen at atmospheric pressure. Both catalyst saturation with hydrogen and hydrogenation is carried out under continuous mechanical stirring. Measurements of the amount of reacted hydrogen are taken continuously every 10 seconds at atmospheric pressure and kinetic curves are calculated from them. Parameters studied are catalyst composition, preparation conditions, quantity used, solvent type, temperature of reaction, composition of unsaturated substances and their structure

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Abstract No : 1082

INFLUENCE OF SCS CONDITIONS ON PROPERTIES OF NANOSTRUCTURED METALS AND ALLOYS

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Metal nanoparticles are very attractive for many applications because of their size- and shape-dependent properties. This has guided their use in many industrial applications including catalysis and medicine. Various catalytic processes use nanostructured metallic catalysts with improved activity such as in thermal decomposition of ammonium perchlorate [1]. Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosize materials [2]. A large variety of different organic compounds (which results in the synthesis of oxides) such as urea, glycine, alanine, asparagine, serine, methyl cellulose, ammonium acetate, ammonium citrate, citric and succinic acids and ammonium tartarate have already been explored as fuels. Although complex fuels favour formation of nanoparticles, in many cases a further calcination is required to form organic-free pure nanocrystalline powders. Initial batch composition and the nature and amount of fuel are two of the most important factors in controlling the combustion process and final product composition during SCS. Single step preparation of porous nanostructured metals and alloys is possible with a proper selection of the combustion parameters.

During the synthesis of nickel nanopowders reported by previous authors [3], mixed valence copper oxide phases and metallic copper was demonstrated by varying the fuel (carbohydrazide) to oxidizer ratio. N-tertiarybutoxy-carbonylpiperazine was used as a fuel for the first time for the preparation of porous Cu, Ni and CuNi bimetallic particles [4].

The objective of this work is to use SCS to produce nanomaterials of pure metals and metal alloys using solution combustion synthesis and we report on the production of finely dispersed copper, copper oxide, and copper-nickel bimetallic particles. The overall aim is to optimise the reaction yield and study the factors which contribute to the nanostructure of the nanomaterials by adding additives and by changing the ratio between the fuel and the oxidiser.

The above nanomaterials are generally synthesised by the combustion of stoichiometric amounts of aqueous solutions of metal nitrates. Each experiment consists of stoichiometric amount of one or two metal nitrates ($\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ - $\text{Al}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$ - $\text{Fe}(\text{NO}_3)_3$) and a reducer (glycine, urea, aminobenzoic acid, carbohydrazide). The suitability of the reducer and its percentage in the initial batch (20-80%) has been examined. In every experiment series the influence of temperature has been studied in the range 350°C to 650°C. XRD, SEM, TEM, FT-IR, BET, TGA have been used to identify and characterise the compounds and alloys produced.

Based on XRD analysis, the influence of glycine concentration in the initial solution on the lattice spacing of Cu and on the crystallite size of Cu, Ni, FeNi_3 are shown in Figures 1 and 2 respectively. It was found that at stoichiometric ratio between fuel and oxidiser, the particle size increases due to sintering processes at high temperatures.

The optimum SCS conditions were found for maximum yield of metal nanopowders of Cu, Ni and FeNi_3 and regulation of their particle size and structure.

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Abstract No : 1107

EVALUATION OF SHS POWDER COMPOSITION UNIFORMITY USING SPECTRAL ANALYSIS

METHODS

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One of the most important factors affecting the self-propagating high-temperature synthesis (SHS) occurrence, as well as structure and properties of the synthesized products, is the initial blend uniformity (e.g. see [1]). In the present work approaches are proposed with respect to evaluation of precursor SHS powder compositions using such methods as Laser-Induced Breakdown Spectroscopy (LIBS) and Energy-Dispersive X-Ray Analysis (EDAX). The advantages and limitations of the methods are discussed including their combined use for e.g. optimization of the modes for mixing components into the blend.

The LIBS method employing a laser source for emission spectra excitation allows evaluating the uniformity of the SHS elemental compositions without defining concentrations of the blend constituents. Therefore, it is introduced such parameter as X_{av} , which represents the ratio of the arithmetical mean intensities of spectral lines I_{el} of a particular selected chemical element from those constituting the blend and the intensity of the spectral lines of the reference element I_{av} :

$$X_{av} = \bar{I}_{el} / \bar{I}_{av} \quad (1)$$

As a rule, the reference element is another element, whose mass portion is the largest in a particular SHS composition. Following such an approach, the blend uniformity can be estimated based on the variation coefficient V , which is the ratio of the mean square deviation σ of the chosen element spectral line intensity variability to the parameter X_{av} :

$$V = \sigma / X_{av} \times 100 (\%) \quad (2)$$

The proposed approach to the evaluation of SHS composition uniformity using the EDAX technique, which is, in particular, implemented in the majority of scanning electronic microscopy devices, deals with the analysis of certain component content in superficial and sub-superficial layers of the blend dependently on the scanned area scale (at different magnification degree). Such analysis allows defining a length of the uniform area via a numerical value of the size factor, which is determined by the notion "the correlation radius" L from the theory of fractals [2]. This factor characterizes the behavior of the heterogeneous system properties in case of the scanning scale diminishing and corresponds to the transition from the uniform behavior to fractal one. At scales larger than L heterogeneous systems behave like uniform ones, i.e. their properties don't depend on a sampling size. At scales less than L the system properties depend not only on the sampling size but also on the sampling coordinates (see fig.1). The less is the correlation radius, the longer is the uniform area of the SHS composition.

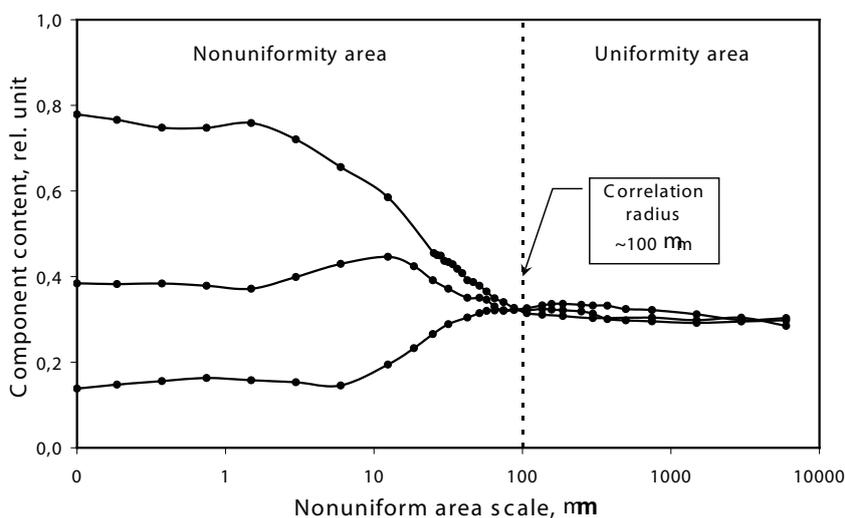


Fig.1. Example of correlation radius determination for two-component SHS composition

The combination of the said approaches to uniformity evaluation allows matching the advantages of the LIBS, which is suitable for characterization of the material volume unit uniformity, and the EDAX, which allows evaluating the uniformity of superficial and sub-superficial layers of the blend with a high degree of the discretization and localization.

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Abstract No : 1118

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF TITANIUM NITRIDE OVER AMMONIUM CHLORIDE

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The use of gasifying additives such as ammonium chloride and fluoride at SHS of silicon and aluminum nitrides is known to influence structure formation mechanism, provide an increase of the specific surface area of the obtained samples, and allow synthesizing compounds with finer structure.

The classical SHS method does not allow obtaining so fine powders of titanium nitride, as due to high synthesis temperatures crystallites of 10-20 mkm in size are formed, and the product is partially sintered. The synthesis should be carried out at low temperatures in order to result in obtaining fine titanium nitride powders.

The paper demonstrates the investigation results of titanium combustion in nitrogen over ammonium chloride with the aim of producing fine titanium nitride powder. The processes occurring at titanium powder combustion with addition of NH_4Cl in nitrogen can be presented by the equation

$$\text{Ti} + \text{NH}_4\text{Cl} + \text{N}_2 \rightarrow \text{TiN} + \text{HCl} + \text{H}_2$$

The influence of the amount of NH_4Cl on the parameters of the green mixture combustion and synthesis product characteristics has been studied.

It has been established that at SHS of TiN over ammonium chloride, the combustion temperature decreases greatly, sintering of synthesized particles is avoided, and specific surface area of the synthesized titanium nitride is increased. A remarkable increase of the specific surface area is observed at NH_4Cl content of 40 mass %. In the range of NH_4Cl concentrations under study, titanium nitride powders of the specific surface area of 3-24 m^2/g were obtained. It has also been established that the value of specific surface area depends on the initial titanium powder microstructure. The highest value was achieved when titanium powder with fullfledged and dendrite particle structure was used. Electron microscopy shows that the synthesis product consists of titanium nitride nano-structured particles of equiaxial shape of 50-200 nm in size, Fig. 1.

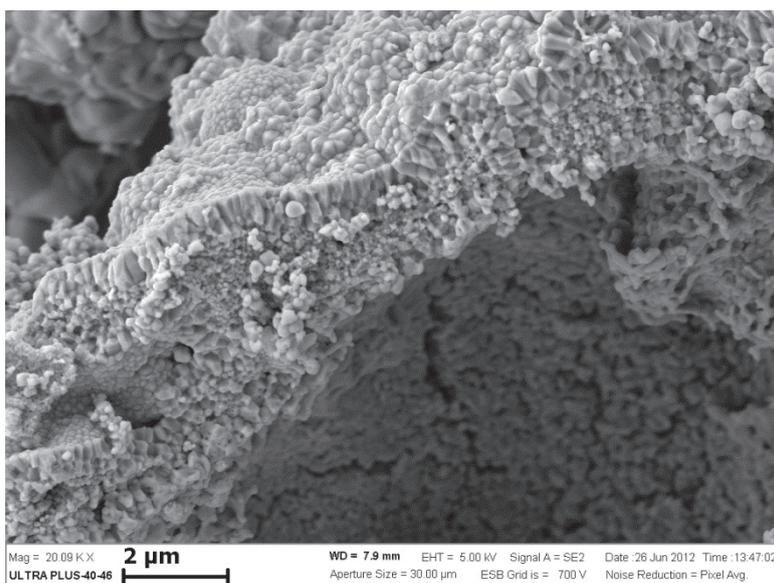


Fig. 1. Nano-structured particle of titanium nitride.

Our investigations have shown that in the case of titanium combustion in nitrogen over ammonium chloride, gas-phase synthesis of titanium nitride is partially realized. The synthesis product (nano-TiN+NH₄Cl) precipitates as a black or dark-green coat on the cold walls of the reactor and reaction boat.

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Abstract No : 1129

COBALT CATALYSTS SYNTHESISED BY SOLUTION COMBUSTION FOR DRY REFORMING OF METHANE

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The mitigation and utilization of the greenhouse gases CO₂ and CH₄, are among the most important challenges in the area of energy research. CO₂ reforming of CH₄ has received much attention from both an environmental and an industrial perspective because the reaction can convert these greenhouse gases into synthesis gas with a low H₂/CO ratio.

This paper presents the results of a catalytic investigation of cobalt-based catalysts produced by solution combustion synthesis (SCS). The catalysts were synthesised from cobalt, alumina, manganese, magnesium nitrates and urea (as reducer) at a pre-heating temperature of 500°C. Properties of the catalysts studied include microstructural morphology (SEM, EDAX), atomic structure and phase distribution (XRD) and porosity and specific surface area. The catalytic reaction was carried out at 750, 800, 850 and 900°C using as feed gas a mixture of CO₂:CH₄:N₂ in the ratio 1:1:1 and the reaction products were analyzed by gas chromatography.

The basic reaction of CO₂ reforming of CH₄ is: CO₂ + CH₄ → 2CO + 2H₂. The basic reaction of CO₂ reforming of CH₄ is: CO₂+CH₄→2CO+2H₂. Apart from the reforming process which is desired, by-products can form by following reactions: CO₂+CH₄→2C+2H₂O, CO₂+CH₄→CO+C_xH_y. Such by-products were observed for most catalysts in very small quantities, indicating very high selectivity of CO and H₂ estimated at about 95-100%. CO and H₂ yield and CH₄ and CO₂ conversion are also very high up to about 100% depending on the system, as shown in Figures 1 and 2. The calculated activity for H₂ and CO for the catalysts of the system Co-Al-O are presented in Figure 3.

In addition to the above systems, active catalysts for many other reactions have been produced by SCS on the basis of many different compositions such as spinels and their mixtures with other oxides and metals. The work is continuing.

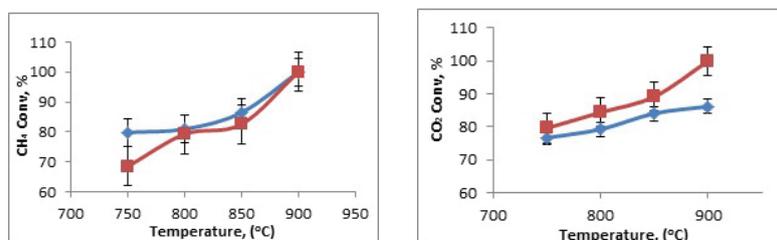


Figure 1: Conversion of CH₄ and CO₂ by SCS cobalt catalysts (60% Co(NO₃)₂-Al(NO₃)₃-urea -◆ curves, 30% Co(NO₃)₂-Al(NO₃)₃-urea -■ curves)

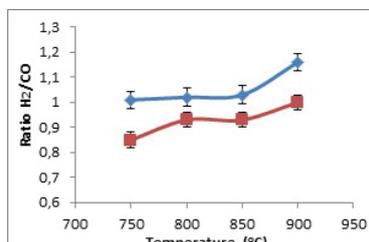


Figure 2: Ratio H₂/CO by SCS catalysts in the systems Co-Al -O (60% Co(NO₃)₂-Al(NO₃)₃-urea-♦curves, 30% Co(NO₃)₂-Al(NO₃)₃-urea -■curves)

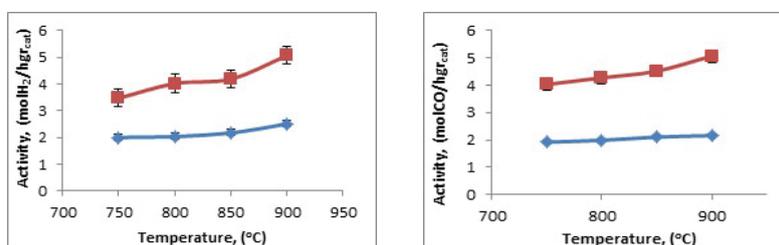


Figure 3: Activity (mol/hgrcat) H₂ and CO by SCS catalysts in the systems Co-Al -O (60% Co(NO₃)₂-Al(NO₃)₃-urea-♦curves, 30% Co(NO₃)₂-Al(NO₃)₃-urea -■curves)

Abstract No : 1015

SYNTHESIS OF SINGLE-PHASE NIOBIUM SILICIDE BY SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS WITH USING PRELIMINARY MECHANICAL ACTIVATION

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Obtaining single-phase product is the important result for the chemical synthesis. The different methods and techniques receipt are use for these purposes. Obtaining single-phase synthesized product using preliminary mechanical activation (MA) is difficult by the fact that the treatment of the powder mixture in the activator is associated continuous change of the composition of the activated mixture due to the sticking of powder mixture on the balls and the walls of the drums [1]. The change in composition and the sticking of powder mixture on the balls and the walls of the drums take place during mechanical activation of Nb and Si powder mixture. The powder mixture is sticking irregularly because one of components is more inclined to stay on the balls and the walls than the other. The change of such a component can be take place during different periods of MA. Figure 1 shows the part of the XRD pattern with different intensity peaks of Nb and Si at different mechanical activation time.

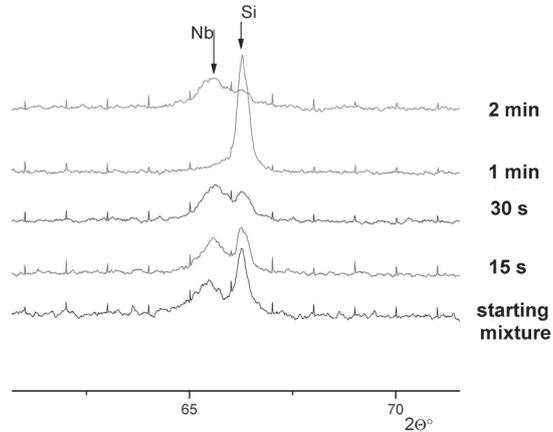
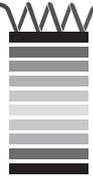


Fig. 1. Fragments of XRD pattern of powder mixture of the Nb - 62.3 mass. %, Si - 37.7 mass.% composition after various time MA.

The difference between the composition of the powder mixture inside of the activator and powder mixture on the walls and balls is come from 5 to 15 % after 30 s MA.

The niobium powder is prevalent on the walls of the drums after this time MA. Still more niobium sticks on the walls after 1 min of the MA and powder mixture with prevalence of silicon is remains inside activators. The change the stuck component takes place between 1 and 2 min of MA.

Niobium is returned in the powder mixture into activator, come off from the walls, and silicon begins stick to walls and balls.

The quantity of the silicon in powder mixture is reducing by 5 - 10 % after 2 min MA. Therefore, the activated composition pour out from activator is differing from starting stoichiometric composition. The composition has significant impact on the following synthesis of single-phase product. Obtaining single-phase product is possible when the quantity of the starting silicon increase to 5 - 6 wt.% over to the stoichiometric composition NbSi_2 and 2 minutes MA. There are only peaks of niobium silicide NbSi_2 take place in this case.

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4. SHS of bulk materials (advanced functional and constructional materials, including biomaterials, intermetallic alloys, composites, foams etc.)

Abstract No : 1011

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF BIOCERAMIC MATERIALS IN THE Ti-C- $\text{Ca}_3(\text{PO}_4)_2$ SYSTEM

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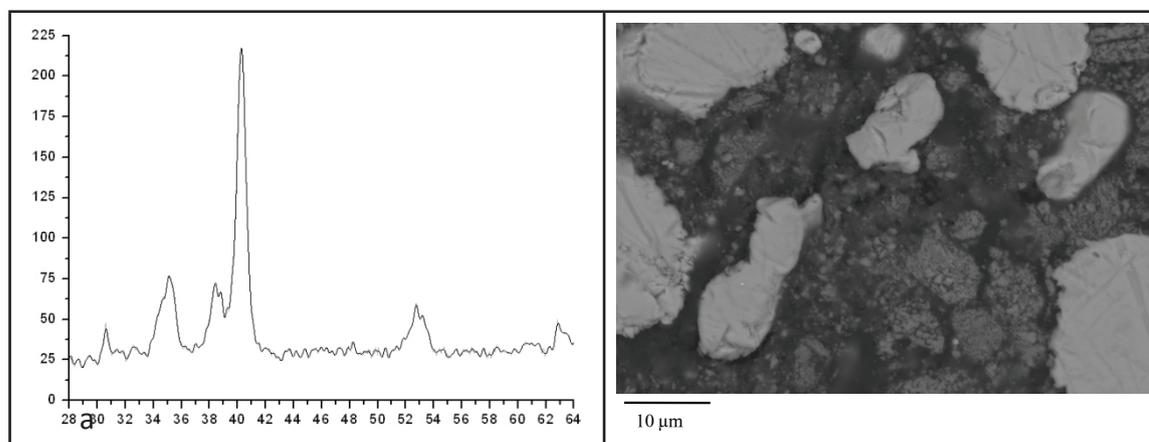
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Tricalcium phosphate (TCP) - $\text{Ca}_3(\text{PO}_4)_2$ is a well-known biomaterial that used to replace or repair damaged or missing bone tissue and can be employed as a component of the coating for bone prostheses. TCP is an antigenic, non-toxic and non-carcinogenic biomaterial that is widely used in orthopaedics, dentistry, and reconstructive surgery, due to its similarity in chemical composition to that of bones [1]. Improved biocompatibility and bioactivity of implants can be achieved by deposition of coatings using the magnetron sputtering technology with targets based on nonstoichiometric titanium carbide with functional additives of Ca, P, C, O in a given ratio [2].

The work is devoted to experimental studies of SHS ceramic materials in Ti-C- $\text{Ca}_3(\text{PO}_4)_2$ system. Green compositions were taken according to the formula $(100\% - X) (\text{Ti} + 0.5\text{C}) + X\% \text{Ca}_3(\text{PO}_4)_2$ ($X = 10-30\%$). The effect of initial temperature of SHS process and the reactionary mixture composition on kinetic parameters of the combustion process was studied. The additives of TCP to the reaction mixture reduced combustion temperatures and rates. In the mixture with $X = 20\%$, the combustion process initiated at $T_0 = 298\text{ K}$ and still occurred in the stationary mode, which indicates that Ti exothermically interacts with TCP.

In the case of $X = 20$ and 30% the stages of the structural and phase transformations were studied by dynamic X-ray diffraction and by the stop combustion front (SCF) method (Fig. 1). The characteristic regions of the combustion front were assessed using electron microscopy. Parallel chemical reactions between Ti and C with the formation TiC and between Ti and $\text{Ca}_3(\text{PO}_4)_2$ with the formation CaO and Ti_3PO_x occur in the combustion wave (Fig. 1b, e). The presence of the CaTiO_3 phase suggests that an interaction between calcium oxide and unreacted titanium takes place in the post-reaction zone (Fig. 1c, f).

Dense ceramic materials consisting of round-shaped grains of $\text{TiC}_{0.55}$ - $\text{TiC}_{0.6}$ surrounded by a titanium phosphate (Ti_3PO_x) binder with inclusions of calcium oxide (CaO) have been synthesized using the forced SHS pressing technology. The physical properties of the materials were studied. Increasing of parameter X from 10 to 30% reduces the grain size and hardness of final product, but increases the residual porosity.



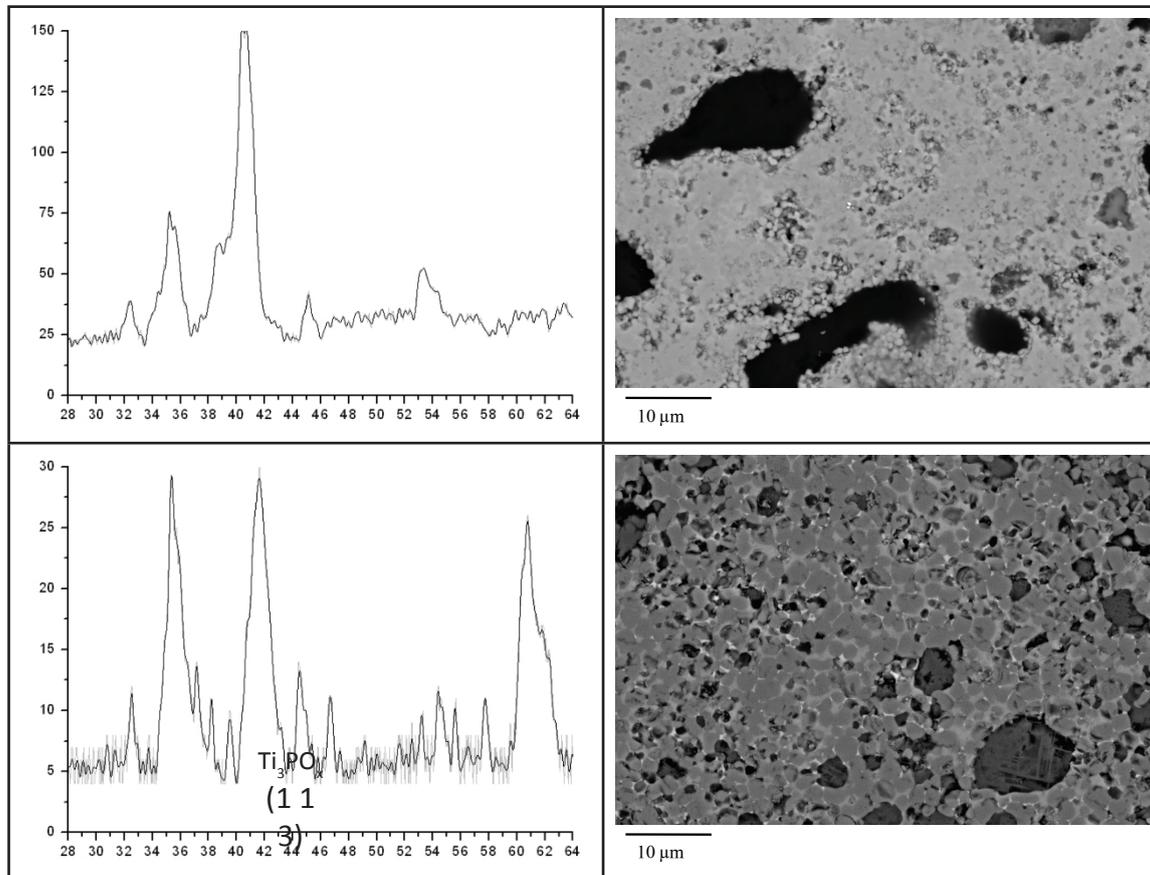


Fig. 1. A selected series of dynamic XRD patterns of combust sample at X = 20 % (a-c) and microstructures of SCF in different zones of combustion wave: d - initial mixture; e - post combustion zone; f - final product.

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Abstract No : 1017

SYNTHESIS OF MATERIALS IN Ti-Cr-C-Me SYSTEM

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In line with the scientific and technical development of materials science, it is important to elaborate effective technologies for production of new multifunctional materials which can work in extreme conditions [1]. Besides the elaboration of effective technologies for production new materials, the other goal of modern scientific research is focused on the elaboration of energy and resource saving, ecologically safe technologies and their realization. In this point one of the prospective directions for reduction of electrical energy and the duration of technological cycle is the Self-propagating High-temperature Synthesis (SHS). The method can be characterized with high productivity, low energy consumption, with high quality of the product and ecological purity [2].

The process ongoing in the synthesis wave can be divided in 4 zones: those are heating zone, component interaction or heat emission zone, the zone of interaction finishing among components and the zone of formation of the final structure [3].

In the first zone there are no chemical reactions, but the initial components are heated. In the second zone of heat emission, there are chemical reactions and significant amount of heat is emitted which ensures the propagation of synthesis wave. The interaction among the components are finished in the final zone, with formation of final phase content of the product[4,5].

The work describes some characteristics of phase formation in Ti-Cr-C-Me and Ti-Cr-C-Mo-Me systems by SHS. The paper also describes the physical and mechanical and specific properties of obtained materials. It is shown that physical and mechanical properties of hard alloys, in particular exploitation strength, is significantly stipulated by the strength of, on the one hand, among I phase of hard component, and II and III phases of joint components and on the other hand among the adhesion strength between I, II and III phases. In the presented work the possibility of increasing adhesive strength among I, II and III phases in Ti-Cr-C-X18H15 system is studied by creation ring-shaped structure, achieved by alloying of initial mixture with Molybdenum (Mo).

The other typical property of hard alloys is their resistance in different media, especially resistance against oxidation on air at high temperatures, which significantly increases the areas of application of such materials. The materials with high oxidation resistant properties in open air can be used for preparation of stamps, high-temperature isostatic stamping, also for rolls, cutting tools, peep-holes and etc.

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Abstract No : 1018

SYNTHESIS OF GRADIENT MATERIALS ON THE BASIS OF INTERMETALLICS

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We are first proposing two technologies of fabrication of single-phase components made from Ti-Al compounds, which are compacted and pore-free. These technologies are performed in two modes: combustion and thermal explosion. The material has fine microstructure, and in particular cases even nanostructure, which makes them very attractive because of expected increase in strength and plastic characteristics of the material. Because of peculiarities of Ti-Al compound formation in the developed equipment of SHS in the mode of thermal explosion, at first stage of the process the starting materials (Ti and Al) are pressed at 0.25 - 2 Kbar.

The experiments which were carried out to obtain single-phase compositions enabled us to determine the conditions and optimal characteristics to obtain desired single-phase composition [1]. The idea of obtaining nanostructure materials in Ti-Al system proposed by us is that during mixing of components high quality deformation is performed, after that pre-compaction and plastic deformation takes place under high pressure. At the next stage the high speed heating process is realized in thermal explosion regime, which is possible during realization of SHS for high exothermic chasm. As soon as the process is finished the sample is finally compacted and plastically deformed under high pressure.

As far as we are using high exothermic chasm for obtaining TiAl and Ti₃Al in thermal explosion mode, during the synthesis high energy is exhausted, it becomes possible to obtain the high quality deformed and compacted sample of Ti-Al system in 4-8 seconds [2-3].

After heating to definite temperature with the definite rate of heating, the synthesis in the mode of combustion or thermal explosion with subsequent compacting takes place [4]. After the synthesis of the compounds in the mode of thermal explosion, a compacting at high temperature, 1300 - 1600°C is performed. This causes plastic deformation of dislocation structure and formation of new grain boundaries, resulting in grain size refinement and formation of very fine microstructure with the dimensions, ~80nm. The above leads to the conclusion that the developed technology makes it possible to produce nanostructure single-phase Ti-Al intermetallics. These materials can be successfully used in space technologies for protection from radiation and meteorites.

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Abstract No : 1019

TECHNOLOGY FOR SYNTHESIS OF MULTIFUNCTIONAL CERAMIC MATERIALS

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The main objective of modern scientific research is to orientate industry onto development and realization of resource-saving, environmentally friendly technologies [1-3]. Among these directions is Self-propagating High-temperature Synthesis (SHS), which is characterized by high productivity, low power input, high quality of the obtained produce and ecological efficiency.

Synthesized by the SHS method hard alloys and composite materials based on carbides, borides and carbon-nitrides are characterized with high values of physical and mechanical properties as hardness, compression stress, wear-resistance, resistant to oxidation on air, resistance to aggressive areas. At the same time they preserve these properties at a high temperature [4]. Therefore they are largely applied in different spheres of techniques. However, their consumption is limited due to their brittleness, which make them inefficient to resist serious impact stress [5].

The knowledge of transformation of initial components to the final product gives us possibility, on the one hand, to the optimal parameters and technological parameters to obtain materials, also to make prognosis about exploitation properties of those materials.

In the heating zone start the processes of melting of Copper and Titanium and capillary flow in one case on the particles of boron nitride, and in another case on the particles of boron nitride and carbide. In the next, active heat educing zone there is active interaction between Titanium and Boron Nitride in one case and between Titanium, Carbon and Boron Nitride in another case.

According to the interaction of particles we may say, that the formation of final product in the first case there is boron interaction to the melted titanium, as a result we obtain titanium boride and there is dismissal of boron nitride by active separation of Nitrogen and by interaction of Nitrogen melted Titanium, we obtain Titanium nitride.

In the second case during the synthesis takes place by interaction of boron nitride containing boron, carbon particles with melted Titanium, afterwards by interaction of separated nitrogen with Titanium Carbide, is obtained titanium carbide nitrides. By the end of reaction, practically all titanium is converted in ultrafine state and is presented as titanium borides, nitrides and carbon-nitride form. The pores are filled with melted consolidating alloy. In the zone of crystallization the final process of formation of product structure takes place.

The study of regulations of synthesis in Ti-B-N-Me and Ti-B-N-C-Me systems gave possibility to make conclusions about peculiarities of process. In particular, in spite of that all components in chasm are solid, the character of synthesis is not typical to systems solid-solid, as far as during the synthesis the BN is dismissed by intensive separation of Nitrogen, therefore during the experiments in atmosphere condition there is process of dismissal of nitrogen from reaction zone which causes the decrease of synthesis parameters 2 times for Ti-B-N-Me and almost 4 times for Ti-B-N-C-Me systems. As a result when obtaining material in atmospheric conditions, the speed and temperature is decreased of synthesis, also the content of nitrogen in material is also decreased. On the basis of discussion of presented material we may conclude that by pressing the synthesized hot SHS material, in order to obtain synthetic composite ceramic material, it is very important to select optimal characteristics of time and pressure. After right selection of technological parameters by authors will be obtained ceramic materials with the following parameters in Ti-B-N-Me and Ti-B-N-C-Me systems: practically non porous 0,4% and 1,2% consequently to the systems, hardness- 91,5-92,5 HRA and 92,3-93,3 HRA consequently, density-4,3-4,4 g/cm³ and 4,5-4,7 g/cm³ consequently. These materials can resist single 18000-20000 J energy loads on 68-65kg/m² (6,8-6,5g/cm²).

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Abstract No : 1020

SHS-HEAT INSULATORS BASED ON THE MODIFIED TECHNOGENIC RAW MATERIALS

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Self-propagating high-temperature synthesis (SHS) is one of most effective methods for creation of high-temperature heat insulators and products on their basis. The systems CaO-SiO₂-Al₂O₃ for synthesis under SHS conditions are of great interest, because they allow to obtain composites containing wollastonite, anorthite and helenite. These structural elements provide strength enhancement and thermal resistance of the material. The wastes of a number of industries are characterized by specified by ratio of oxides and in accordance with composition can be used also for synthesis and production of constructional and building materials [1]. Mechanochemical treatment is an effective method for preparation of technogenic wastes when using them as full-value raw material for production of composite systems of different assignment [2, 3].

This work presents the results on the use of mineral and industrial raw material, choice of the composition and mechanochemical treatment of charge mixtures for production of porous ceramics under conditions regime for high temperature thermal insulators. Experimental works were carried out with the use of quartz sand and technogenic wastes (fly ash thermal power plants and waste autoclave aerated concrete). Mechanochemical treatment (MCT) of powders were carried out in a centrifugal planetary mill CPM "Pulverisette 5" producer - FRITSCH. In the course of mechanochemical treatment, the time for grinding and modifying additives in the form of activated carbon and polystyrene $[-C_8H_8]_n$ were varied. Aluminium of the brand PA4 was used as a reducing material in SHS process. The samples obtained as a result of SHS were investigated on density, thermal conductivity, compression strength and phase composition of synthesis products. It is shown, that in the process of mechanochemical treatment of quartz with organic compounds there takes place a complex multi-stage process of formation of new carbonaceous structures on the particle surface. The degree and form of "carbonization" of quartz surface is specified by the used modifier. MCT of aerated concrete results in complete transformation of the composition of the aerated concrete sample. Wollastonite and quartz become the basic phases.

MCT of silicate - containing mineral and technogenic systems provides a significant change in the structure as well and consequently, the activity of the resulting mixture that is evident in the thermokinetic SHS process characteristics based on such systems. The phase composition of combustion products in these cases is presented by a large amount of corundum. Aluminum and quartz are almost completely realized in combustion reactions. In the sample obtained with the help of fly ash and quartz, the quantity of silicon increases and aluminum nitride is formed. By phase composition the samples correspond to the materials with high refractoriness. But their strength was no more than 4 MPa, which indicates about formation of a large amount of gaseous phase loosening the sample during synthesis. Strength of SHS-samples containing aerated and modified polystyrene is increased to 96 MPa. Samples have a fine porous structure with dense walls. The synthesized samples have shown that thermal conduction coefficient is changing within limits from 0.552 to 0.185 W/m•K and correlates with density variation (it means porosity) of SHS-samples. Due to sufficiently low values of thermal conduction coefficient, these samples are heat-insulators.

Thus, the use of wastes of different productions in the composition of the charge mixture and realization of mechanochemical treatment of charge mixtures can be quite effective in production of SHS thermal insulators. As can be seen from the obtained results, the favorable factor for synthesis process is the content of aerated concrete in the charge and its modification with polystyrene. The synthesized material shows a rather low thermal conductivity, is characterized by a fine porous structure with high strength. According to the X-ray phase analysis such material consists essentially of aluminum oxide and also contains aluminum nitride, i.e. refers to the category of refractory systems.

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Abstract No : 1026

FABRICATION OF MAGNESIUM SILICIDE VIA MECHANICALLY ACTIVATED SHS FOLLOWED BY SHOCKWAVE CONSOLIDATION

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Harvesting energy from exhaust gases would have a tremendous impact on the economy and the environment. Thermoelectric conversion is being studied extensively for this purpose [1]. Magnesium silicide (Mg_2Si) is a promising thermoelectric material for harvesting energy because it can be used at 300-600°C, i.e., in the operation domain of thermoelectric generators used in exhaust systems and other high-temperature applications [2]. Magnesium and silicon

are non-toxic, abundant, and relatively inexpensive. A low density (1.99 g/cm^3) of Mg_2Si is attractive for automobile waste heat recovery applications. Mg_2Si -based compounds are typically synthesized on a small scale via melt synthesis or casting. Mechanical alloying has been considered for a larger-scale fabrication, but this method requires long milling times, leading to contamination by grinding media [2].

One promising alternative is self-propagating high-temperature synthesis (SHS). Recently, Mg_2Si has been obtained by combustion of Mg/Si mixture [3, 4]. Unfortunately, the reaction between Mg and Si is not very exothermic. The adiabatic flame temperature of the stoichiometric (2:1 mole ratio) Mg/Si mixture is only 1242 K (at 1 atm). This creates difficulties with ignition and may prevent the use of SHS for fabrication of Mg_2Si . To facilitate ignition of low-exothermic mixtures, mechanical activation is often used. Thus, in the present work, Mg_2Si was fabricated using mechanical activation-assisted SHS. Another objective of the present work was to explore the feasibility of using shockwave consolidation for the densification of Mg_2Si obtained by SHS.

Mixtures of magnesium and silicon powders were milled in a planetary ball mill in an argon environment, compacted into pellets and ignited at the top in a reaction chamber filled with argon at 1 atm pressure. Upon ignition of the pellet, a combustion wave propagated downward, leading to the formation of a highly porous, low-density Mg_2Si product.

The product was then compacted into a steel tube in an argon environment. The tube was sealed and placed coaxially within a larger-diameter "explosive" tube, which was then filled with ammonium nitrate fuel oil (ANFO), an explosive material (Fig. 1). A third, "confinement" tube of a larger diameter was installed coaxially and the gap between the explosive and confinement tubes was filled with sand. A detonator at the top was used to initiate the explosion which applied a symmetrical high-pressure pulse that moved inward and down the inner tube, causing the tube to deform and the interior powders to consolidate into a dense, well bonded bulk material. Thermophysical properties of the obtained material were examined using a laser flash apparatus and a differential scanning calorimeter.

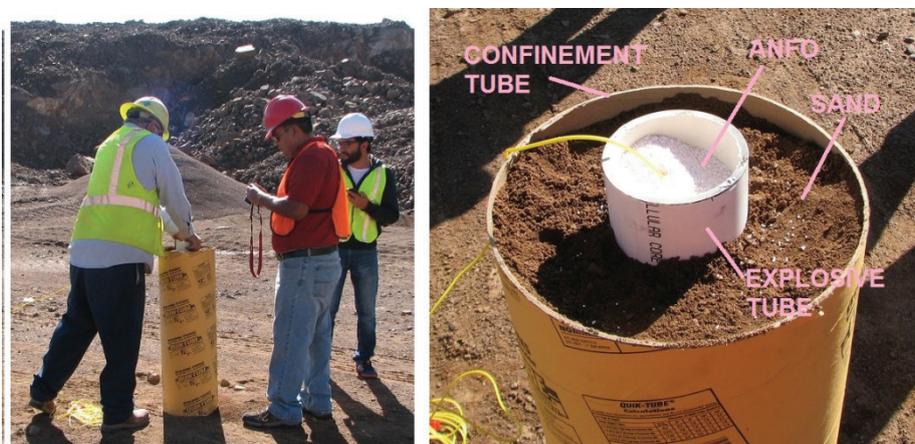


Fig. 1. Shockwave consolidation setup.

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Abstract No : 1032

EVALUATION OF COMBUSTION TEMPERATURE AND COMBUSTION SPEED OF THE PROCESS OF SH-SYNTHESIS OF TITANIUM OXIDE BRONZE

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So-called transition metal oxide bronzes have unique chemical and physical properties. Depending on the composition and structure they are good conductors or semiconductors. Recently the high photothermal effect was found out for the molybdenum oxide bronze used as a photo absorbing addition to cartilage irradiated by laser [1]. Transition metal oxide bronzes have been produced by various synthetic routes. Most of these methods are technically complex and expensive. We have determined the conditions and carry out the SH-synthesis of oxide bronzes of different composition [2].

In this paper we evaluated the temperature and speed of the combustion process in SH-synthesis of titanium oxide bronze with system of optical control parameters SHS with automated analysis of thermal data [3]. The work aims to study the kinetics of SH-synthesis of oxide bronzes and allows to establish the relationship between the composition of the charge and its combustion characteristics, as well as to evaluate the degree of conversion in the reaction.

The mixture of TiO₂, Ti, Cu(OH)₂ and KI was combusted in air. The product was identified by X-ray powder diffraction method as K_{0.12}TiO₂. Thermal measurements were performed using a high-speed camera "VideoSprint" (NPK "Videoscan", Russia). Registration of the SHS process was carried out at 1000 frames per second.

Using system of optical control the dynamics of the maximum temperature of SHS wave on the depending size of the layers of the product from time may be determined. Variability of temperature is associated with variability of the composition and parameters of heat transfer charge in the layers of the product formed at different times. The figure shows a set of thermograms in the system according to a linear set of photocells (3D).

Theoretically, the individual thermograms can be obtained for each point of space at each moment. Analysis of set of thermograms together with information on the structural transformations in the process of SH-synthesis gives the kinetic description of the combustion process.

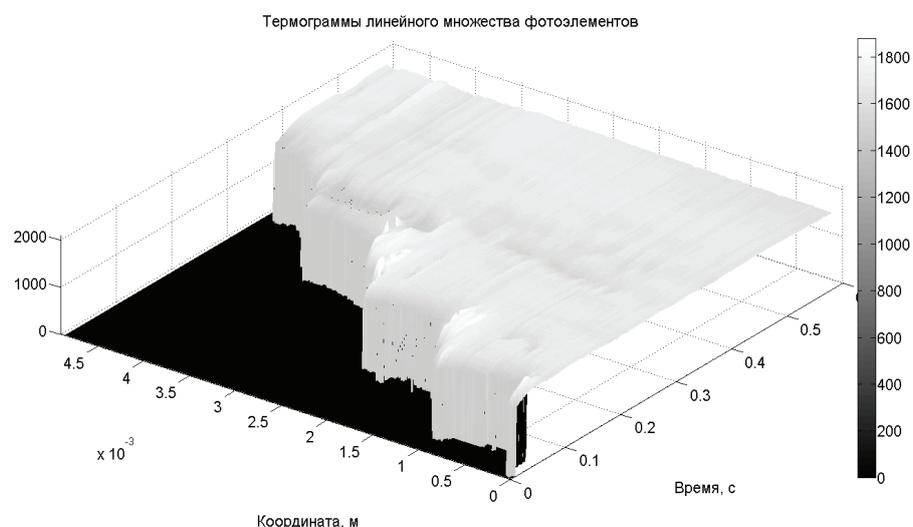


Figure. Set of thermograms on a linear set of photocells (3D)

Reaction runs in a combustion wave during 40-60 seconds and accompanied by the structural transformation of an original tetragonal TiO_2 . The structure of oxide bronze, as rutile, is built from chains of TiO_6 octahedra connected by edges. However the motive location of octahedra chains in rutile differs from motive location in oxide bronze. The structure of oxide bronze may be described as frame-structure with tunnel emptiness. This friable structure is stabilized by introducing of large potassium atoms.

Individual process steps SH synthesis are: 1) the occurrence of oxygen vacancies; 2) diffusion of potassium atoms in the crystal; 3) melting of copper metal formed by the reaction (m.p.1084,6 °C). Restructuring does not occur continuously, but in waves, with the accumulation and ordering of oxygen vacancies and enrichment of the crystal with potassium atoms.

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Abstract No : 1042

STRUCTURAL CHARACTERIZATION AND SUPERCONDUCTING PROPERTIES OF Nb_3Al BY COMBUSTION SYNTHESIS

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In this work we present, the synthesis of superconductive intermetallic compound, of crystallographic structure of type A15 (Nb_3Al) presenting a critical temperature of 18°K. The preparation of mixtures was crushed dry in one steel jar by means of a global crusher in a weak speed of 150Tr x m. Powder her Nb_3Al is compacted under cold conditions united uniaxially in a press (12 tons), pressure of P=2000Psi.

By using the electrothermal explosion (ETE) initiated by the heavy current (400 A), the obtained samples were characterized of the phase composition by the diffraction technique of the X-rays. Further studies have been carried out by field emission scanning electron (FESEM) and optical microscopy. The energy-dispersive X-rays microanalysis (EDX) and Auger spectroscopy was used to determine the phase composition of the phase formation.

Keywords: Thermal explosion, Nb_3Al intermetallic, superconductivity, morphology, phase.

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Abstract No : 1043

FABRICATION OF Cu-20at.% Sb SEMICONDUCTING PROPERTIES BY COMBUSTION SYNTHESIS METHOD

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The direct formation of semiconductor phase by combustion (Self-propagating high-temperature synthesis and thermite explosion techniques) synthesis method of crystalline elemental powder of Cu and Sb with the nominal composition Cu-20at.% Sb. Powder of Cu₂Sb is compacted under cold conditions uniaxially in a press (12 tons), pressure of P=1000Psi. The phase composition after combustion reaction and crystallisation process in situ has been studied using the X-ray diffraction technique. Morphologies and homogeneity of sample are characterized by scanning electron microscopy (SEM). The energy-dispersive X-ray microanalysis (EDX), Auger spectroscopy and atomic emission spectroscopy (AES) was used to determine the phase composition of the phase formation.

Keywords: rapid solidification; Cu₂Sb; semiconductor; phase; X-ray diffraction; SEM.

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Abstract No : 1044

MICROSTRUCTURE EVOLUTION AND MANGNETIQUE PROPRIETIES OF NANOCRYSTALLINE $Fe_{60}Cu_{30}Al_{10}$ PREPARED BY COMBUSTION PROCESSES

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Nanostructureddisorderediron-aluminium-copperalloy of Fe-30% Al-10% Cu composition wasprepared by Self-propagating high-temperature synthesis (SHS) and thermeexplosin(TE) techniques of mechanically activated mixture of Fe, Al, Cu powders.The transformations occurring in the material during combustion were studied with the use of X-ray diffraction.Furtherstudies have been carried out by scanning electronmicroscopy (SEM) to examine the morphology. The energie-dispersive X-ray microanalysis (EDX), augerspectroscopy and atomic emission spectroscopy (AES)was used to determine the phase composition of the phase formation.Finally, the Magnetic properties were also investigated,for combution processers the magnetic behaviors lightly softened becoming a semihard ferromagnetic.

Keywords:combustion processes;noncrystalline; $Fe_{60}Cu_{30}Al_{10}$; morphology;Magnetic.

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Abstract No : 1053

ULTRA-FAST DENSIFICATION OF BORON CARBIDE CERAMICS BASED ON SELF-PROPAGATING HIGH-TEMPERATURE SYSTHESIS

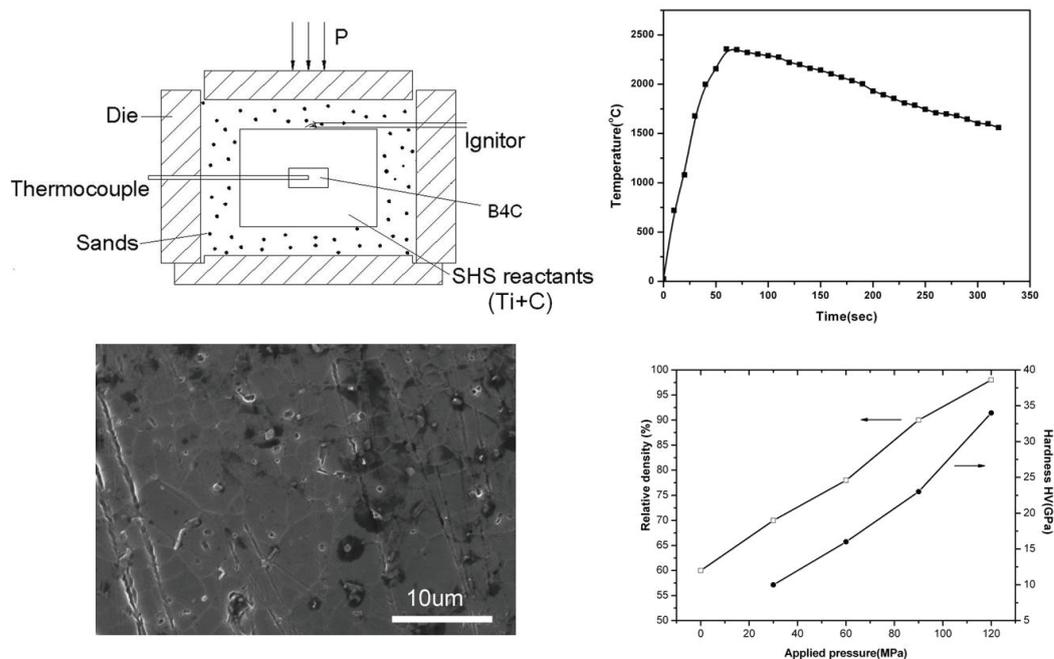
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Boron carbide (B_4C) has been widely used as one of the most important and promising engineering ceramics due to its excellent physical and chemical properties, such as, low density ($\rho_v=2.52 \text{ g/cm}^3$), super hardness, high elasticity modulus, good wear and corrosion resistance, and neutron absorption ability[1]. Due to the presence of high fraction of strong covalent bonding, low plasticity and high resistance to grain boundary sliding, densification of B_4C is difficult. Many efforts have focused on the preparation of dense B_4C by various sintering techniques [1-4]. There were two effective method help to obtain dense B_4C ceramics, one was increase sintering temperature, and the other was adding sintering aid. Although the high temperature and additives were proved to be able to improve the densification, they might also result in grain coarsening and the formation of grain-boundary phases, thereby influenced the mechanical behaviors of B_4C .

In this research, a fast fabrication technique utilizing a very high heating rate and high pressure was developed. The heat generated by combustion reaction or Self-propagating High-temperature synthesis (SHS) was applied to act as high temperature source. A B_4C compact was loaded inside the combustion reactants. The whole reaction system was put into a steel die. A large mechanical pressure was applied, when the sample's temperature reached the maximum. Compared with other fabrication techniques, this method has advantages of higher heating rate (2300 °C/min), shorter densification time and larger pressure (120MPa),

which is predicted to refine the microstructure and enhance the densification. With such an approach, densification of B_4C ceramic can be obtained within two minutes.



The B_4C was densified by the heat from SHS with a heating rate of $2300\text{ }^\circ\text{C}/\text{min}$, and the mechanical pressure of 120 MPa in two minutes. The maximum hardness of the dense B_4C specimen is 34 ± 0.2 Gpa. This method has higher heating rate and shorter sintering time than traditional sintering process, which leads to maximal temperature and minimal grains coarsening.

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Abstract No : 1065

SHS-PRODUCED TRANSITION METAL SILICIDES: SYNTHESIS AND SINTERING

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Ceramic materials based on molybdenum, tungsten, niobium and titanium silicides are characterized by high resistance to aggressive media at high temperatures. They are used for deposition of coatings and manufacturing machine parts operating in extreme conditions.

Such materials can also be produced [1, 2] by SHS metallurgy. In this work, we studied the possibility of producing cast $\text{MoSi}_2\text{-WSi}_2$, $\text{MoSi}_2\text{-NbSi}_2$, and $\text{MoSi}_2\text{-TiSi}_2$ in the form of ingots. The ingots were then milled into powders with a wide particles size distribution and used for deposition of coatings and sintering.

We explored the effect of blend composition on the process parameters, microstructure, and composition of final products. Products $\text{MoSi}_2\text{-WSi}_2$ and $\text{MoSi}_2\text{-NbSi}_2$ could be prepared in any relative ratios. In case of $\text{MoSi}_2\text{-TiSi}_2$ composite, the maximal content of titanium silicide can not exceed 40%.

Some highly caloric mixtures of Mo, W, Nb, Ti oxides with silicon or aluminum were suggested for synthesis of cast composite materials. Since the combustion temperatures exceed the melting points, the final products are formed in their liquid state.

Our experiments were carried out in an 20-L SHS reactor under the nitrogen (or argon) pressure of 4-5 MPa. Synthesized materials (ingots up to 5 kg in their weight) were characterized by elemental analysis, XRD, and EDS.

The parameters of milling in a jaw crusher and ball mill were optimized. The mixtures of milled composites with added magnesium aluminum silicates were sintered in argon at 1650-1800°C to obtain the samples of 70% MoSi_2 /30% WSi_2 ($\text{Mo}_{0.7}\text{W}_{0.3}\text{Si}_2$). Influence of composition and amount of added sintering agent on oxidation in air at 750°C for 100 h was studied. $\text{MoSi}_2/\text{WSi}_2$ composites showed a higher resistance to oxidation than MoSi_2 and WSi_2 . The addition of 20 vol % magnesium aluminum silicate was found to reduce the rate of low-temperature oxidation.

Maximum density and strength were exhibited by the sintered samples of 70/30 $\text{MoSi}_2/\text{WSi}_2$ ceramic composite. This ceramic can be recommended for use as a structural material [3].

This work was partially supported by the Russian Foundation for Basic Research (project no. 13-08-00864a)

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Abstract No : 1068

STRUCTURAL HEREDITY OF ALLOYS OBTAINED BY CENTRIFUGAL SHS: INFLUENCE OF REMELTING TEMPERATURE

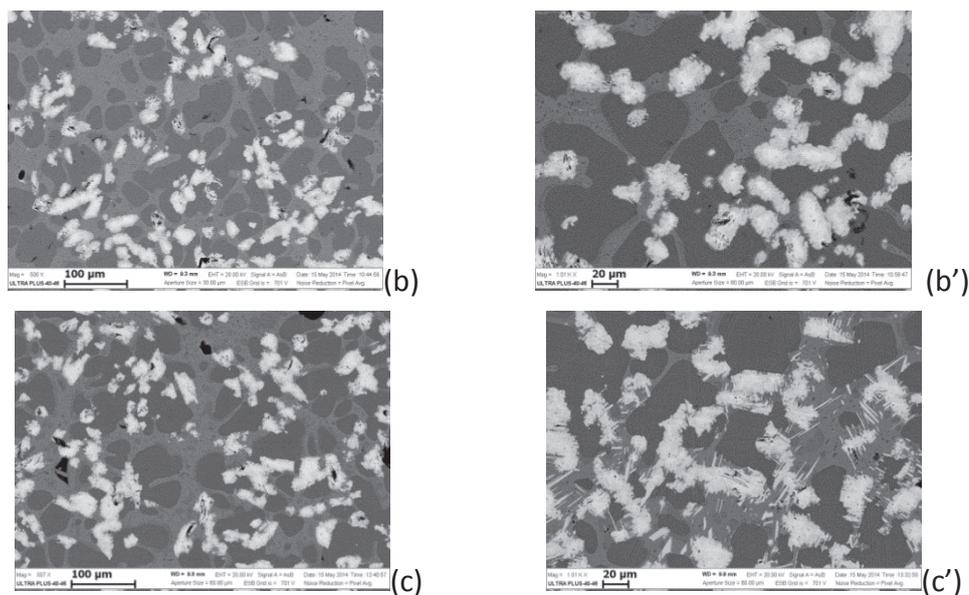
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Items operated at temperature range 700 - 1100 °C made of heat-resistant nickel, cobalt or iron based alloys (superalloys). Despite the emergence of new technologies for manufacturing such products a most massive and manufacturable process still remains casting. Modern production of components from the superalloys by casting generally includes the step of producing cold-charged materials (CCMs) with regulated chemical composition and microstructure and casting the products directly to predetermined shape. The quality and technology of smelting CCMs can have a significant impact on the parameters of casting technology and properties of the final products.

Marked advance in service parameters of final components can be achieved by using the following approach to manufacturing cast materials: (1) synthesis of cast CCMs by centrifugal SHS [1] and (2) their remelting under reduced pressure or in an inert atmosphere followed by casting into a mold with desired geometry.

SHS process was performed at centrifugal accelerations $a = 10-400g$. In this way, we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product structure more uniform. Thus synthesized CCMs exhibited a uniform distribution of the elements over the entire ingot. Experiments were performed the following two composites: Ni alloyed with Al, Cr, Mo, Mn, Hf, and B (alloy I) and Co alloyed with Nb, Cr, Mo, W, Al, and C (alloy II). The influence of CCMs remelting temperature on the phase composition and microstructure of resultant materials was determined by using a VIK-VMR apparatus as described elsewhere [2].

Remelting CCM was carried out at 1700, 1750, and 1800 °C. The results of sample microstructure investigation are exemplified in Fig. 1. An increase in remelting temperature is seen to markedly change the microstructure of the alloys under study.



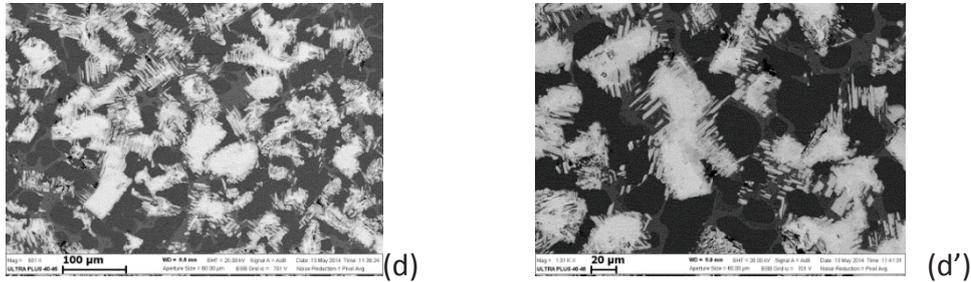


Fig.1. SEM images of alloy I: SHS-produced (a, a') and after remelting at 1700 (b,b'), 1750 (c, c') and 1800 °C(d, d').

Our results can be expected to provide a technological background for a new cost-effective two-stage process: (a) SHS fabrication of refractory alloys with a desired composition and (b) their metallurgical reprocessing into ingots of appropriate configuration.

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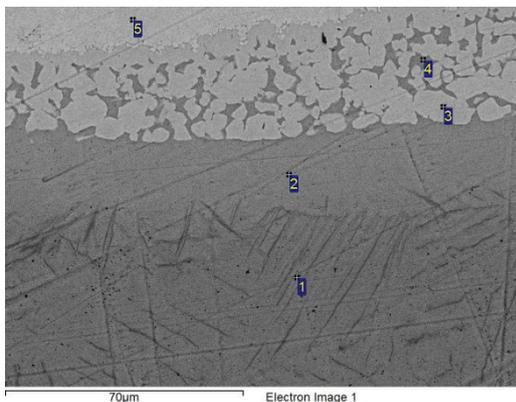
Abstract No : 1072

SHS OF COMPOSITE MATERIALS BASED ON Ti-Co

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Experimental studies for obtaining the porous material on the basis of Ti-Co by self-propagating high-temperature synthesis (SHS) followed by welding of the material with the titanium substrate (BT1-0) have been carried out. The structure and phase composition of the samples were investigated by scanning electron microscopy and X-ray phase analysis. It is shown that the synthesized alloy Ti-Co has a total porosity of 55-70 % with pore size 200-800 μm. The porous material on the basis of Ti-Co with characteristic pore size of 100-200 μm shows a high open porosity (60 %), uniformly distributed on the sample.

Structural characteristics of the materials can be adjusted by changing the synthesis parameters and the initial dimensions of the sample. It is shown that contact zone has no pores or other defects when welding the material on the basis of Ti-Co with titanium substrate (VT1-0).



| Spectrum | Ti | Co |
|----------|-------|-------|
| 1 | 99.73 | 0.27 |
| 2 | 93.34 | 6.66 |
| 3 | 63.78 | 36.22 |
| 4 | 87.70 | 12.30 |
| 5 | 45.98 | 54.02 |

Fig.1. Microstructure of transition zone and EDA data of TiCo titanium substrate.

Abstract No : 1077

SHS OF POLYMETALLIC CATALYSTS WITH MULTIFUNCTIONAL PROPERTIES

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In the research the new class of polymetallic catalysts on the base of complex intermetallides was developed. The catalysts demonstrated high activity and selectivity in oxidation [1,2] and reduction processes [3].

On the first stage, the multicomponent intermetallic precursors were produced by centrifugal termite-type SHS process [2] from oxides of iron group metals (Fe, Ni, Co) with addition of other d-metals and rare earths as promoters. The SHS reaction yielding cast intermetallic alloys can be represented by the following scheme:



where ΣMeO_x is a mixture of oxides of transition metals and rare earths, the intermetallic alloy consisted of "higher" and "lower" intermetallides with unreacted aluminum. After ignition, highly exothermic reaction spread through sample in combustion mode. The temperature reached as high as 2500°C therefore all the products were in liquid state. The total reaction time was only a few seconds. The SHS process was performed at centrifugal accelerations $a = 10\text{-}400 \text{ g}$. In this way, we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product structure more uniform. Thus synthesized multicomponent intermetallic precursors exhibited a uniform distribution of the elements over the entire ingot.

On the second stage, the synthesized polymetallic alloys were leached by alkaline solution to produce the required property of catalysts. The essential feature of the developed method was stabilization of prepared catalysts by treatment of hydrogen peroxide solution. It is necessary to prevent self-ignition of the samples in the air by removing hydrogen adsorbed during leaching and by formation of a thin oxygen layer on the catalyst surface. After that the catalysts were stable even in oxidation processes at high temperatures.

The structure of the catalysts granules included the lower non-leached intermetallides as supports for highly disperse, disordered and partially amorphous metallic phases. Their specific surface reached more than 40 m²/g. Oxo-metallic two-level nanostructures were observed on the surface of the all investigated catalysts. The primary levels of structure were flat hexagons of ~1 μm in diameter and less than 100 nm in thickness. The hexagons consisted of granules of 10-30 nm in size or thin unresolved geometric figures as secondary level structures (Fig.1).

The (Ni, Fe)-Co-Mn(Ce) catalysts have high activity and stability in process of deep oxidation of CO and hydrocarbons up to 450°C. The temperature of 100% conversion was 150-200°C for CO and 250-300°C for propane under gas space velocity 120,000 h⁻¹ [1,2].

The cobalt based catalysts with promoters such as V, Zr, Ce, La were tested in Fischer-Tropsch (FT) process and demonstrated high activity (~70% CO conversion) and a very high selectivity to heavy hydrocarbons (up to 94%). The value of ASF chain growth factor α reached 0.94 and the product contained a large amount of solid paraffins [3]. The samples of the catalysts were not subjected to any preliminary activation by hydrogen treating at 400°C in contrary to the traditional supported cobalt catalysts.

Other samples of polymetallic catalysts were tested in the process of hydrodesulfurization (HDS) of heavy oil fractions as well. Mo-Ni catalyst was very active in purification of diesel fraction at 350°C, weight velocity of 1 h⁻¹ and hydrogen consumption of 300 ncm³/cm³. The total sulfur content was reduced from initial 9900 ppm to 31 ppm. The catalyst was used without preliminary treatment by sulfur compounds and calcination.

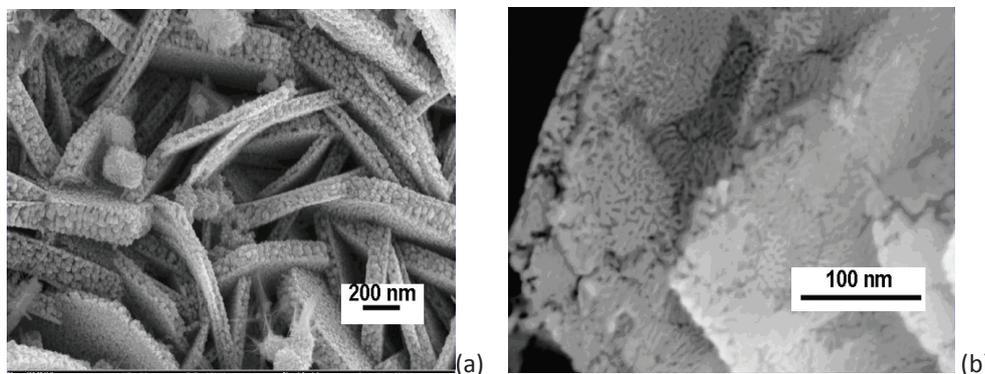


Fig. 1. SEM micrograph of Fe-based (a) catalyst surface for deep oxidation and (b) Co-Ce catalyst for FT process

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Abstract No : 1084

NOVEL SHS INDUSTRIAL REFRACTORIES BASED ON CHROMITE AND FERROUS WASTES

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High-temperature industrial furnaces require refractory linings which can withstand the, often corrosive, operating conditions. Chrome-containing refractories are suitable for linings because apart from high performance they are also stable to chemical agents that exist in metallurgical processes. In addition, chromite refractories generally have high melting points, moderate thermal expansion and very good thermal shock resistance [1].

The conventional process of producing high-temperature refractories involves four stages: raw material processing, forming, firing and finishing. This process takes a few days to complete and demands great amounts of energy which translates to high cost [2]. This necessitates economies of scale and over the last years, only a few major companies around the world are left producing commercial refractories. In Europe, these are mainly located in Germany, Poland, Czech Republic and Turkey.

SHS has been used to synthesize many types of refractories in the past [3, 4] and industries in Kazakhstan (among other countries) have used SHS technology commercially for the production of various types of refractories often based on local raw materials. Because of the many advantages of SHS production, as well as large mineral (chromite and other) local deposits and extensive inorganic industrial solid wastes, it would be beneficial to introduce SHS manufacturing technology of refractories into Greek industry.

In this paper we present the current state of development of high-temperature chromite-based refractories on the basis of Greek raw materials and wastes for industrial kiln lining in extraction industries.

With respect to previous reports related to refractory production by SHS, a basic refractory composition of chromite-MgSO₄-Al has been used. Various types of ball-milled chromite ore with grain size less than 250 microns were mixed with magnesium sulfate and aluminum powder and cold-pressed in cylindrical compacts. Various concentrations of

the mixtures have been examined while keeping the aluminium content at 12 wt%. SHS synthesis was carried out at different pre-heating temperatures from 650 to 900°C with 4 minutes of pre-heating. At each firing temperature several refractory materials were produced and subjected to characterisation by determining their density, porosity, microstructural morphology, atomic structure (XRD) and thermal and mechanical properties. Indicatively, the compressive strength and density/open porosity are shown in Figures 1 and 2 as functions of chromite content and pre-heating temperature.

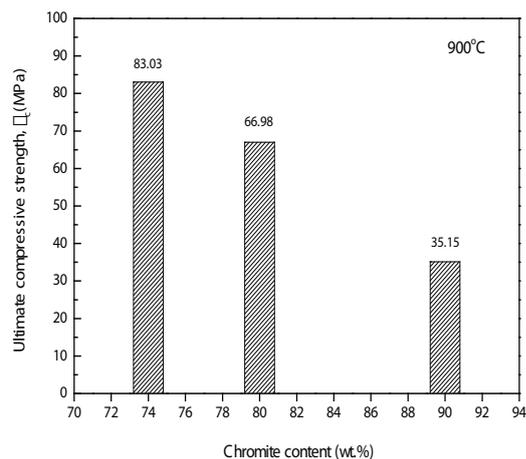


Figure 1. Ultimate strength in compression of SHS refractories synthesized at 900°C as a function of chromite content (wt.%).

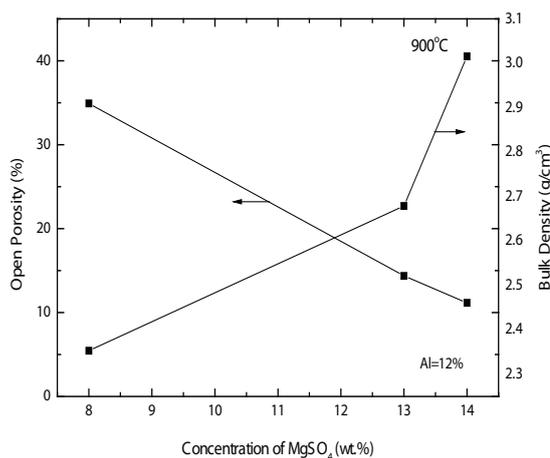


Figure 2. Influence of magnesium sulphate concentration on the open porosity and bulk density of refractories synthesized at 900°C.

In addition to chromite, various additives of magnesia and ferrous wastes were mixed with the initial composition and refractories were synthesised using SHS. In nearly all cases, refractoriness was found to be over 1700°C and ultimate compressive strength reached over 60MPa. The bulk density of most of the refractories was measured to be above 3g/cm³ while the open porosity was less than 15%. Thermal conductivity in most cases was measured at less than 2 W/mK. The work is continuing but results to date indicate that the SHS method is capable of producing high quality refractories based on Greek chromite and inorganic industrial wastes. Products display similar or better thermodynamic properties than the traditional high-temperature refractories. Finally, a first order techno-economic analysis indicates that the new SHS refractories are cost-competitive due to the low aluminium content of less than 12wt.% as compared with commercial products which generally are made with higher cost ores. The method can be adapted easily for the commercial production of orthogonal and trapezoidal blocks as used in kiln linings for extraction metallurgy.

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Abstract No : 1094

IMPROVEMENT IN THE DURABILITY OF ALUMINIDE INTERMETALLIC COATINGS BY MICROWAVE-ASSISTED COMBUSTION SYNTHESIS STRATEGIES

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Aluminide intermetallic compounds and phases are widely employed as high temperature protective coatings, mainly due to their low densities, high melting temperatures and the high aluminium content, which guarantees excellent high temperature oxidation resistance [1, 2].

However, one major problem concerns the long-term durability of these intermetallic coatings as a result of interdiffusion processes between the aluminide coating and the substrate, occurring during exposure at high temperatures. Indeed diffusion of Al from the coating to the substrate usually results in depletion of Al in the major part of the coating [3].

This inward diffusion of Al toward the substrate and the subsequent formation of micro-pores in the interdiffusion zone, probably represent the main degradation modes of aluminide coating.

Some of the present authors already exploited microwave (MW)-assisted combustion synthesis to obtain a NiAl intermetallic coating on grade 2 titanium substrate, with improved performances due to the formation, during synthesis, of an interfacial Ni-Al-Ti reaction layer [4], which demonstrated the ability to decrease interdiffusion phenomena at high temperatures [5].

The aim of the present work is to propose a similar approach in order to create opportunely designed barrier layers to the inward diffusion of Al, thus significantly increasing the durability, of FeAl-, NiAl- and CoAl-based intermetallic coatings, on technologically relevant substrates, like Ni-based superalloys, and different stainless steels, in order also to evaluate the outward diffusion of some elements possibly found in the substrate.

Moreover the powder metallurgy-based strategies, like combustion synthesis, easily allow to opportunely tune the composition of the starting powders mixture, thus to study the effect of added elements on the interdiffusion process. The formation of an efficient protective intermediate thermal layer, which hinders the inward Al diffusion, can prolong the lifetime of aluminide coatings.

Furthermore, the use of microwave ignition strategy will also permit to continuously transfer energy to the reactive system also after ignition, thus modifying the reactivity, the consequent adhesion and diffusion phenomena. The results obtained by using different incident microwaves frequency (namely 2.45 GHz and 5.8 GHz) will be fully detailed.

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Abstract No : 1095

SHS OF CAST NiCrCoFeMnAl_x NANO-STRUCTURED HIGH ENTROPY ALLOYS AND COATINGS OF THEM

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High entropy alloys (HEAs) or multi-component alloys are a new effort in materials science and engineering. The standard definition of an HEA is an alloy that contains at least five major metallic elements ($n \geq 5$), each with concentration between 5-35 at.% [1]. The configuration entropies of HEAs ($S_{\text{conf}} = R \ln(n)$ where R is the universal gas constant) assuming the alloys in a fully (close-to fully) random state (random solid solution), are much higher than those of conventional alloys with one or at most two principal elements, and here comes the definition of HEAs. Depending on the alloy compositions, HEAs can possess many interesting mechanical and physical properties, and particularly they have great potentials to be used as high temperature materials, or coating materials requiring high hardness and high wear resistance. Nevertheless preparation of the multicomponent materials is not easy science and technological task. We should promote high homogeneity (fine distribution of all elements into volume of alloy). Besides if the alloy content high chemical active component (Ti, Al, Zr, Hf etc.) it require use expensive mold materials and complicated techniques.

In this work we investigated a cost-effective SHS process for fabricating cast NiCrCoFeMnAl_x high-entropy alloys through the following aluminothermic reaction:



where (MeO) - NiO, Cr₂O₃, Fe₂O₃, Co₃O₄, etc.; Al-metal reducer, FA is an additive facilitating phase segregation, and Q the reaction heat.

The process flowsheet is: after initiation with an igniting coil, SHS reaction frontally propagates downward. Because the attained temperatures (up to 3000 °C) are well above the m.p. of reaction products, the melt represents a mixture of multicomponent mutually insoluble metals (HEAs) and oxide (Al₂O₃) phases. Due to strongly different specific weights, these phases undergo gravity-assisted phase separation. As the result, the cast multicomponent HEAs are formed. Combustion was performed at centrifugal acceleration $a = 10\text{-}400 \text{ g}$ [2]. In this way we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product composition more uniform.

As follows from the SEM micrograph the cast synthesized NiCrCoFeMnAl_x HEAs exhibit a clearly pronounced nanostructure. Increasing of Al content into HEA was found to markedly change the microstructure and phase composition of HEAs. The Vickers hardness of synthesized HEAs was found to vary between 400 and 800 Hv.

On the second stage we carried out a search for the reactive systems and process parameters that would be favorable for deposition of protective coatings of HEAs directly onto commercially available Fe and Ti alloys. It was released by putting the Ti (Fe) alloy substrates into bottom of mould. The cast protective coatings are formed due to strongly heat exchange between high temperature alloys and substrate (Fig.1). The optimal experimental parameters for production of the cast protective coating were verified experimentally. The phase composition and microstructure of protective coatings was investigated. The gradient concentration of components over height of coatings was revealed (Fig.2). The Vickers hardness of SHS coatings of the cast HEAs was found to vary between 240 and 450 Hv. This makes such coatings promising candidates for use in marine and aerospace propulsion engineering, power engineering, gas/oil transportation, structural engineering materials etc. This work can be regarded as the first positive experience of SHS surfacing by HAE.

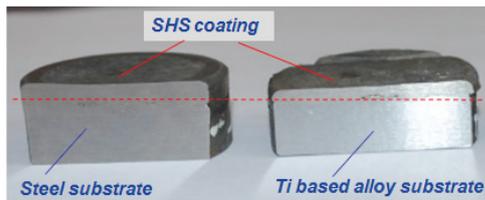


Fig. 1. Exterior view of samples after SHS surfacing (cut-to-cross)

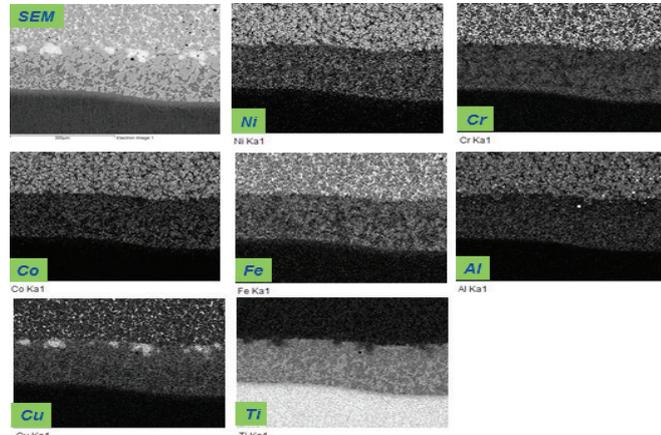


Fig. 2. X-ray element maps of SHS coating HEA / Ti alloy substrate

The work was supported by the Russian Foundation for Basic Research (project RFBR no. 14-08-00694)

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Abstract No : 1100

STRUCTURE FORMATION IN THIN LAYERS OF BALLS AT AXIAL COMPACTION. I. CYLINDRICAL MATRIX

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The SHS method allows obtaining long-sized items with $l/D \gg 1$ [1]. High homogeneity of items is achieved due to the use of initial billets obtained by the method of step-by-step pressing of thin layers of powders into long-sized forms (with $l_0/D_0 \gg 1$). The method allows achieving structural ordering of particles of SHS mixture components by the compact volume, especially in the mixtures of titanium-boron with dendritic particles [1], and in the model mixtures of titanium-boron with spherical particles [2-3]. The paper discusses the peculiarities of structure formation in thin layers of the model system consisting of monodispersed calibrated steel balls of $d=1000 \pm 5$ mkm with particle diameter in the cylindrical matrix ($D_0/d > 1$). The ball filling was subjected to densification by the scheme of axial unilateral compaction in cylindrical matrix-molds with the internal diameter $D_1=4\text{mm}$ ($D_1/d=4$); $D_2=10\text{mm}$ ($D_2/d=10$); $D_3=15\text{mm}$ ($D_3/d=15$). The steel balls were not deformed substantially or damaged. The number of balls (N) in the filling was varied in a wide range; it allowed obtaining compacts (thin layers) in which the structures containing from one up to six ball monolayers were formed by the height H of the layer ($D \gg H, D > H, D \sim H$). Before the compaction the matrix was inclined relating to the vertical axis with the preset angle α . Varying the degree of unhomogeneity of the initial filling with the balls in the cross section of the matrix in such a way, we determined its influence on structure formation at compaction for three values of the angles - $\alpha=0^\circ$, $\alpha=45^\circ$, $\alpha=90^\circ$. The dependences of heights of the compacted thin layers $H=f(N)$ and their relative densities were obtained $\rho_0=\rho_0(N)$ (Fig. 1). The curves $H=f(N)$ are of the rising type for all the values of the matrix slop angle α . The specific feature of these curves is a periodic sudden increase of the thin layer height after monotonous growth at the specific values of N .

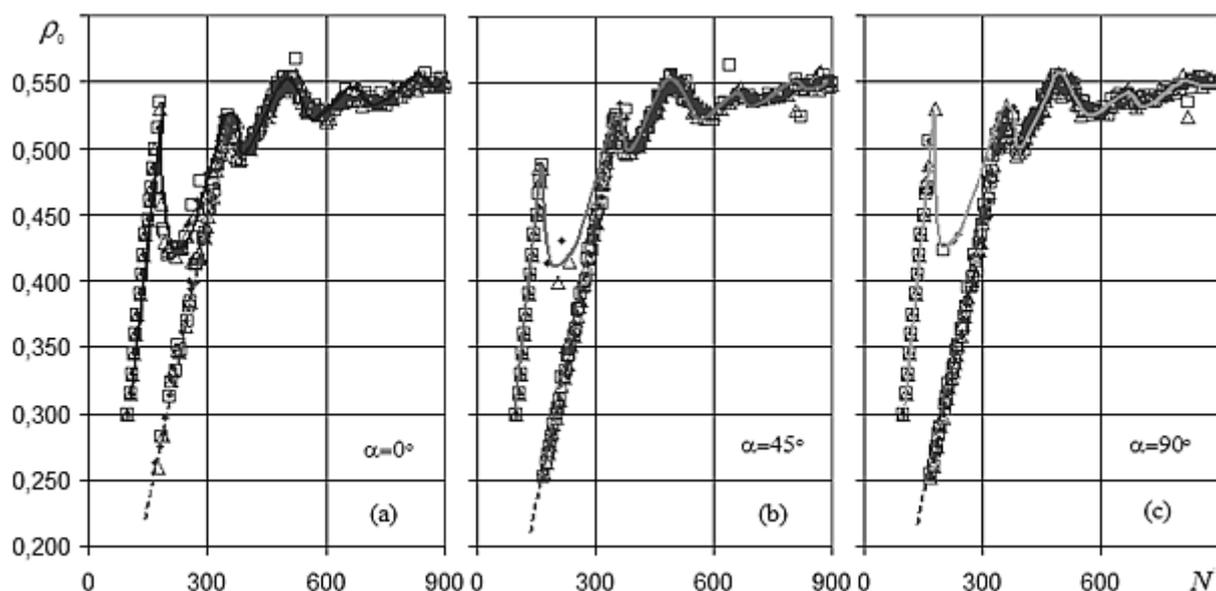


Fig.1. Relative density r_0 of compact as a function of N ($D_3=15\text{mm}$):
a) $\alpha=0^\circ$; б) $\alpha=45^\circ$; в) $\alpha=90^\circ$.

$\rho_0 = \rho_0(N)$ dependences have well pronounced extremes - density maximum and minimum. They are analogues to the extremes in the theoretical dependences of packing density of ideal balls in the thin layer endless in the horizontal direction. [2]. The coordinates of density extremes are practically constant for all α , and keep their position at any increase of densification effort. Formation of substantially loose and unhomogeneous structures is possible, $\rho_0 = \rho_0(N)$ in Fig.1. These points are seen in on the dash-line.

The work has been carried out with the support of the grant No11-03-00572-a of the Russian Fund of Fundament Investigations.

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Abstract No : 1102

STRUCTURE FORMATION IN THIN LAYERS OF BALLS AT AXIAL COMPACTION. II. MATRIX OF SQUARE SECTION

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Homogeneity of initial billets of powder mixtures is very important for obtaining high homogeneous items by the SHS method. Such billets usually have a rather complicated form of their cross section and high length-diameter ratio ($l/d \gg 1$) [1]. The method of step-by-step compaction of thin powder layers into tough forms allows solving the task of homogeneity of long-sized cylindrical initial billets. At step-by-step compaction of powder SHS mixtures it is possible to achieve ordered arrangement of component particles in the sample volume at some specific terms (dispersion, particle form-factor) [1-3]. Structuring at compaction of bidispersed mixtures with large spherical particles of one of the components is especially obvious [3]. Investigation of the influence of the form of the press-mold cross section on mixture particles ordering and that of uniformity of the initial distribution of some low mixture fillings by the matrix cross-section is of great interest. Some experiments on unilateral compaction of fillings of monodispersed calibrated steel balls (as a model system) in the matrix of square cross-section (square side $L=14\text{mm}$, $d=1000 \pm 5 \text{ mkm}$, $L/d=14$) were

carried out. While changing the angle of matrix slope in relation to the vertical direction, the initial nonuniformity of ball filling distribution in the matrix was set (for $\alpha=0^\circ$, $\alpha=45^\circ$ and $\alpha=90^\circ$). The fillings were compacted due to ball structuring (without their deformation or damage). Dependences of heights (H) on the number of balls (N) were obtained for five monolayers of balls ($D \gg H$). The curves $H=f(N)$ are of the rising stepped type for all the values of α . The dependence of the layer relative density $\rho_0 = \rho_0(N)$ in Fig.1 is rather complicated. It can be explained by the appearance of various structures a in the thin layer of balls for fillings of various sizes. On the other hand, in the fillings with the same N , both dense and loose structures were observed (shown with dash lines) - with different degree of probability at different α .

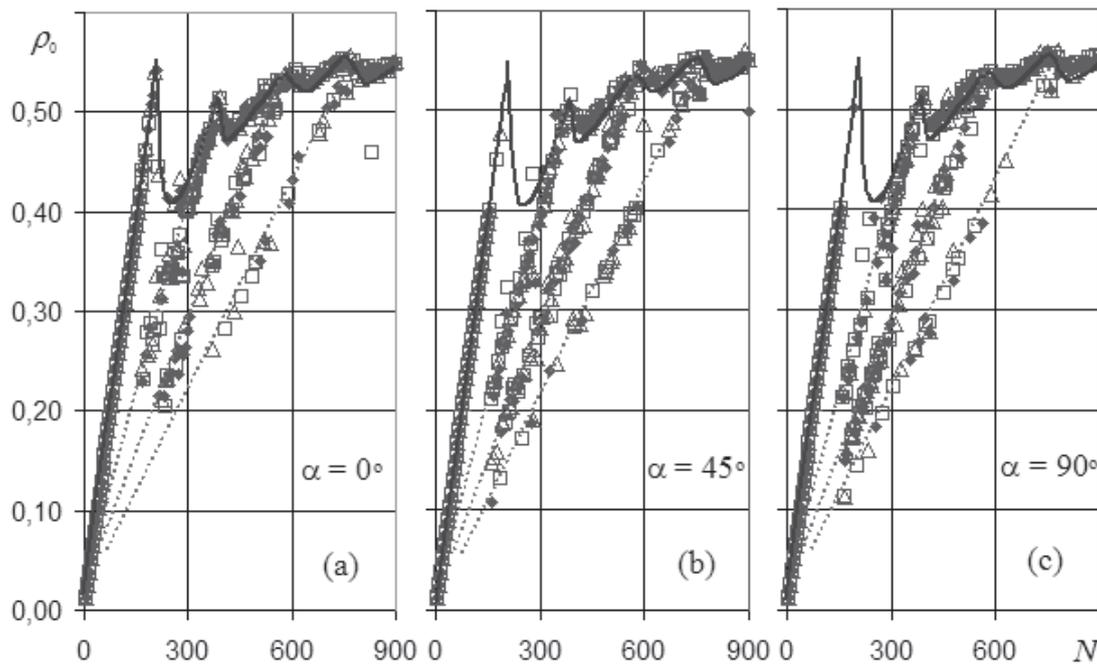


Fig.1. Relative density of the compact r_0 as a function of N ($L=14\text{mm}$): a) $\alpha=0^\circ$; b) $\alpha=45^\circ$; c) $\alpha=90^\circ$.

The upper part of the plot has experimental points corresponding to dense structures (ordered and disordered); the curve passing these points has well pronounced extremes - density maximum and minimum for the theoretical dependence of packing density of ideal balls in the endless thin layer [2]. With an increase of the matrix slope angle the layout of the curve $\rho_0 = \rho_0(N)$ does not change significantly but the number of points belonging to the curve decreases, while the probability of loose layer appearance increases. The coordinates of density extremes (except the first one) remain constant for all the values of α .

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Abstract No : 1104

STRUCTURE FORMATION IN THIN LAYER OF BALLS AT AXIAL COMPACTION. III. MATRIX OF HEX-TYPE CROSS SECTION

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High uniform long-sized items ($l/D \gg 1$) can be obtained by the SHS method from the initial billets formed by step-by-step portion compaction [1]. In this case it is possible to achieve structure ordering of particles of reaction powder mixture components in the compact volume. Structure ordering was obvious when such model mixtures (Ti+2B, Ti+Al, Ni+Al) were used in which particles of one of the component are much larger than other particles of the mixture [1-3]. The main factor in this case is monodispersity of large particles and their spherical shape [2-3]. There are some other principal parameters - a form of the cross section of the press mold and uniformity of powder portion distribution in the press mold before compaction. This paper studies the peculiarities of unilateral compaction of small billets of monodispersed particles in the matrix of hex-type cross section (characteristic parameters $L=15$ mm; $L/d=14$; L - diameter of the incircle, d - particle diameter). Calibrated steel balls were used as model particles ($d=1000 \pm 5$ μ m). The matrix slope angle α was varied in the experiments ($\alpha=0^\circ$, $\alpha=45^\circ$ и $\alpha=90^\circ$). The ball distribution from the initial billed by the matrix cross section was varied in such a way. Densification appeared to be without deformation and particle destruction - only as a result of structuring of a thin layer of balls. There could be up to five structured ball monolayers by the height H of the pressed thin layer ($L \gg H$). The dependences of relative density of the thin layer $\rho_0 = \rho_0(N)$ some extremes - density maximums and minimums. When the thin layer was densified, both dense (solid lines) and loose (dash lines) structures were obtained. Loose nonhomogeneous structures were mainly achieved between the first and the second maximums of density at all the values of α . The possibility of loose structure formation in this plot increases with an increase in α . Density extreme coordinates (except the first one) remain constant at all the values of α . $\rho_0 = \rho_0(N)$ dependences are analogues to the theoretical dependences of density of ideal ball packing [1]. Maximum values of density are higher than the analogous values obtained in matrixes with round or square cross section.

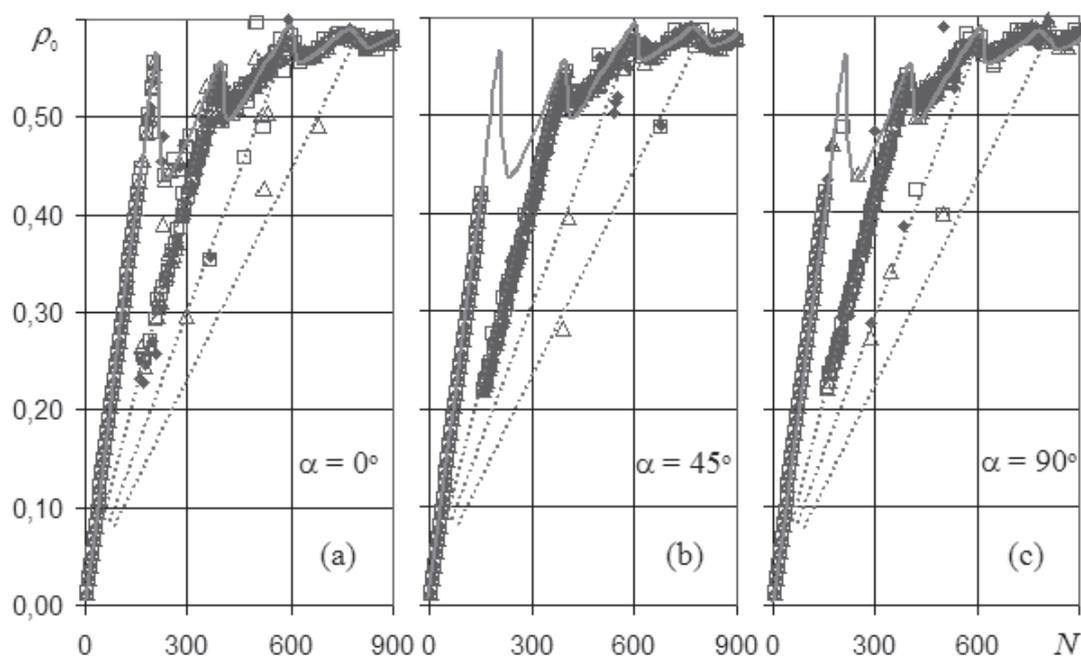


Fig.1. Relative density of the compact r_0 as a function of N ($D_3 = 15$ mm):
a) $\alpha=0^\circ$; б) $\alpha=45^\circ$; в) $\alpha=90^\circ$.

The work has been carried out with the support of the grant No. 11-03-00572-a of the Russian Fund of Fundament Investigations.

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Abstract No : 1105

SHS OF COMPOSITE MATERIALS BASED ON Ti+2B MIXTURE CONTAINING TITANIUM PARTICLES OF SPHERICAL AND DENDRITE SHAPE

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The peculiarities of SHS of composite materials from the mixture of Ti+2B, influence of the mixture quality, particle dispersion and shape of its metal component on the synthesis and its product structure are of great interest [1]. The initial mixtures consisted of black amorphous boron (particle size < 10 mkm) and a metal component of two types - titanium with spherical particles and titanium with dendrite particles. Monodispersed titanium (average particle size - 290 mkm) was obtained by plasma spraying. Three types of titanium powder with dendrite particles were used: PTC type - average particle size-120 mkm, PTM type - average particle size-100 mkm, and a fine fraction of PTM type - average size-100 mkm. Reaction mixtures were made of the powders: $a(\text{Ti}(290\text{mkm})+2\text{B})+(1-a)(\text{Ti}(\text{PTC})+2\text{B})$; $a(\text{Ti}(290\text{mkm})+2\text{B})+(1-a)(\text{Ti}(\text{PTM})+2\text{B})$; $a(\text{Ti}(290\text{mkm})+2\text{B})+(1-a)(\text{Ti}(40\text{mkm})+2\text{B})$, the variation range was $a=0-0,8$. The mixtures were pressed into cylindrical quartz forms (internal diameter $D = 4.0-4.4$ mm, external diameter - 7.8 mm, total length - 43mm) by step-by-step layer-by-layer portion compaction (the height of a single layer - 1200-1400 mkm) [2]. Availability of titanium with dendrite particles allowed realizing SHS in structured samples with large spherical particles of titanium without preliminary heating, i.e. at the combustion mode at the initial temperature $T_0=20^\circ\text{C}$. With an enlargement of the portion of large spherical particles of titanium in the mixture composition, the average combustion rate was decreasing from 5 cm/s at $a=0$ to 0.6-1 cm/s at $a=0.6$. At $a>0.6$ after the synthesis wave propagation to 1-3 mm, the combustion stopped. The maximum temperature T_b in the SHS wave was decreasing with an increase in the portion of titanium spherical particles in the green mixture, e.g. in the case of $a(\text{Ti}(c\phi 315)+2\text{B})+(\text{Ti}(\text{PTC})+2\text{B})(1-a)$ T_b decreased from 2260°C at $a=0$ to 2050°C at $a=0.4$. The temperature profiles in the combustion (measured with W-Rh thermocouples with the junction of 0.25 to 0.35 mm in diameter) demonstrate nonmonotonous temperature growth to its maximum. In $T=f(t)$ curves there are some minimums and maximums connected with a number of stages inherent to macrokinetics of the synthesis process in the combustion wave in the samples under study - within the first stage the mixture is warmed up and a chemical reaction occurs between boron and relatively small titanium dendrite particles with the following formation of matrix around titanium spherical particles: within the next stage titanium spherical particles are warmed up and melt then the forming melt spreads into the matrix - titanium reacts with the matrix substance. In place of titanium spherical particles spherical macropores of 200-250 mkm in diameter remain. A macropore (a) and the internal surface of a pore (b), the synthesis product structure around pores (c, d) are shown in Fig.1.

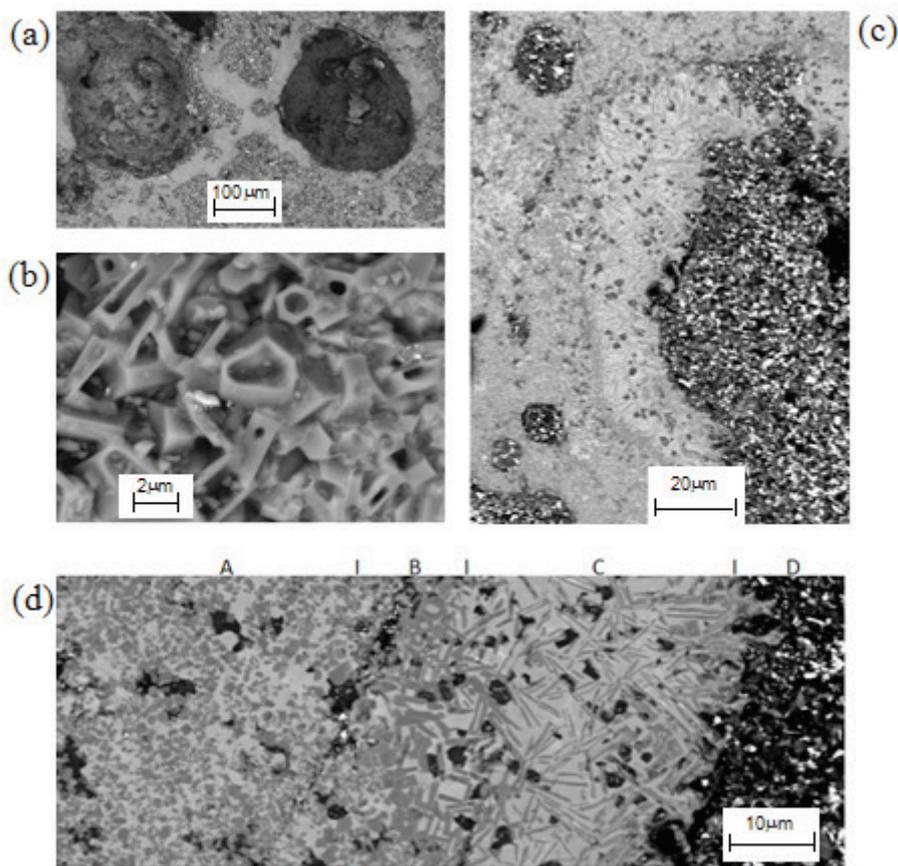


Fig.1. Product microstructure (0,4(Ti(290mkM)+2B)+0,6(Ti(40mkM)+2B)).

The work has been carried out with the support of the grant No. 13-03-12061-ofi-m of the Russian Fund of Fundament Investigations.

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Abstract No : 1106

SHS OF Ti-Al-B SYSTEM FROM Ti+2B MIXTURE WITH ALUMINUM-CLAD TITANIUM SPHERICAL PARTICLES

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The work studies the peculiarities of synthesis of composite materials by the SHS method from powder green mixtures of (Ti+2B)+(Ti+Al) composition; they consisted of aluminum-clad large titanium spherical particles and titanium-boron mixtures. The influence of the mixture composition on synthesis and product structure was studied. The initial mixtures (Ti+2B) consisted of black amorphous boron (particle size < 10 mkm) and titanium powder of PTC type (average particle size – 120 mkm) with dendrite particles. Large granules of Ti+Al were monodispersed titanium spherical particles (average size – 290 mkm) cladded with aluminum of 20-30 mkm in thickness. For obtaining these granules, loose compacts of the mixture of titanium spherical powders (prepared by plasma spraying) and fine aluminum of the type of ACD4 (Ti+Al) were heated up to 700°C in argon atmosphere [1] and then ground. Reaction mixtures were made from the cladded granules and (Ti+2B) mixture: $a(\text{Ti}(290\text{mkm})+\text{Al})+(1-a)(\text{Ti}(\text{PTC})+2\text{B})$, the variation interval $a=0-0.8$.

The mixtures were pressed into quartz cylinders (internal diameter $D=4.0-4.4$ mkm, external diameter - 7.8 mkm, total length – 43 mm) by step-by-step layer-by-layer portion compaction (the height of a single layer – 1200-1400 mkm) [2]. Availability of high-reactive mixture of Ti(PTC)+2B allowed realizing SHS in structured samples without preliminary heating, i.e. at the combustion mode at the initial temperature $T_0=20^\circ\text{C}$. With an enlargement of the portion of large spherical granules of (Ti(290 mkm)+Al) in the mixture composition, the average combustion rate was decreasing from 5 cm/s at $a=0$ to 1.5 cm/s at $a=0.5$. The maximum temperature T_b in the combustion wave was decreasing with an increase in the portion of cladded granules in the mixture from 2260°C at $a=0$ to 1515°C at $a=0.5$. The temperature profiles in the combustion wave demonstrate nonmonotonous temperature growth to its maximum at various a . Such development of temperature is connected with the stage character inherent to the synthesis process: within the first stage the chemical reaction occurred in boron and titanium mixture surrounding a spherical granule; within the next stage the granules melt and aluminum reacts with titanium, simultaneously the forming melt spreads into the surrounding matrix and reacts with the matrix substance.

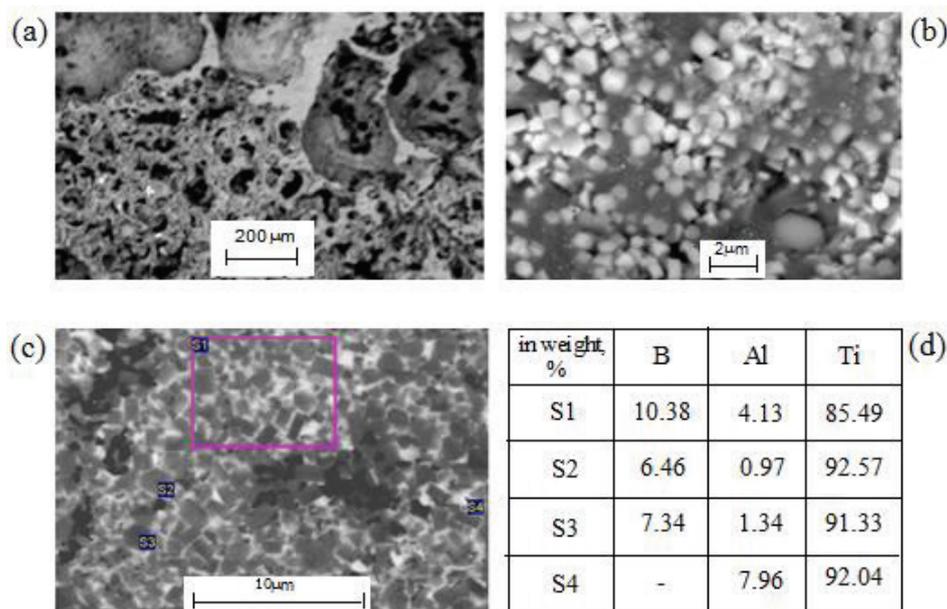


Fig.1. Synthesis product structure: a) macropores, b) macropore surface, c, d) material microstructure and elemental composition ($a=0.8$).

Macro- and microstructure of the synthesis product are shown in Fig.1. The product has pores of three sizes. Around spherical macropores we can observe both high content of titanium and boron – it corresponds to titanium boride matrix (TiB_2 phase according to X-ray analysis), and some zones with high content of titanium and aluminum – titanium aluminides (Ti_3Al и $TiAl$ according to X-ray phase analysis) appearing as a result of capillary spreading of Ti+Al melt in matrix pores.

The work has been carried out with the support of the grant No. 13-03-12061-ofi-m of the Russian Fund of Fundament Investigations.

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Abstract No : 1108

MECHANICALLY ACTIVATED SHS OF TARGET MATERIALS IN Ti-Al-C AND Si-B-C SYSTEMS FOR PVD OF TRIBOLOGICAL COATINGS

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The synthesis of advanced multicomponent coatings by physical vapor deposition (PVD) for different industrial applications requires the development of new composite targets which already contain all necessary elements in their composition. Required multicomponent compositions can be readily produced by self-propagating high-temperature synthesis (SHS) as a promising method for target fabrication, which provides a highly dense, uniform structure with required mechanical, thermal, and electrical properties. One of the most actual problems in the field of SHS is the investigation of peculiarities and mechanisms of combustion, phase and structure formation processes during the synthesis of composite materials, as knowledge in this area, allows effectively control the structure and properties of synthesized materials. Mechanical activation (MA) of the reactionary mixtures can significantly reduce their heterogeneity, increase rate and depth of the chemical transformations due to the energy accumulation on the defect structure of the reactants [1]. Also MA allows to reduce the initial temperature of the reaction and ignition.

The first part of the study is devoted to the experimental investigation of the combustion process in Ti-Al-C system with the formation of $M_{n+1}AX_n$ -phase namely Ti_3AlC_2 , which is of great practical interest for the deposition of tribological coatings for cutting, stamping, and bearing conditions, resistant against humidity, corrosive environments, and temperature fluctuations [2]. In the second part much attention is paid to the experimental investigation of feasibility of MA SHS in the Si-C-B system. SiC based ceramic materials is of great practical interest for the deposition of amorphous coatings due to their high temperature stability up to 1800 °C and high-temperature oxidation resistance, high hardness, creep resistance at elevated temperatures and low coefficients of thermal expansion and thermal conductivity. The combination of these properties is very important for protective coatings of carbon-carbon composite materials as well as products of high-temperature micro- and optoelectronics [3].

We explored the effect of MA on the structure, morphology and heating capacity value of green reactionary mixtures in both systems. Kinetics and mechanisms of the combustion process were studied, with special emphasis on the effect of the initial temperature (T_0) on combustion temperature (T_c) and rate (U_c). The effective activation energy of the combustion process was calculated. The staging of structural and phase transformations during synthesis were studied by the method of combustion front quenching in a copper wedge followed by SEM and EDS investigations of the sample characteristic areas. Also time resolved XRD analysis was used. The phase composition and structure of the final synthesis products were also studied.

Multicomponent targets for PVD were fabricated by hot pressing of the SHS powder products in the case of Si-C-B system, and by the technology of force SHS- pressing from the reactionary mixtures in the case of Ti-Al-C system.

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Abstract No : 1112

SHS SURFACING WITH THERMITE NiO-AL MIXTURE

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The important problem of modern materials science is a creation of layered composite materials have a balance of high strength metals and high hardness, wear resistance and high temperature corrosive environment, based on ceramics of carbides, borides and intermetallic compounds, as well as high-tech high-performance technologies for their preparation. The main task objective of this work was investigation of regularities and mechanism of autowave synthesis on the surface of a metallic substrate, with special emphasis on the formation of melted combustion products and characterization of thus prepared layered coatings.

In our experiments we used thermite mixtures yielding Ti-Ni intermetallics, molybdenum carbides, and chromium carbides. Titanium plates were used as a substrate.

We explored the combustion of high-caloric NiO-Al mixture on the surface of Ti substrate. After ignition, the combustion wave propagates over the sample surface leaving behind a two-phase melt with metal droplets distributed over the layer bulk. After combustion the two-phase mixture of "hot" combustion products comes into contact with the "cold" substrate [1, 2]. Then the following sequence of events takes place in the system:

- intense heat "hot" layer of combustion products from the "cold" metal substrate, resulting in a layer of product cools and heats up the foundation; heating leads to melting and movement of the melting front deep foundations
- gravitational separation of metal and oxide phases in the layer of the combustion products leads to formation a metal layer of the product on substrate, and the oxide phase is displaced in the upper layer
- exothermic chemical interaction of the melt with active metal base to form a two-phase solution

The final result is the formation of the metal substrate-metal alloy- oxide coating. Most important results of our study are: (i) strong adhesion NiTi with a Ti substrate and (ii) and preparation of lightweight durable coating.

ACKNOWLEDGMENTS

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Abstract No : 1113

SYNTHESIS OF CAST OXIDE MATERIALS IN THE Al-O-N SYSTEM

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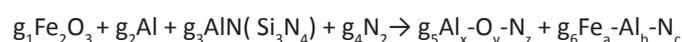
In ISMAN investigations of synthesis of cast oxynitride ceramics have been recently performed in the combustion regime via the SHS route [1, 2]. This approach allows production of nitrogen-containing compounds and materials in the liquid (cast) state using highly exothermic mixtures of a thermite type.

In the present investigation two possible versions of synthesis of cast aluminum oxynitrides are considered. In one case, synthesis proceeds along the following scheme:



The aluminum content in the initial exothermic mixture from 25.2 up to 50.3 wt% and variation of the initial nitrogen pressure within 0.1-10 MPa provide the condition of generating combustion temperature higher than the melting points of the final products and formation of both metallic and ceramic cast products. The combustion velocity of as arranged compositions (u) does not exceed 0.3cm/s and the process is accompanied by slight dissipation of the combustion products. The resultant cast oxynitride ceramics contains up to 2 wt% bound nitrogen. Its presence is determined in the gas-transport reactions.

A specific feature of the other version is the possibility of additional introduction of nitrogen-containing components (aluminum or silicon nitrides, AlN or Si_3N_4) into the green exothermic mixture. The chemical scheme of the process is as follows:



The Fe_2O_3/Al compositions added with AlN and Si_3N_4 can burn at the additive content no more than 50 wt%. In this region, after the process initiation a combustion front formed propagates along the mixture. The combustion front velocity is determined by the amount of the additive introduced. In the vicinity of the combustion limit it is equal to 0.1-0.2 cm/s. At the AlN and Si_3N_4 content of no more than 10 wt%, the combustion process yields cast products that form individual metallic and ceramic layers.

At the additive content > 10 wt%, the combustion products are casts formed by a mixture of metallic and oxynitride phases. At the increase in the AlN and Si_3N_4 content an average linear velocity of combustion diminishes from ~1.0 down to ~0.1 cm/s. The relative mass loss is slightly reduced and constitutes 1-2 wt%. A combined scheme of the synthesis run provides the increase in the bound nitrogen portion in the cast oxynitride ceramics up to 7 wt%. Its content in the cast ceramics depends on both the initial nitrogen pressure and the amount of the nitride additive in the green exothermic mixture.

An X-ray analysis of the final cast oxynitride ceramics shows that the following main phases $Al_{2.81}O_{3.56}N_{0.44}$; $Al_8O_3N_6$; $Al_9O_3N_7$; $Al_{2.78}O_{3.65}N_{0.35}$ can be synthesized dependent on the variation of the experimental conditions. Optimization of the synthesis conditions may bring about formation of a cast one-phase aluminum oxynitride of the $Al_{2.78}O_{3.65}N_{0.35}$ phase composition.

This work was done within frames of PRAS № 20

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Abstract No : 1119

FORMATION OF ULTRAFINE GRAIN STRUCTURE IN THE SHS-PRODUCED CAST Co-Cr-Mo-ALLOY BY PLASTIC DEFORMATION

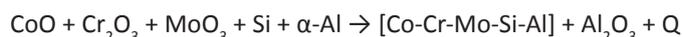
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Producing of refractory alloys based on multicomponent systems, which have a unique set of mechanical, chemical and physical properties, is a promising area of researches. However, industrial methods of obtaining such materials economically very costly because they require the use of sophisticated vacuum technology and high power consumption. One of the most cost-effective ways to obtain refractory materials is a method that combines the SHS and metallurgy, later called "SHS-metallurgy" [1, 2]. SHS-metallurgy method allows obtain multicomponent alloys with homogeneously distributed components, but due to the nature of combustion processes the formation of microstructure during the

crystallization and cooling cannot be fully controlled. Often the structure of obtained ingot is heterogeneous and has a pronounced porosity in the surface layers that excludes the possibility of finish treatment.

Such structure significantly limits the use of SHS alloys and it requires an additional thermomechanical processing (TMP) to obtain a uniform sub microcrystalline or ultrafine-grained state in the material.

In this work, we explored alloy based on Co-Cr-Mo system (Co; 28,0Cr; 6,0Mo; 1,0Si; 0,5Al) obtained by centrifugal casting through the SHS reaction:



where $\alpha\text{-Al}$ is selected based on the results of thermodynamic and actual analyze of composition of the alloy.

We used a previously obtained experience [3, 4] to achieve a significant structure refinement in the material synthesized by SHS-metallurgy method. Synthesized material was subjected to the deformation by rolling into rods.

In addition, synthesized cast alloy was investigated using SEM and XRD methods before (after SHS synthesis) and after TMP. It has shown on fig.1 that alloy samples have single-phase and ultra-fine grain structure formed after TMP. Ultra fine grain structure formed during the processing of cast alloy has an average size of the structural elements about 500 nm.

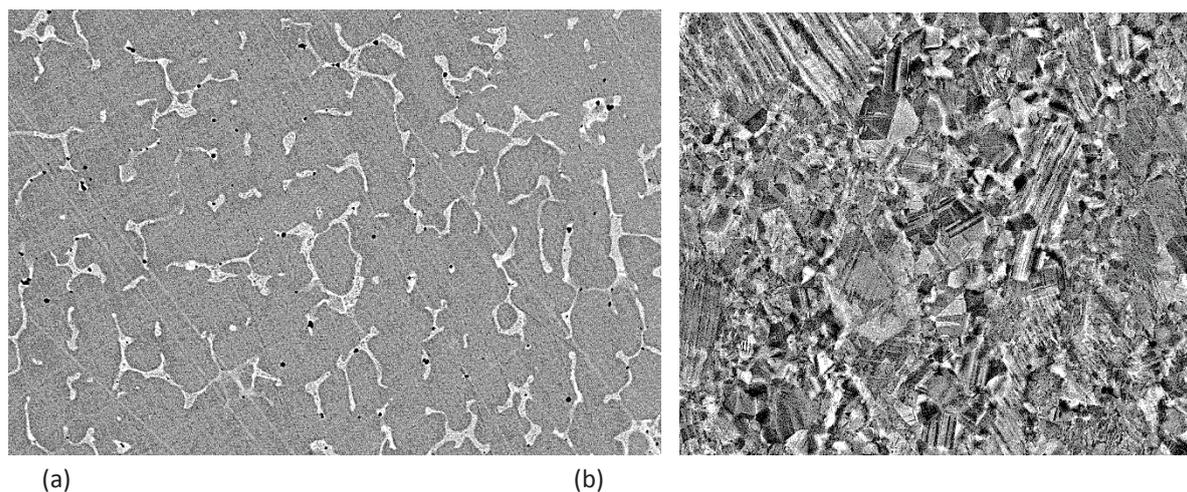


Fig. 1. Microstructure of SHS-synthesized alloy (a) and SHS-alloy after thermomechanical processing (b).

In this work, it is shown for the first time that one of the effective ways to solve the problem of increase consumer properties of cast material products is the development of an integrated technology, which allow produce cast materials combining the stage of SHS and the subsequent stage of thermomechanical processing while reducing energy and material costs of its production.

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Abstract No : 1132

INFLUENCE OF MECHANOCHEMICAL TREATMENT OF Ni+Al POWDER MIXTURES ON PHYSICAL AND CATALYTIC PROPERTIES OF COATINGS PRODUCED BY “CAFSY” METHOD

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Nickel-aluminide coatings have attracted significant attention because of their technological and scientific applicability. Combustion-assisted flame spraying (“CAFSY”) has recently [1] been demonstrated to successfully coat metallic substrates with hard, strong and wear resistant coatings in the Ni-Al system using only Ni and Al base-metal powders and a simple hand-held type flame oxy-acetylene flame spray gun. This method can be used for many other intermetallic systems, eliminates the need for expensive pre-alloyed powders and allows tailoring of the properties of the coatings according to the needs of the ultimate application. The intermetallic coatings produced by CAFSY exhibit very high integrity, with good adhesion and high surface hardness at a substantially lower cost than equivalent coatings using pre-prepared alloy powders. In this work CAFSY was used to produce catalytic coatings in the Ni-Al system.

In order to improve the contact between the initial Ni and Al powders and enhance the in-flight combustion reactions, a series of experiments were carried out using mechanically and mechanochemically treated powder mixtures. Mechanical treatment in a ball mill influences particle size (Figure 1). The milling in planetary mill was performed using tungsten carbide balls at a rotation velocity of 350 RPM for one hour. The mass of the milled powders were 12.5 g, using a ball to powder ratio of 15:1. As some sticking might happen during milling, we only take the powders that pass through a 300 μm sieve. For aluminium-rich mixtures, sticking is extensive and less than 10% goes through the sieve for the aluminium richest case. For this reason, for more than 25 g of large powders, an additional milling for 10 minutes is performed using the same mass of balls with the BPR ranging from 5.8 to 7.5.

The results using PVA as binder are shown in figure 1c. It appears that mechanochemical treatment from 10 min to 60min leads to a preferential SHS reaction between Ni and Al probably because this reaction is initiated at the lowest preheating temperature and highest adiabatic temperature from all nickel-aluminides (Figure 1a). Stoichiometric compositions (65% Ni for NiAl and 86.8%Ni for Ni₃Al) lead to much higher presence of these compounds in the coatings. On the other hand, increasing concentration of NiAl₃ in the coating with increasing Ni concentration in the spray mixture happens because under the conditions of thermal spraying the limiting factor is concentration of Al, since Al is highly reactive and it is important that in the short period Al must be surrounded with as much nickel as possible.

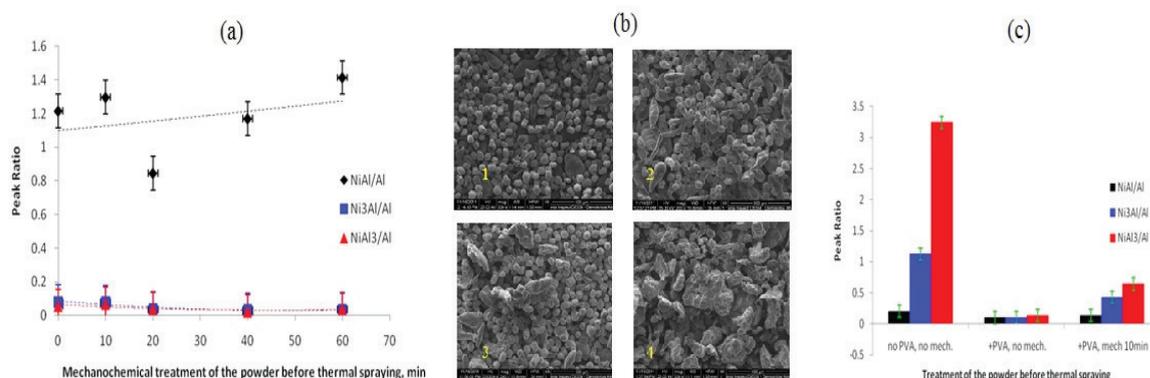


Figure 1. (a) Influence of mechanical treatment of the initial powders Al+Ni before thermal spraying on the final composition of the coating, (b) SEM photos: 1) without mechanochemical treatment, 2) 20min, 3) 40min and 4) 60min and (c) influence of synthesis conditions on the concentration of intermetallic compounds in the catalysts

The original decision to use PVA was connected with increasing of possibility of reaction between Ni-Al powders when they are bonded by PVA, but in practice PVA gave negative results (Figure 1c). It appears that PVA produces a thermally insulating coating reducing synthesis and Ni+Al agglomerated particles encapsulated by PVA go through the combustion zone but don't have enough temperature and time to react. Thus, the best yield of intermetallics was received without PVA and without mechanochemical treatment.

Catalysts prepared by CAFSY method with preliminary mechanical and mechanochemical treatment have been tested in for dry reforming of methane and for oxidation of CO with very promising results . It was found that the activity of catalytic CAFSY coatings depends on the conditions of preliminary powders treatments. The work is continuing.

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Abstract No : 1133

STUDY OF CATALYTIC ACTIVITY OF COATINGS PRODUCED BY CAFSY METHOD IN DRY REFORMING OF METHANE

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Ni-Al composite coatings were produced by in-flight SHS during flame spraying. As an advanced coating process, combustion-assisted flame spraying ("CAFSY") combines conventional flame spraying of coatings and SHS reaction into a single step [1].

The mitigation and utilization of greenhouse gases, CO₂ and CH₄, are among the most important global challenges. CO₂ (dry) reforming of CH₄ has received much attention from both an environmental and an industrial perspective because the reaction can convert these greenhouse gases into synthesis gas with a wide range H₂/CO ratio. However, traditional catalysts have not been successful for this reaction because of the double obstacles of coke deposition and relatively low H₂/CO ratio.

Combustion synthesis (SHS and SCS) produces materials that are characterised by particularly heavily distorted atomic structures, with a very large proportion of stable active centres, ideal for many catalytic reactions. Many SHS or SCS catalysts display very much enhanced activity than the same materials produced by traditional means, even at much lower specific surface area [2]. For example, it has been reported that many SHS catalysts based on Co-Al-O exhibit very high catalytic activity for dry reforming of methane with minimal coke production [3].

This work presents the results of Ni-Al catalysts sprayed as coatings by CAFSY. A range of carriers were used for thermal spraying (65.1% Ni-34.9%Al composition, ratio O₂/ C₂H₂=1.56, mechanical treatment of initial batch 10 min, thermal spray distance 4cm, substrate temperature 600°C) of nickel and aluminum and the products of in-flight SHS which were deposited on the surface were studied. The influence of number of coatings on the catalyst composition were also studied (Figure 1) and the influence of carrier on the catalytic activity of the CAFSY coatings are presented in Figure 2.

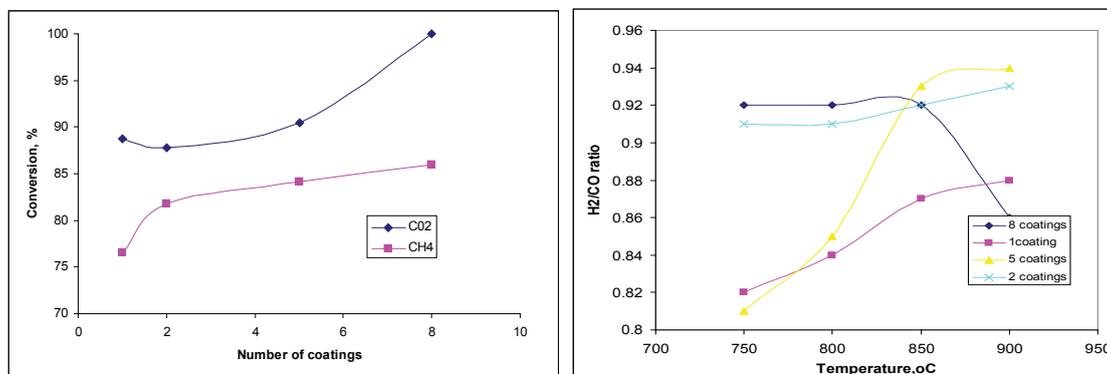


Fig1. Influence of number of coatings during preparation of catalysts on carrier (on the base of MgO-MgAl₂O₄) on conversion CH₄, CO₂ and H₂/CO ratio.

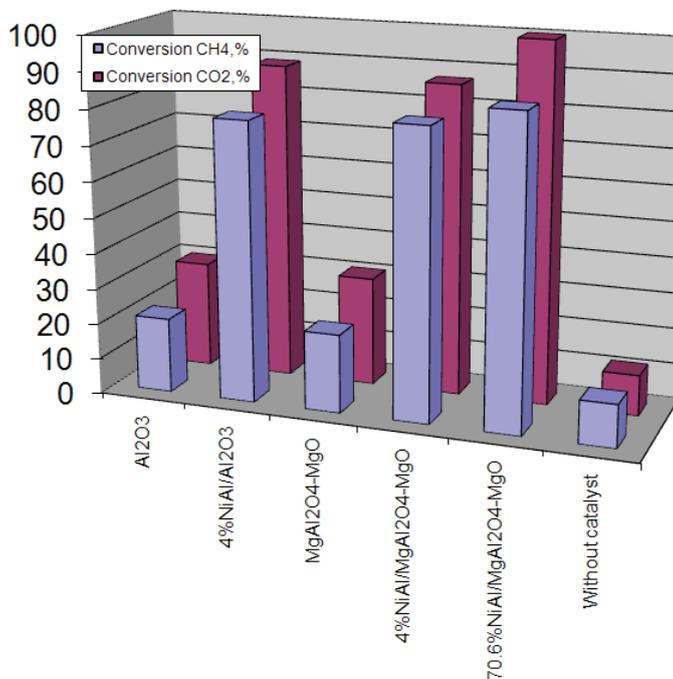


Fig.2. Influence of carrier on the catalytic activity of coatings produced by CAFSY method.

The Ni-Al composite coatings produced by CAFSY have shown very high catalytic activity for dry reforming of methane. The results show that CAFSY produces very active catalysts in this case and they indicate that it may be used for preparation of active catalysts on carriers for different processes.

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Abstract No : 1146

EFFECT OF MECHANICAL ACTIVATION OF Ta-Zr-C MIXTURES ON PHASE COMPOSITION OF SHS-PRODUCTS

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(Ta,Zr)C carbide compound attracts high interest in aerospace and cutting-tools production industries because of its high melting point, hardness, resistance to corrosion and ablation (radiation-induced evaporation), these properties being higher in ternary carbide TaC-20%ZrC than in binary carbides TaC and ZrC [1,2].

Mechanically activated SHS (MA-SHS) [3] of super-refractory ternary carbide (Ta,Zr)C is a nouvelle route of obtaining this compound, firstly described in [4].

Aim of this work was to investigate more detail the effect of mechanical activation conditions of reactive mixture Ta-Zr-C in order to obtain synthesized carbide ceramics with increased content of (Ta,Zr)C solution and to decrease content of ZrO₂ impurity.

Zirconium (PTsrK-1 grade), tantalum (TaPM grade), and soot (P804T) powders were used as initial reagents. Mechanical activation was performed in two types of planetary centrifugal mills: AIR-0.015 (milling atmosphere - air), Aktivator-2S (milling atmosphere - Ar and vacuum) with centripetal acceleration along the drum axis 250 m/s² and the ratio between the ball weight and weight of the raw mixture 20:1. Microstructure of activated mixtures and synthesized carbide compounds was investigated using scanning electron microscopy (SEM) Hitachi S-3400N. Energy-dispersive spectroscopy (EDS) of the characteristic SCF areas within activated mixtures was performed. The heat of combustion of activated mixtures was studied using high speed combustion calorimeter BKS-2X. The phase composition of the combustion products was studied by X-ray diffraction analysis (XRD) using monochromatic CuK α radiation. Microhardness of synthesized (Ta,Zr)C was measured by PMT-3M microhardness tester.

By variation of milling conditions, mixtures with different microstructure, phase composition and reactivity were obtained. To analyze the efficiency of mechanical activation, rate of lattice deformation, size of SCF and specific combustion heat of activated mixtures were examined. Critical mechanical activation time was found after that time first traces of carbides were identified, showing that chemical reaction within planetary mill was started. Microstructure, phase composition and mechanical properties of SHS product were found to be in strong relation with conditions of mechanical activation. A variety of phase compositions of synthesized ternary carbides was obtained: single-phase ternary carbide with uniform distribution of Zr; mechanical mixture of independent carbide phases with only traces of ternary carbide on grain boundaries; multi-phase solid solutions with various content of Zr within. During the mechanical activation, oxygen was adsorbed on newly produced surfaces of powders, and as a consequence, it led to the problem of contamination of synthesized product by ZrO₂, caused by inevitable oxidation of Zr during the combustion. This problem was also resolved by adaptation of milling conditions. Microhardness of obtained ternary carbide products varied from 7,01 to 12,47 GPa, specific density - from 0,41 to 0,62, lattice parameter - from 0,4454 to 0,4474 nm, Zr content in ternary carbide - from 0 to 9 at.%.

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Abstract No : 1150

OPTIMIZATION OF PARAMETERS OF FERROMOLYBDENUM PRODUCTION VIA METALOTHERMIC REDUCTION PROCESS

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In this study, production conditions of ferromolybdenum alloys by metallothermic reduction process were investigated. The formation of FeMo was tried to practice by using technical grade MoO₃, granulated Fe₂O₃, steel scrap, aluminum, ferrosilicon, CaO and CaF₂ powders.

Effects of the crucible volume, addition of Ca based fluxes, stoichiometric ratio of Al, FeSi and addition of the steel scrap on the metallothermic experiments were investigated, respectively.

Metallothermic reduction experiments were realized in Al₂O₃ lined crucible in open air. At the end of the experiments, solid alloy and slag products were obtained. These products were crashed and metal-slag separation was done. Alloys and slag were characterized by separately. Due to the high exothermic characteristic of the reaction, some of the MoO₃ was scattered from the crucible.

In the experimental studies, the conditions for producing of ferromolybdenum that provides the world standards were investigated. All the experiments were realized with 300g of MoO₃ addition. Different ratios of CaO, CaF₂, Al, steel scraps and FeSi were tried to produce ferromolybdenum. Ferromolybdenum alloys and the slag obtained from the experiments were characterized by using EPMA and AAS techniques.

At the end of the experiments, ferromolybdenum alloys had 87 % of Mo recovery were produced by the metallothermic reduction without using any dust collector or electrostatic precipitator used in industrial applications. When 90 % of steel scrap to total Fe ratio was used, Mo recovery was obtained as 80.87 %. Molybdenum recoveries were calculated as 86.86 % and 79.41% with the addition of 10 % and 2 % of CaO/Al ratios, respectively. Molybdenum contents of alloys were calculated between 62.0-68.2 wt.%, and SHS alloys were produced within the molybdenum standards.

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Abstract No : 1151

PRODUCTION AND IMPROVEMENT OF THE Ni-Cr-B ALLOYS VIA SHS

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In this study, Ni-Cr-B alloys were synthesized using a mixture of NiO-Cr₂O₃-B₂O₃ powders reducing with Al powders by a metallothermic process which is a high energy efficient, fast and low-cost production technique for synthesis of cast alloys. Detailed thermodynamical studies were simulated by using FactSage 6.2 Thermochemical software in order to calculate adiabatic temperature of the reactions and effects of initial molar composition on the final products. In the SHS experiments, effects of initial mixture ratios (NiO:Cr₂O₃:B₂O₃) on the metal recovery and compositions of final alloys were carried out. Final products were characterized by using AAS, XRD, EPMA and microhardness techniques.

In the SHS experiments, NiO, Cr₂O₃, B₂O₃ and Al powders were used in order to produce Ni-Cr-B alloy. The raw materials have over 96 % purity and 200 μm average grain sizes. The initial mixtures were calculated and prepared to produce alloy containing 80-15% Ni, 15-80% Cr, and 5% B by weight. The advanced thermochemical simulations of the reactions were investigated in detail including different ratios of initial mixtures, and their effects on metal recoveries, metal distributions and alloy compositions were carried out.

The reaction mixtures were mixed thoroughly 15 minutes in a turbula mixer and powder mixtures (approximately 150 g) were charged into Cu crucible and compacted. Cr-Ni wire was placed at the top of copper crucible and the reaction realized by passing current through the wire. After initiation, a highly exothermic reaction became self-sustaining and propagated throughout the SHS mixture. The obtained SHS products were discharged from the crucible after cooling. Nickel and chromium recoveries were measured as 51.8% and 37.9%, relatively without using any flux by using a mixture of 3 mole NiO, 1 mole Cr₂O₃, 1 mole B₂O₃ and 6 mole Al. With the addition of SiO₂ and CaO into the green mixture, Ni and Cr recovery ratios were increased; however there was not any positive effect of Al₂O₃ additions. Higher metal recoveries were obtained at 5% flux addition into the green mixture, and the highest Ni and Cr recoveries were measured as 70% and 51% relatively, with the addition of 5% of SiO₂ into the green mixture by weight. Metallic losses due to the scattering were also decreased with the flux additions.

Two phases and a eutectic formation were detected in the electron microscope image. EPMA/WDS analyses of the pointed areas showed that the matrix of the alloy is (Ni) solid solution, the secondary phase is Cr₂B₃, and the eutectic phase includes Cr₃B₄ and (Ni) solid solution. There were also seen micro-segregations in the Cr₂B₃ phase due to the speed cooling.

Metallic distributions into alloy, slag and scattered parts obtained by different initial mixtures were investigated. With the increasing in Cr₂O₃ ratio in the green mixtures, Cr recoveries were increased despite that B recoveries were decreased. B and Al contents were also decreased with the increasing in Cr₂O₃ ratio. Due to the metallic leaks into the slag during rapid cooling, Ni and Cr contents in the slag were measured at higher degrees.

The comparisons of the microstructures of the alloys obtained after SHS and after refining processes were investigated. The sizes of the Cr₂B phases were grown with the increasing in Cr content in the final alloy. After refining process, alloys became more homogeneous. B and Cr were dispersed similar with each other. In the Cr and B rich areas, Ni content was measured at its lower degree.

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Abstract No: 1169

DIFFERENT IGNITION STRATEGIES IN THE COMBUSTION SYNTHESIS OF Ni-Ti INTERMETALLICS

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Near equiatomic NiTi intermetallic phase is widely employed in a plenty of high technological application fields, including aerospace, automotive and medical ones, mainly as a consequence of its superelasticity, shape memory effect, high recovery strength, wear resistance, relatively low Young's modulus and its biocompatibility [1].

Several manufacturing methodologies of both porous and nonporous NiTi intermetallic are possible [2-4], representing combustion synthesis (CS) between elemental Ni and Ti powders still the most advantageous one due to its doubtless time and energy saving characteristics, together with the relatively simple experimental approach and the possibility for a subtle control over the porosity. Since all of these advantages are surely to be attributed to the harnessing of heat derived from exothermic reactions, the necessity for an equiatomic mixture of Ni and Ti to be pre-heated [5], in order to be self-sustained, due to the relatively low exothermic character of the reaction (see eq. 1), surely contributes to partially hide all the benefits of this technique.



In this latter framework the use of alternative energy forms as ignition source could potentially and partially overcome this limitation. Particularly, the peculiar heating mechanism at the basis of direct microwaves-matter interaction [6] has been deeply investigated in the present work, as an innovative ignition strategy for the combustion synthesis of Ni-Ti intermetallics, and has been compared to a laser assisted ignition strategy [7, 8].

Indeed, although combustion synthesis of these materials has been deeply investigated through experiments performed in both self-propagating high-temperature synthesis (SHS) and thermal explosion (TE) way of combustion, employing several ignition strategies, to the best of authors' knowledge the use of microwave energy in this particular reactive system has scarcely been reported. Moreover, results obtained by positioning the reactive specimen in the regions of predominant electric or magnetic field will be reported and explained on the basis of the intrinsic characteristic of microwaves-based heating mechanism of being based on the energy transfer from the electromagnetic field directly into the matter.

Two different frequencies have been employed to reach ignition and the differences in the combustion synthesis parameters will be discussed in detail.

Reacted samples were analysed for macroscopic characteristics, such as shape and porosity.

After that, selected samples were sectioned and prepared for several microstructural investigations devoted to phase identification, phase content estimation, and shape memory behaviour, in order to establish a correlation between these features and microwave assisted combustion synthesis parameters. X-ray diffraction analyses, differential scanning calorimetry analyses and optical microscope observation were first performed. More detailed analyses were performed with field emission scanning electron microscope equipped with EDS and EBSD detectors. The results indicate the presence of shape memory NiTi intermetallic as main phase, even if the amount is varying between 50 and 90 % depending on compaction degree and preheating/reaction history. Work is going on in order to better understanding the observed phenomena.

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Abstract No: 1170

INFLUENCE OF LASER PARAMETERS ON POROUS NiTi₂ SHAPE MEMORY ALLOY PRODUCED BY SHS

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Shape memory alloy NiTi is widely employed in a several fields, including aerospace, automotive and medical ones, mainly as a consequence of its superelasticity, shape memory effect, high recovery strength, wear resistance, relatively low Young's modulus and its biocompatibility [1]. Commercially available material is rather expensive (ranging from 200-1000 €/ kg and even more) due to the cost of starting materials (especially titanium) and also production route, involving VR or VIM melting. This fact, combined to the general small size of NiTi components, hardly heavier than few grams, fostered the research for alternative, direct and near net shape production routes.

Several manufacturing methodologies of both porous and nonporous NiTi intermetallic are possible [2-4], representing combustion synthesis (CS) between elemental Ni and Ti powders still the most advantageous one due to its doubtless time and energy saving characteristics, together with the possibility of obtaining porous materials.

It is well known that in order to obtain self propagating combustion, a suitable preheating is required, due to the relatively low exothermic behaviour of Ni-Ti reaction. Moreover it is well known that preheating temperature affects the porosity of the product: too high preheating temperature leads to swelling of the pellet and hence nearly zero porosity products [5].

In literature, ignition of powders is performed by using several methods, most of which involve the use of a tungsten wire filament, placed nearby or in contact with the pellet to be ignited. This could led to over heating or even contamination of the upper part of the pellet, hence reducing the feasibility of near net shape products.

An alternative to W-filament ignition can be LASER ignition. This technique has already proven to be a valid alternative for ignition of several shs reactions [6-8]. In these works, the attention was primarily focussed on studying the ongoing process and reactions.

In the present work, a different approach is attempted in order to establish correlations between laser parameters and obtained products. The main aim is to gain sufficient understanding of the interaction between laser ignition and SHS process in order to eventually apply it to commercially available laser systems.

Design of experiment was applied to laser ignition parameters of elemental Ni and Ti mixed powders, mixed with equiatomic ratio. The effect of preheating temperature (between 250 and 350°C) and ignition conditions, means laser power shot and laser time shot on pore characteristics, microstructure and martensitic transformation of porous NiTi SMAs were studied. It was found that the minimum laser power/ignition time required to ignite the sample is related to preheating temperature. XRD, SEM and EDX analyses confirmed that for all reacted samples, the main phases realized were NiTi matrix and small amounts of secondary phases, including NiTi₂, Ni₃Ti and Ni₄Ti₃. The characteristic temperatures of the martensitic transformation were not significantly influenced by the process conditions, investigated in this work. DSC results demonstrated that transformation temperatures, means M_s, M_f, A_s and A_f were almost equal for the various preheating temperatures and all ignition conditions, whereas both forward and inverse transformation enthalpies had highly scattered values.

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Abstract No: 1171

FORMATION OF (Ti,Zr)B₂ SOLID SOLUTIONS BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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TiB₂ and ZrB₂ are two of the most stable and most widely used binary metal borides commercially. They have very high melting points and have other excellent properties such as wear resistance, hardness, thermal conductivity, chemical stability, strength and electrical conductivity. Some applications of TiB₂, ZrB₂ containing materials are cutting tools, crucibles for handling molten metal, jet engine components, refractory linings, nozzles, armor, thermal protection, electrodes, etc [1].

Although, TiB₂ and ZrB₂ solid solutions keep the potential of exhibiting superior properties, there is a limited number of studies in the literature. In the study of Mroz [2] (Ti,Zr)B₂ solid solutions were prepared by pressureless sintering and hot press. Mechanical properties of the end members (TiB₂ and ZrB₂) were compared with those of solid solutions. Single phase solid solutions were prepared by borothermic reduction of oxide starting materials at 1975°C. It was reported that a hardness value of to 2200 kg/mm² was obtained from single phase Ti_{0.5}Zr_{0.5}B₂ solid solution, while hardness values of pure ZrB₂ and TiB₂ were 1200 and 1800kg/mm², respectively. Devon has prepared solid solutions of zirconium diboride and other transition metal borides by hot pressing at 2150°C, in order to investigate their thermal properties [3]. In the study of Zdaniewski [4], (Ti,Zr)B₂ solid solutions were prepared by hot pressing and their lattice constants were reported. In the present study, (Ti,Zr)B₂ solid solutions were prepared by self-propagating high-temperature synthesis (SHS). Initial experiments were performed by combustion synthesis, exploiting the reaction of titanium oxide, zirconium oxide and boron oxide with magnesium. It was seen from the results of the XRD analyses that formation of ZrB₂ and TiB₂ occurred as separate phases. The same mixture of starting powders were used for obtaining (Ti,Zr)B₂ solid solutions through mechanochemical synthesis. The results of the experiments conducted by high-energy milling of the starting powders revealed that a solid solution between TiB₂ and ZrB₂ was not formed.

Elemental powders of Ti, Zr and B were used for the formation of (Ti,Zr)B₂ solid solutions by SHS. After weighing and mixing of the powders, a loose pellet was formed by slightly pressing the powder mixture to about 60% of theoretical density. XRD patterns of pure TiB₂, pure ZrB₂ and (Ti,Zr)B₂ samples containing 25, 50 and 75at.% ZrB₂ are presented in Fig. 1. When 25 at.% was added into TiB₂ structure, a single phase solid solution was obtained (Fig.1b). The wide peaks in Fig.1c indicate the presence of a solid solution ((Ti_{0.5}Zr_{0.5})B₂) and separate phases of end members; ZrB₂ in this case. Sample containing 75 at.% ZrB₂ was composed of mostly ZrB₂ phase and minor amount of solid solution. It was reported in the study of Mroz [2], that slow cooling resulted in the formation of single phase solid solution, whereas a fast cooling rate produced two phases. This suggests that sufficient time at high temperature is necessary for diffusion and for the formation of single phase solid solution. Although the temperatures attained in the SHS process is high, the dwell time at that temperature is short and the cooling rate is intrinsically fast. This may be the reason for the lack of single phase solid solutions of (Ti,Zr)B₂ in some of the SHS products.

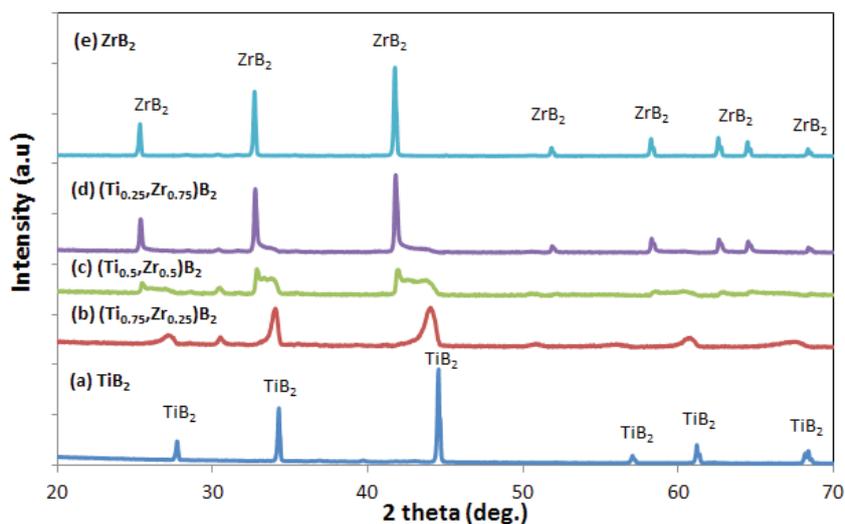


Fig.1 XRD patterns of (a) TiB_2 , (b) $(\text{Ti}_{0.75},\text{Zr}_{0.25})\text{B}_2$, (c) $(\text{Ti}_{0.5},\text{Zr}_{0.5})\text{B}_2$, (d) $(\text{Ti}_{0.25},\text{Zr}_{0.75})\text{B}_2$, (e) ZrB_2

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5. Boron related SHS materials

Abstract No : 1023

MECHANICALLY ACTIVATED SHS OF MOLYBDENUM BOROSILICIDE BASED MATERIALS FOR ULTRAHIGH-TEMPERATURE STRUCTURAL APPLICATIONS

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The thermal efficiency of gas-turbine power plants could be dramatically increased by the development of new structural materials based on molybdenum silicides, which can operate at temperatures higher than 1300 °C with no need for cooling [1-3]. A major challenge, however, is to simultaneously achieve high oxidation resistance and acceptable mechanical properties at high temperatures. For example, molybdenum disilicide (MoSi_2) has excellent oxidation resistance and poor mechanical properties, while Mo-rich silicides such as Mo_3Si and Mo_5Si_3 have much better mechanical properties but poor oxidation resistance. The addition of boron to Mo-rich silicides improves their oxidation resistance through the formation of a borosilicate surface layer. In particular, Mo_5SiB_2 (called T_2) phase and alloys based on this phase are promising materials that offer favorable combinations of high temperature mechanical properties and oxidation resistance.

The synthesis of Mo-Si-B multi-phase alloys is usually difficult because of their extremely high melting temperatures. Mechanical alloying has been considered as a promising method for manufacturing these materials [4-6]. This method, however, requires long milling times, leading to large energy consumption and contamination of the product by grinding media.

In the present paper, alloys of T_2 phase and TiB_2 have been fabricated from Mo, B, Si, and Ti using mechanically activated self-propagating high-temperature synthesis (MASHS). Mo/Si/B mixtures for the formation of Mo_5SiB_2 - TiB_2 materials exhibited spin combustion. XRD analysis has shown that along with the desired Mo_5SiB_2 and TiB_2 , the products contain Mo_5Si_3 , Mo_3Si , and MoSi_2 phases.

The chemical oven technique, recently used for synthesis of a single T_2 phase [7], has enabled fabrication of α -Mo/ Mo_5SiB_2 / Mo_3Si (Mo-12Si-8.5B) alloys (Fig. 1), which are promising materials for ultrahigh-temperature structural applications.

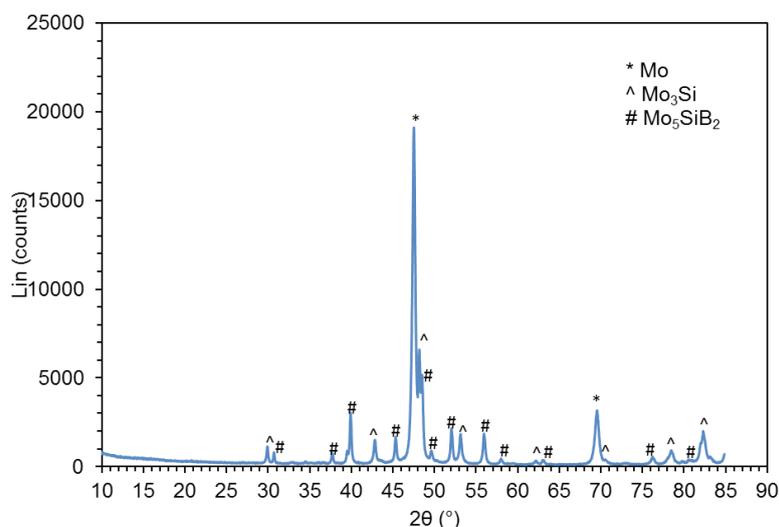


Figure 1: XRD pattern of products obtained by combustion of Mo-12Si-8.5B mixture.

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Abstract No : 1028

OBTAINING OF BORON CONTAINING MATERIALS BY SHS

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Production of materials containing boron isotope ¹⁰B is currently restrained because of its high production cost, complicated technology and considerably low quality of the end product [1].

Preliminary study of this task has shown that using of starting materials containing boron isotope ¹⁰B provides production of multifunctional material, including nanostructure, radiation-resistant, metal-ceramic materials with high resistance to impact blow, and fabrication of components using a Self-Propagating High-Temperature Synthesis (SHS). This means the synthesis of compounds (or materials) in a wave of chemical reaction (combustion) that propagates over starting reactive mixture owing to layer-by-layer heat transfer, so that high technological and economic efficiencies are intrinsic to this (SHS) method. Intensive heat generation during chemical reaction between the initial ingredients, instead of heating from outside source, provides production of the material and the end product in one technological cycle, possessing a desired shape, dimensions, properties and microstructure. The method is considerably low cost and environmentally safe in comparison with the conventional technologies[2].

At present fabrication and application of ¹⁰B containing materials are restricted due to the difficult technologies of their production and high cost price. [3,4]. In order to obtain such materials we use SHS technology.

The main innovation in the work is based on the technological method: to obtain low cost priced materials and product, which contain boron isotope ¹⁰B.

After applying each technological direction we obtain different type of materials and product. In particular, powders, moulds, compacts (among them gradient nanostructure), also porous and nonporous composite materials, containing ¹⁰B.

The application of the above SHS technology, using the high-pressure reactor, ensures 90% extraction rate of boron after chemical-thermal treatment of the end product (KBF₄ is used as an initial raw material). In the process of ligature production in the system Fe-B and Ni-B, which are used for alloying of special steels, the end product does not contain any ingot- or edge-to-center segregation, and energy consumption is minimal. In addition, a by-product of the process, KF, is used for production of KBF₄. While using the SHS technology of compacting in the modes of burning, unique nonporous bulk materials and functionally graded boron-containing materials are obtained. This technology ensures production of bulk metal-ceramic materials resistant to impact blow, so that the loss of boron in this technology is less than 1%. The SHS technology under atmospheric conditions provides production of porous, heat-resistant composites.

The peculiarities of the suggested technology allow varying the gas permeability of the material from 400 units to 0. Fabrication of components with the shape of cylinder, barrel, cap and plate is possible, and loss of boron is less than 1%. The advantage of the proposed technology is a possibility of production of boron-containing, multifunctional (including nanostructure), radiation-resistant materials and components made of them, resistant to impact blow. The advantages are also: reduction of loss, increase of boron extraction rate, and fabrication of material and the end product with the specified shape, dimensions, properties and microstructure in a single technological cycle.

The produced materials will be relevant to nuclear reactor's requirements dealing with radiation shielding, and to space technologies dealing with radiation- and meteorite protection.

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Abstract No : 1031

SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS OF COMPOSITES ON THE BASIS OF ZrB_2 - Al_2O_3

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Transition metal borides are of special interest due to their unique physico-chemical properties and are widely used as the most promising materials in many branches of engineering, machine building, electronics, power industry [1]. However, strong covalent bonds inherent to phases of pure diborides of transition metals lead to low plasticity and low strength, thereby limiting the field of their use to a great extent. In this connection, at present great attention is paid to the technology of production of multicomponent composition materials containing metal borides in combination with more plastic materials playing the role of a binder. These can be, for example, aluminium or magnesium oxides which play the role of a high temperature binder and filler decreasing the content of expensive diboride, when producing composition materials [2, 3].

The aim of this investigation is self propagating high temperature synthesis (SHS) of composition materials with a wide range of phase composition using borate ore of Inder deposit of the Republic of Kazakhstan. The ores of Inder deposit are represented mainly by asharite, hydroboracite and ulexite [4]. The average content of B_2O_3 in Inder ores makes up 15-27.5%. In relation to the fact that borate ore of Inder deposit is distinguished by a considerable content of gypsum, the initial raw material was concentrated, the maximum content of boron oxide after concentration of ore made up 40 mass.%.

SH-synthesis was carried out in the system $ZrSiO_4 + Al + B_2O_3$, (where B_2O_3 is in the composition of borate ore). The samples were prepared from the charge containing aluminium (99% purity), borate ore of Inder deposit (the content of boron oxide up to 40%), natural mineral-zirconium $ZrSiO_4$ (98.8%), preliminary mechanical activation was carried out in a high power planetary-centrifugal mill. The prepared samples were burnt at room temperature in air initiating ignition by magnesium.

High temperature phase: zirconium diboride, corundum, zirconium silicide were determined in SHS products by the method of XRD analysis.

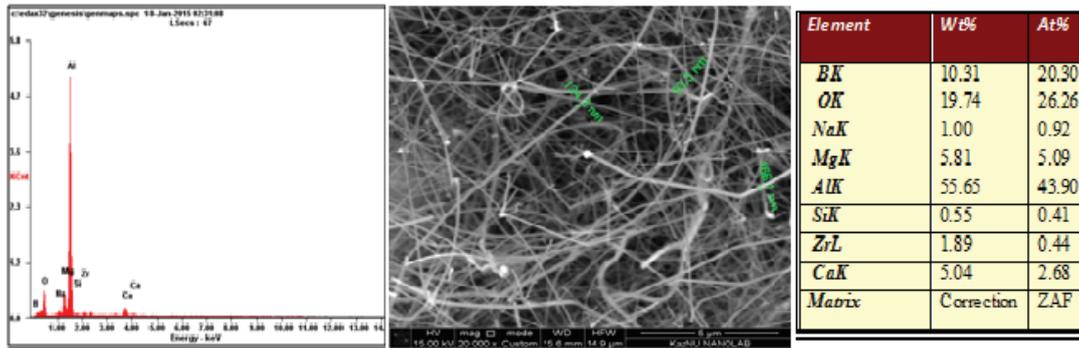


Figure 1 – The microstructure and elemental analysis (SEM, EDAX) of SHS products of the system $ZrSiO_4 + Al + B_2O_3$ (in borate ore)

Investigation on the microstructure surface of compositions allowed to reveal formation of filamentary crystals from aluminium oxide (Figure 1).

Thus the possibility of using borate ore of Inder deposite and mineral-zirconium for synthesis of refractory composite on the basis of $ZrB_2-Al_2O_3$ is shown.

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Abstract No : 1045

EFFECTS OF BORONIZING COMPOSITION ON AISI 8620 STEEL CAM SHAFT

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Boronizing of an AISI 8620 steel cam shaft was performed by immersion in molten salts. These were based on a borax containing five reducing agents: Na₂CO₃, CaCl₂, NaCl, NaOH and ferro-silicium. Also the cam shaft was bronized with pack bronizing method using different mixture compositions such as boron carbide (B₄C), borax, Na₂CO₃, and silicon carbide (SiC). This work gives a survey on the nature and quality of the layers which were obtained according to the boronizing composition. The mechanical features (hardness and wear resistance) of the deposited layers are discussed according to the experimental conditions used for their characterization. Effects of the boronizing bath composition on the obtained layers' quality are also discussed. According to the borax's reducing agents, the boronized layer deposited on the AISI 8620 steel was either single- or double-phase. All the layers were of comparable hardness which was about 900-1250 HV on the samples for the boride FeB and 750-1050 HV for the boride Fe₂B at 950°C and 5 hours. Also hardness profile of the boronized samples was compared with traditional gas cemented cams.

Key words: Boronizing, composition, cam shaft.

Abstract No : 1047

EFFECTS OF BORONIZING COMPOSITION ON AISI 1045 STEEL CAM SHAFT

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Boronizing of an AISI 1045 steel cam shaft was performed by immersion in molten salts. These were based on a borax containing five reducing agents: Na₂CO₃, CaCl₂, NaCl, NaOH and ferro-silicium. Also the cam shaft was bronized with pack bronizing method using different mixture compositions such as boron carbide (B₄C), borax, Na₂CO₃, and silicon carbide (SiC). This work gives a survey on the nature and quality of the layers which were obtained according to the boronizing composition. The mechanical features (hardness and wear resistance) of the deposited layers are discussed according to the experimental conditions used for their characterization. Effects of the boronizing bath composition on the obtained layers' quality are also discussed. According to the borax's reducing agents, the boronized layer deposited on the AISI 1045 steel was either single- or double-phase. All the layers were of comparable hardness which was about 850-1200 HV on the samples for the boride FeB and 700-1000 HV for the boride Fe₂B at 950°C and 5 hours. Also hardness profile of the boronized samples was compared with traditional gas cemented cams.

Key words: Boronizing, composition, cam shaft.

Abstract No : 1049

EFFECTS OF BORONIZING COMPOSITION ON GGG 60 CAM SHAFT

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Boronizing of a GGG 60 steel cam shaft was performed by immersion in molten salts. These were based on borax containing five reducing agents: Na_2CO_3 , CaCl_2 , NaCl , NaOH and ferro-silicium. Also the cam shaft was boronized with pack boronizing method using different mixture compositions such as boron carbide (B_4C), borax, Na_2CO_3 , and silicon carbide (SiC). This work gives a survey on the nature and quality of the layers which were obtained according to the boronizing composition. The mechanical features (hardness and wear resistance) of the deposited layers are discussed according to the experimental conditions used for their characterization. Effects of the boronizing bath composition on the obtained layers' quality are also discussed. According to the borax's reducing agents, the boronized layer deposited on the GGG 60 steel was either single- or double-phase. All the layers were of comparable hardness which was about 850-1150 HV on the samples for the boride FeB and 750-1000 HV for the boride Fe_2B at 950°C and 5 hours. Also hardness profile of the boronized samples was compared with induction hardened cams.

Key words: Boronizing, composition, cam shaft.

Abstract No : 1090

INFLUENCE OF SYNTHESIS CONDITIONS ON BORON CARBIDE SHS

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Boron carbide is a widely used material with a number of valued properties. Its structure is extensively investigated for over than 100 years and now everything is clearly in general: the structure is consist of icosahedra and linear groups. However following questions are still discussed in the literature: (1) lower and upper limits for carbon concentration in boron carbide; (2) limits for carbon intrusion into icosahedron and linear groups; (3) too large spread in the reported values of lattice parameters for boron carbide of the same composition [1].

But there is no proved interpretation of the above-mentioned questions in numerous papers on research of boron carbide structure. Suggested explanations [2, 3] for the above situation – synthesis conditions, structural deficiency, impurities, inexact results for chemical composition and lattice parameters – have not been confirmed by detailed analysis and reliable explanations.

In this work we studied the influence of synthesis conditions on lattice parameters of SHS-produced boron carbide.

Boron carbide samples were prepared through the magnesiothermic SHS-reaction with various temperatures. In order to raise combustion temperature, the additive of magnesium perchlorate was added to initial mixture that resulted in generation of additional heat. For decreasing of combustion temperature, we used the inert additive of magnesium oxide.

XRD investigations were carried out on automatic powder diffractometer (CuK α -radiation) using internal standard method.

Figure 1 presents the comparison of the cell parameters and reflection (104) half-width of boron carbide synthesized in identical conditions (2000 °C) in paper [1] and synthesized at various temperatures (1500-2500°C) in present work. These graphs convincingly demonstrate that the values of boron carbide cell parameters and (104) half-width markedly depend on synthesis conditions.

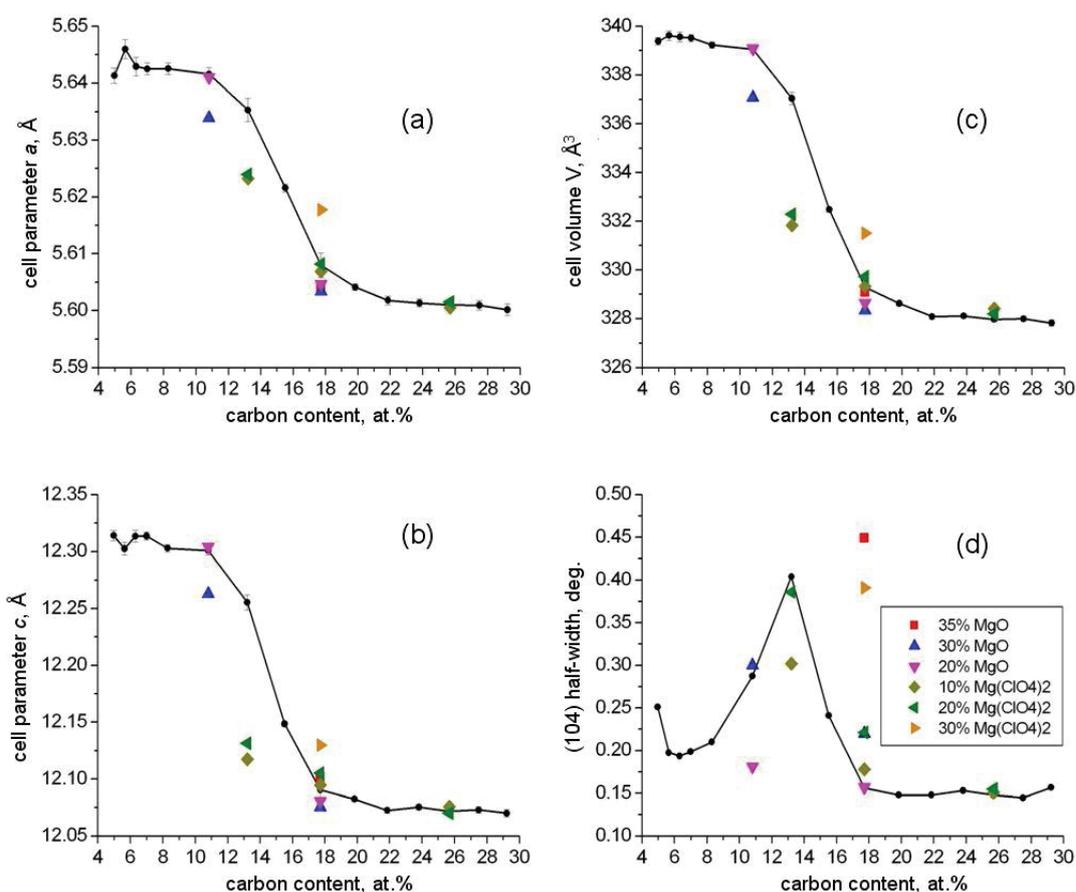


Figure 1. Cell parameters (a–c) and half-width of (104) reflection (d) for boron carbides synthesized at 2000°C in paper [1] (solid lines) and at 1500–2500°C (symbols).

Thus, variation in synthesis temperature for boron carbide of the same composition leads to variation in the values of cell parameters and XRD-lines half-width, that reflecting the influence of synthesis conditions on the boron carbide structure. This confirms suggested in [1] explanation of wide spread of boron carbide cell parameters by the diversity of carbon ordering in the crystal structure of boron carbide. These results can give an opportunity for regulating the structure and properties of boron carbide.

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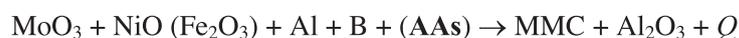
Abstract No : 1114

CAST Mo_2NiB_2 AND Mo_2FeB_2 METAL-MATRIX COMPOSITES BY COMBINED CENTRIFUGAL CASTING-SHS PROCESS

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It has been found [1-3] the metal-matrix composites (MMCs) on the base the complex borides (Mo_2NiB_2 , Mo_2FeB_2 etc) possess a unique combination of properties: high strength and excellent corrosion resistance in conditions of heavy loading and friction at high temperatures. Nevertheless, these materials have not yet found their wide application largely because of complicated technology for their production. Their high melting point is an obstacle for using conventional metallurgical processes. These materials are normally fabricated by the methods of powder metallurgy, hot isostatic pressing, reactive sintering, spark sintering, etc. whose drawbacks are high energy requirements, complexity, and expensive equipment.

In this work, we attempted to fabricate cast MMCs containing *I*- Mo_2NiB_2 and *II*- Mo_2FeB_2 by centrifugal SHS casting [4,5]. The SHS reaction yielding cast MMCs based on Mo_2NiB_2 and Mo_2FeB_2 can be represented in the form:



where MMC = $\text{Mo}_2\text{NiB}_2 - \alpha\text{Ni}$ or $\text{Mo}_2\text{FeB}_2 - \beta\text{Fe}$, alloying agent AA = Cr_2O_3 , V_2O_5 , MnO_2 , etc., and α , β stand for respective mass fractions.

To make the process much more effective, SHS was carried out in conditions of high artificial gravity created by centrifuge machine. Combustion was performed under normal pressure of atmospheric air at centrifugal acceleration $a = 10-200 g$.

The results of chemical analysis are presented in Table 2. The amounts of Mo and Ni are close to nominal values. The B content is slightly lower (by 0.2%) probably due to occurrence of redox reactions with metal oxides competing for Al. This also explains the presence of Al (~1 wt %) in the resultant ingots.

The XRD and SEM data suggest that the cast MMC *I* is formed by orthorhombic Mo_2NiB_2 and intermetallic compound MoNi_4 with insignificant admixture of the MoNi phase. The material has a clearly pronounced composite structure. Detailed SEM/EDX element distribution analysis has confirmed that the material of matrix is largely Ni filled with Mo_2NiB_2 particles 20–30 μm in their size uniformly distributed over the volume of cast material. The Al-rich areas were found to coincide with the Ni-rich ones.

Comparative analysis of the XRD data and SEM/EDX element distribution images clearly shows that the *MMC II* has a Fe matrix impregnated with Cr and Ni in the form of solid solutions (F_{ss}). The boride Mo_2FeB_2 acts as a filler. Its particles about 10 μm in size are uniformly distributed all over the volume of cast material. The alloying agents, Cr and Ni, are distributed largely in a metal matrix and tabular eutectic deposits. Again, the Al-rich areas were found to coincide with the matrix ones (Fe and Ni-rich areas).

The influence of alloying agents (**AAs**) on the composition/morphology of complex borides was explored. We attempted to introduce **AAs** (such as Cr_2O_3 , V_2O_5 , MnO_2) into green mixtures, prior to combustion synthesis. It was found that the addition of **AAs** strongly affects the composition/morphology of Mo_2NiB_2 -containing MMCs. It follows that the addition Cr and V changes a structural type of boride cell from the orthorhombic to tetragonal one.

The hardness of synthesized MMCs is rather high and attains as large value as 1200 H_V . The highest hardness is exhibited by MMCs alloyed with Cr and V.

Cast Mo_2NiB_2 and Mo_2FeB_2 based metal-matrix composites (MMCs) with good service parameters were prepared by metallothermic SHS for the first time. The process can be recommended for practical implementation in production of cutting tools, tribological materials, moulds, and deposition of protective coatings. The present results can be expected to make a theoretical background for industrial-scale manufacturing of new tungsten-free MMCs with valued properties.

Acknowledgments

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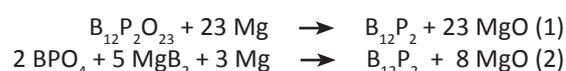
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Abstract No : 1145

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF BORON SUBPHOSPHIDE $B_{12}P_2$

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Icosahedral boron subphosphide $B_{12}P_2$ is a promising superhard material with theoretical hardness $H_v = 37$ GPa [1] and high thermal and chemical stability [2]. Two new methods to produce $B_{12}P_2$ nanopowders by self-propagating high-temperature synthesis have been proposed, according to the following reaction schemes:



where $B_{12}P_2O_{23}$ is a boron phosphate glass, produced by evaporation of a mixture of boric and orthophosphoric acids in distilled water. After uniaxial pressing of the powder mixtures in a steel die (10t, f=20mm, h=4mm), the samples were ignited in a SHS chamber under dynamic argon atmosphere [3]. After reaction, the products were leached using boiling 20% hydrochloric acid for 30 min and analyzed by X-Ray Diffraction (XRD), Scanning Electronic Microscopy (SEM) and Raman Spectroscopy.

Relatively low (50-75%) yields of the desired product by reactions (1) and (2) are due to a number of side reactions (the formations of magnesium phosphide, diboride and borate; boron and phosphorus oxides, etc.), which, however, as in the case of BP [4], is compensated by the simplicity of the method and availability of the reagents used.

The product synthesized according to reaction scheme (1) yielded $B_{12}P_2$ containing not more than 3% BP (Fig. 1a). As a comparison, similar pellets annealed at 870 K in a closed crucible in a muffle furnace for 20 min resulted in a greater yield (65% instead of 51%) but with BP impurity level of up to ~10%. Scheme (2) yield was even better (76%), with no detectable BP impurity (Fig 1b). For this reaction scheme, the use of SHS reaction is undoubtedly preferable, as similar pellets annealed at 870 K resulted in a lower yield (71%) with a high BP impurity level (16%).

The results of SEM observations, Raman spectroscopy and DSC/TG analysis of synthesized boron subphosphide will also be presented.

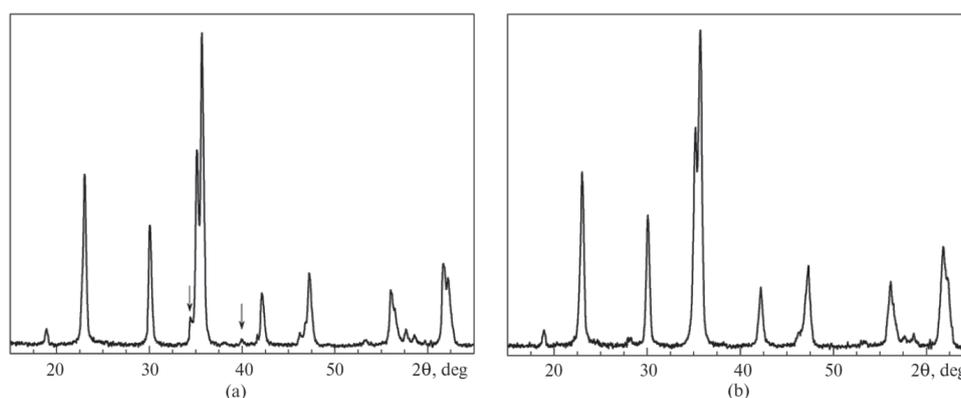


Fig. 1. Diffraction patterns of washed $B_{12}P_2$ samples produced by SHS according to reaction schemes 1 (a) and 2 (b). Arrows show locations of 111 and 200 diffraction lines of BP.

This work was financially supported by the Agence Nationale de la Recherche (grant ANR-2011-BS08-018) and DARPA (grant W31P4Q1210008).

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6. Novel approaches and SHS related processes (SHS and shock waves, sol-gel auto-combustion synthesis, SHS in nano-systems etc.)

Abstract No : 1024

COMBUSTIBLE MIXTURES FOR HYDROGEN AND IODINE GENERATION BASED ON MECHANICALLY ALLOYED REACTIVE MATERIALS

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Because of their high energy density, easy ignition, and good storability, mechanically alloyed reactive materials have the potential to improve the performance characteristics of energetic and gas-generating materials [1-6]. Here, the use of these materials is explored in combustible mixtures for generation of hydrogen and iodine.

Combustible mixtures of water and nanoscale aluminum powder are of interest for propulsion and hydrogen generation applications [7, 8], but nano-Al powders are relatively expensive, difficult to handle, and have substantially reduced active aluminum content. Replacing nano-Al with a micron-sized metal powder is, therefore, desirable provided this does not deteriorate the combustion performance. The mechanically alloyed Al•Mg powder consists of relatively large particles and the fabrication method is simple and readily scalable [1-3]. Thus, it is of interest to explore combustion characteristics of its mixtures with water and their potential for generating hydrogen.

The mixtures for hydrogen generation included water, polyacrylamide as a gellant, and mechanically alloyed Al•Mg powder. Hydrogen-generating mixtures were ignited by a CO₂ laser in a reaction chamber filled with argon. The hydrogen generation experiments have shown that mixtures of Al•Mg powder with gelled water are combustible, with the front velocities exceeding the values obtained for the mixtures of water with nanoscale Al. At the same time, no reaction was detected between mechanically alloyed Al•Mg powder and hot water, which indicates that the mixtures can remain stable for a long time.

Halogen-containing reactive materials could be used for mitigating the spread of hazardous biological microorganisms aerosolized as a result of explosion. Different methods of incorporating halogens in reactive materials have been considered. The approach explored in this research effort involves incorporating halogens into metal fuel, which then can be mixed with a metal oxide. Specifically, mechanically alloyed Al•I₂ powder [3-5] was studied in the present work.

The mixtures for iodine generation included mechanically alloyed Al•I₂ powder and oxides of iron, bismuth, and copper. Iodine generation experiments were conducted in air, in a sealed chamber designed to enable laser ignition and collection of condensed products for chemical analysis. Mixtures of mechanically alloyed Al•I₂ powder with Bi₂O₃ and Fe₂O₃ did not exhibit rapid ignition and steady combustion, while its mixtures with CuO readily ignited and burned rapidly and steadily, similarly to Al/CuO mixtures.

This research was supported by the U.S. Department of Defense (Grants No. W911NF-12-1-0056 and No. W911NF-14-1-0034; Grant Officer's Representative: Dr. Ralph A. Anthenien of the Army Research Office; Co-GOR: Dr. Clifford D. Bedford of the Office of Naval Research).

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Abstract No : 1052

FEATURES OF SYNTHESIS OF MATERIALS DURING ALUMINOTHERMIC PROCESS IN CONDITIONS OF ROTATION

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The analysis of the aluminothermic system SHS mechanism inside a heat insulated cylindrical reactor rotating around the vertical axis has been described. A model considering interaction of the D'Alembert forces with the mass rotation forces, namely centrifugal and Coriolis forces, as well as generated by them hydrodynamic resistance forces has been built up. One should take into account that these forces interact only within a narrow combustion front zone where a smelt of the reaction products such as reduced metal and aluminum oxide is formed. Presence of the resistance forces causes the combustion products separation within the SHS wave front. However, the key point in the mechanism of the rotation forces effect is removal of emerging metal particles from the wave front to the pores of the fresh mixture boundary zone thus causing ignition. The depth of the particles penetration into the fresh mixture increases according to the propagating front coordinate growth inside the reactor. This phenomenon results in the situation when the temperature conductivity role decreases from the front up to the fresh mixture as it is then followed by explosive combustion.

Contribution of the mass rotation forces to the reaction products enthalpy is of a Lagrangian type. Their share in the equation for the reaction rate in the case of restricted heat loss allows for assumption that the explosive combustion is characterized by a superadiabatic mode. Such mode considerably decreases both the lower and uponversion per limits of the combustible mixture burning process. Within the established fuel mixture conversion mechanism all the metal mass contained in the sample reaches the last layer in the form of a cluster. In this case the energy of the clusters leaving the sample consists of the thermal ($T \approx 2500-3300$ K) and kinetic components. The latter reaches 94 m sec^{-1} when the revolutions number is 3 thousand per minute and the rotation radius is $R_x \approx 30$ cm. The clusters flow energy potential can be used in the same reactor so as to initiate by means of a shock the reactions with a high Arrhenius barrier that reaches 1 MJ and maybe even more. This technology has multiple application possibilities. As an example, the article includes a reference to earlier published results of the synthesis based on the attack of $\text{Al}_{20}\text{B}_4\text{O}_{36}$ with a free electronic spin by the reaction mixture ($\text{B}_2\text{O}_3 + \text{Al}$). There is a potential to produce more accelerated clusters to synthesize non-trivial materials. In this paper, which is similar [3] and which was performed on tungsten clusters, the examples of the impact of the flow of copper clusters on loose macrocrystalline quartzite are showing (figure a) and on the dense viscous Plexiglas are showing (figure b) also.



Figure-Penetration clusters of copper in a layer of quartzite (a) and (b) Perspex

Study on combustion processes of the layered oxide systems in conditions of rotation resulted in the following important conclusions. The mass transfer participates in SHS-process under the influence of centrifugal acceleration as opposed to the SHS-process under the conditions of normal gravitation. As opposed to the steady conception, in our case the superadiabatic combustion progresses with the broadening of the combustion front, but not with the contraction. Particles, born at the moment of the initiation process, then increase in quantity by the spread of combustion wave along the cylindrical sample prior to the release of the last layer of the reaction mixture. Energy of this entire mass is determined by maximum distance from the rotational axis. So, the particles of the metal of the first and of the next layers have the identical kinetic and thermal energy on coming out of the sample.

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Abstract No : 1054

INFLUENCE OF DISPERSITY ON EXPLOSIVE SOLID-STATE SYNTHESIS IN THE Al-S SYSTEM

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As is known, shock wave loading opens up wide horizons for synthesis of new smart metastable materials in controlled non-equilibrium conditions. The initiation and onset of shock-induced reactions are defined not only by the temperatures attained but also by the dispersity of initial reagents. In contrast to SHS research where computer-aided simulations for multicomponent systems are widespread, similar models of explosive solid-state synthesis are scarce.

In this work, we report on numerical simulation of explosive solid-state synthesis in the Al-S system in terms of a multicomponent model [1] with special emphasis on the influence of green mix dispersity.

Numerical computations were performed for 0.65 wt % Al + 0.35 wt % S powder mixtures corresponding to Al_2S_3 as a reaction product. The computations gave the horizontal and vertical components of the pressure acting during propagation of detonation wave at velocity D [2]. According to [2], D was taken to have a value of 3.3 km/s.

It was also assumed that the reaction initiated at some applied pressure P_h . For coarse Al-S mixtures (particle size $<100 \mu m$, hereinafter mix I), we used the following parameters: $P_h = 1.6 \text{ GPa}$, $K_0 = 240.8 \text{ GJ}/(\text{kg s})$, and $K_p = 2.0$. For finely dispersed Al-S mixtures (particle size $<20 \mu m$ mix II), $P_h = 0.9 \text{ GPa}$, $K_0 = 260.8 \text{ GJ}/(\text{kg s})$, and $K_p = 2.0$. As for temperature, the reaction in both mixtures was assumed to onset at $T_h = 933 \text{ K}$ (melting point of Al). The initial porosity of initial powders was 40%.

Figure 1 shows the evolution in the degree of conversion (h) at the upper (1), middle (2), and lower (3) parts of ampoule for mix I (a) and mix II (b).

In mix I, the reaction is seen (Fig. 1a) to onset in all three parts of the ampoule because applied pressure P is above P_h . The step in curve 1 (Fig. 1a) is formed because at this point P becomes less than P_h and temperature T still remains smaller than T_h . Within the mid part (curve 2 in Fig. 1a) the reaction proceeds at a lower rate but without a stage of intermediate retardation. As follows from curve 3, the reaction in the lower part of the ampoule stops for a longer period and resumes when T begins to exceed T_h . These results imply the shock-induced synthesis of Al_2S_3 may proceed either in three stages (curves 1 and 3) or in two stages (curve 2).

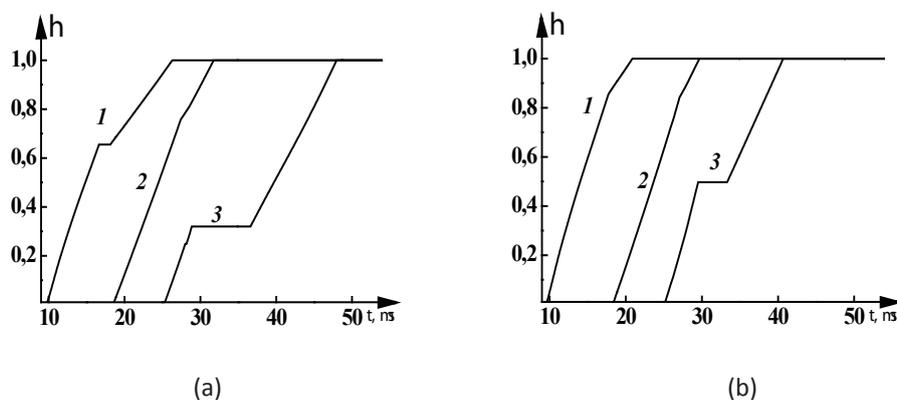


Fig. 1. Evolution in extent of conversion h at the upper (1), middle (2), and lower (3) part of the ampoule for mix I (a) and mix II (b).

Figure 1b presents similar results for mix II. In this case, the reaction is two-stage at the top and middle (curves 1 and 2) and three-stage at the bottom. The use finely dispersed mix II accelerated the reaction and markedly shortened the retardation stage in curve 3 and cancelled it in curve 1 (Fig. 1b).

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Abstract No : 1075

CATALYSTS PRODUCED BY SOLUTION COMBUSTION SYNTHESIS FOR LOW TEMPERATURE CO OXIDATION

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Oxidation into CO₂ is a major solution to CO abatement in air depollution treatments. The development of catalytic converters led to an extraordinary high number of publications on metal catalysts during the last fifty years. In recent years, increasing attention has been focused on the catalytic oxidation of carbon monoxide at ambient temperature due to its important applications in mine rescue devices for human safety, carbon dioxide lasers, proton exchange membrane fuel cells as well as many other applications in air purification devices, CO sensors, and even the burning of a cigarette. Currently, the oxidation of CO to CO₂ is catalyzed over noble metals. The cost of noble metals does not make it economically feasible to be used in the catalytic oxidation of CO. The development of active and stable catalysts without noble metals for low-temperature CO oxidation under an ambient atmosphere is a significant challenge. In general, the catalytic activity for the CO oxidation over transition metal surfaces is determined by the propensity of the metal surface to dissociate oxygen molecules and counter balanced by the bond strength of the active oxygen species on the metal surface. The transition metals with half-filled d-bands reveal the highest activity, where the dissociation probability is not too low and the adsorption energy is not too high. Nanosized materials are characterized by unique, essential and important applications especially in the field of catalysis. An important class of the materials that are rich in oxygen and yet contain O atoms with no O-O bonds are the metal oxide such as iron oxide, Fe₂O₃ or cobalt oxide Co₃O₄. One of the methods used for synthesis catalysts for CO oxidation are self-propagating high temperature synthesis [1], solution combustion synthesis [2] is used for synthesis of nanocatalysts [3].

In the present study, catalytic oxidation of CO over nanocrystallites of oxide and spinel materials studied. The purpose of this investigation was to obtain active catalysts with high surface area for low temperature CO oxidation. The influence of different factors as catalyst composition, crystallite size, temperature of catalysis, parameters of crystal lattice and quantity of catalysts on the conversion of CO were investigated.

The reactor consisted of a quartz tube 2.3 cm in diameter and 25 cm long, of which 5 cm was filled with the catalyst pellets and placed in furnace, temperatures of experiment variate from 50 °C to 350°C. The gases used were 1% CO and 99% air. The inlet section of the reactor was filled with glass fibers, creating a preheating area for the reactants and used as holder for catalysts pills. CO concentration was detected at the outlet by gas analyzer. The reactant flow rate (36000 h⁻¹) was measured individually with a reometer. Measurements at each temperature were done after 30 min. The reactor was operated at atmospheric pressure.

The catalysts used in this study were prepared on the base of systems: Cu-Cr-O, Cu-Cr-Ce-O, Cu-Zn-O, Cu-Ce-O, Cu-Ce-Si-O, Cu-Fe-O, Ce-Cu-Ni-O, Cu-Ce-Ti-O, Co₃O₄, Co-Ce-O, Co-Ce-O, Mn-Ce-O, Cu-Mn-O, Fe-O. After the combustion was completed, the resulting materials were characterized by XRD (CuKα1 radiation), SEM, and EDS. Further analyses were carried out by using FTIR spectroscopy and the size was calculated by XRD peak broadening analysis. Catalysts were

prepared by solution combustion method. Optimization of catalysts preparation methodology was done by changing of composition of initial batch, ratio oxidizer/fuel, preheating temperature, cooling time. Technology of impregnation of different compositions honeycomb structure carries was also developed. It was found number of catalysts which are active in CO oxidation process at low temperatures.

Acknowledgement.

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Abstract No : 1101

THE INFLUENCE OF ELECTRON IRRADIATION ON THE OXIDATION AND BURNING OF METAL NANOPOWDERS

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At the moment ultradispersed and nanosized metal powders are considered as perspective components of high-energy condensed systems such as explosives, propellants, pyrotechnic structures[1]. In this regard, there is a significant interest of nano- and ultradispersed metal particles obtained by electric explosion of wire in gas-inert conditions [2]. The main characteristic property of the nanopowders is their high energy capacity revealing in combustion, explosion or detonation processes.

The aim of this work is to analyse the influence of irradiation by accelerated electrons on parameters of oxidation activity and characteristics of crystal lattices of energy saturated metal nanopowders.

The initial nanopowders were irradiated by an electron beam with the energy of 4 MeV and the radiation doses of 1, 5 and 10 Mrad on the electron accelerator ELU-6. The crystal lattice parameters of the initial and irradiated nanopowders were determined by the X-ray diffractometer DRON-4. The oxidation activity of metal nanopowders was measured by differential thermal analysis (DTA) method on SDT Q600 in air and calorimetric method on bomb calorimeter PHYWE Systeme.

According to scanning electron microscopy (SEM) results the sizes of ultradispersed metal particles were varied within ranges from 50 to 150 nm. The results of X-ray analysis show the changes in the internal structure of nanoparticles. Electron irradiation decreases interplanar spacings in crystal lattices of metal nanoparticles compared to nonirradiated samples of nanopowders. After irradiation the interplanar spacing values of irradiated nanopowders approach to the values of standard samples of massive metals (Table 1).

Electron irradiation of metal nanopowders reveals essentially in the significant increase of the thermal effect of oxidation of metals. For example, the specific thermal effect of oxidation of iron nanopowder irradiated by the dose of 10 Mrad is 2.5 times more than that of the initial nanopowder.

Table 1 - The interplanar spacings of initial and irradiated iron and molybdenum nanopowders with BCC-lattice

| Plane (h k l) | Fe, Å | Fe (10 Mrad), Å | Standard Fe, Å | Mo, Å | Mo (5 Mrad), Å | Standard Mo, Å |
|---------------|-------|-----------------|----------------|-------|----------------|----------------|
| (110) | 2.055 | 2.026 | 2.010 | 2.254 | 2.238 | 2.225 |
| (200) | 1.435 | 1.433 | 1.430 | 1.576 | 1.578 | 1.574 |
| (211) | 1.173 | 1.171 | 1.170 | 1.286 | 1.289 | 1.285 |
| (220) | 1.011 | 1.011 | 1.010 | 1.114 | 1.113 | 1.113 |

In all irradiated metal powders the increase of heat oxidation effects was occurred in 1.5-2 times. These results indicate considerable amount of stored energy in the irradiated nanopowders. This stored energy makes an additional contribution to the heat oxidation or burning.

Thus, obtained results are of interest for study of the self-propagating high-temperature synthesis (SHS) process in energy saturated systems based on ultradispersed and nanosized metal powders.

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Abstract No : 1124

NANOSTRUCTURED MATERIALS FROM IMMISIBLE METALS BY A COMBINATION OF HIGH-ENERGY BALL MILLING AND SPARK PLASMA SINTERING

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Due to excellent combination of high thermal and electrical conductivities, high temperature resistant Cu-based alloys from immiscible metals find a variety of applications including heat-sink elements in microelectronic devices, contacts in high-voltage circuit breakers and nozzles for rocket engines. The fabrication of pseudo-alloys has been reported for different binary system such as W-Cu [1-3], W-Ag [4,5] and Ta-Cu [6].

In present work, a combination of high-energy ball milling (HEBM) and spark plasma sintering (SPS) methods has been shown to be suitable for the production of Cu-Cr, Cu-W and Cu-Mo nanostructured dense bulk materials.

HEBM leads to deformation and multiple flattening of Cu particles, while the Cr, W or Mo particles are crushed into smaller ones. The initial components intermixed and formed agglomerates. It has been shown that after 60 min of MA the grain size of Cr (W or Mo) was in the nanometer range (Fig.1. a).

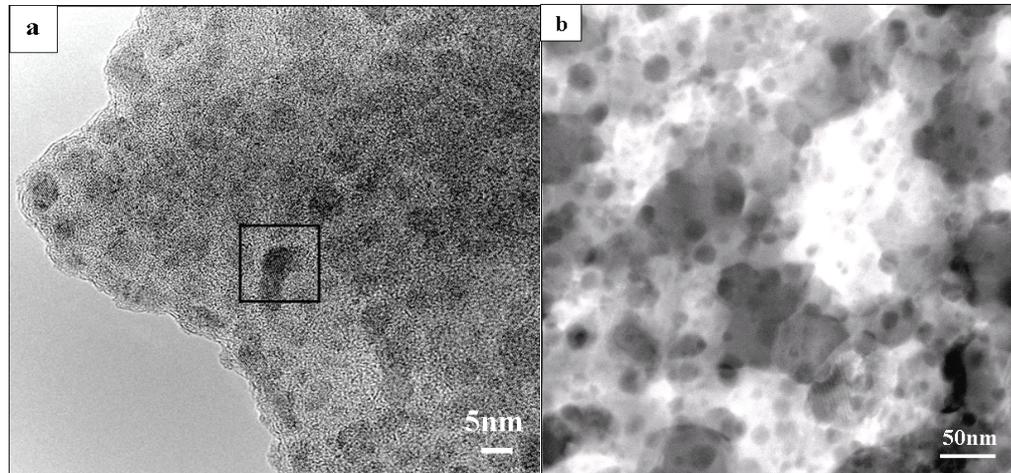


Fig.1. HRTEM images of Cu-Cr pseudo alloys formed at: (a) $s = 60$ min of HEBM, (b) $s = 60$ min of HEBM and SPS-consolidation at 700°C

After milling Cu-Cr, Cu-W and Cu-Mo powders were sintered into bulks by SPS on a Labox 650 (Sinter Land, Japanese) System in a vacuum chamber at different sintering temperatures ($300^{\circ}\text{C} - 950^{\circ}\text{C}$).

SPS is a newly developed process which makes it possible for sintering at low temperature, inhibiting of grain growth and preservation of microstructure. Microstructure, crystal structure, and local atomic structure of pseudo-alloys were characterized by XRD, high-resolution SEM, and high-resolution TEM. Based on experimental results of spark plasma sintering of mechanically milled Cu-Cr mixtures, we have come to conclusion that SPS allows to consolidate Cu-Cr bulk material with porosity less than 1%, microhardness of 5.12 GPa and preserving of mechanocomposite nanostructure (Fig.1. b).

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Abstract No : 1125

HIGH ENERGY BALL MILLING AND SPARK PLASMA SINTERING OF NANOSTRUCTURED W-Cu-Cr COMPOSITE AND ITS CHARACTERIZATION

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Despite the wide range of materials for electrical contacts for various purposes, the problem of creating highly reliable electrical contacts until the end and not solved, because the requirements for the material of contacts depends on the type of the switching device. As for Cu-Cr composite materials, they have turned out to be especially suitable for vacuum power switches with an average voltage in the range of 12 kV-30kV and higher, and contactor from Cu-W materials used in the low voltage range < 1kV [1,2]. Due to the contradictory properties of the pure refractory components W and Cr, it's difficult to contact materials for the remaining gap between 1kV and 12 kV, which are able to meet the ever increasing requirements for vacuum contacts. Meet these requirements may materials characterized by an optimized structure and the corresponding set of properties, durability, and reliability of contacts.

In the present study W-Cu-Cr composite was investigated and conducted in a high-energy planetary ball mill "Activator 2S" type in argon. The milling times varied from 15 to 120 minutes. Nonmilled and milled W-Cu-Cr powders were then consolidated in a vacuum in spark plasma sintering (SPS) system (Labox 650, Sinter Land, Japan).

The structure of the initial Cu-W-Cr powder mixture undergoes a substantial evolution during high energy ball milling. The set of randomly distributed particles transforms into a layered structure and the average layer thickness decreases with increasing milling time.

X-ray diffraction analysis showed that nonmilled W-Cu-Cr mixture exhibits strong and narrow peaks of W, Cr and Cu, while the HEBM powders demonstrate gradual broadening of the diffraction peaks accompanied by a decrease in their intensity. This can be caused by a decrease crystallite size and raise of defects density and lattice strain. Further increase in milling (to 30-120 min) leads to the vanishing of (111), (200) and (220) peaks for Cu, (110) and (220) peaks for Cr. Furthermore, the W peaks during HEBM shifted towards a larger angle, indicating a change in the in the W lattice. Such a behavior of the XRD peaks coincides with the formation of nano-scaled W-Cu-Cr structure.

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Indeed, while the unprocessed Cu-Cr mixture exhibits strong and narrow peaks of Cr and Cu, the HEBM powders demonstrate gradual broadening of the diffraction peaks accompanied by a decrease in their intensity. This can be caused by a decrease crystallite size and raise of defects density and lattice strain. Further increase in s (to 30-60 min) leads to the vanishing of the (200), (220), and (200) peaks for Cu, while the Cu (111) and Cr (110) peaks undergo broadening and partial overlapping. Such a behavior of the XRD peaks coincides with the formation of nano-scaled Cu-Cr structure (Fig. 1d and e).

Abstract No : 1126

A NOVEL PREPARATION TECHNIQUE OF METAL AND METAL OXIDE MICROSPHERES BY SOLUTION COMBUSTION IN ULTRASOUNDIC - GENERATED AQUEOUS AEROSOLS

*German Trusov*¹, Alexey Tarasov², Alexander Rogachev¹, Alexander Mukasyan³

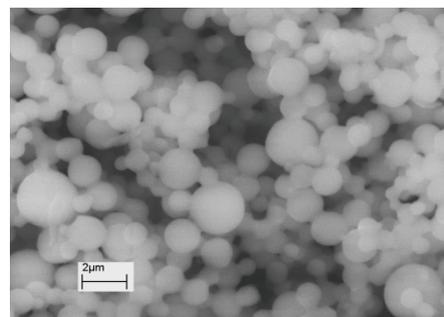
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Pure metal and metal oxide nanoparticles are most demanded magnetic materials for scientific and industrial applications. They are widely used also in different forms and modifications as pigments, conducting paints, catalysts, for medical purposes in magnetothermia etc [1]. Although many different approaches are developed to obtain such nanoparticles with required properties, any new technique allowing a direct synthesis of single-phase nanomaterials still attracts a significant attention.

As it has been shown, a "solution combustion" technique is one of the most promising candidate for different pure metal and oxide materials production with controllable properties, like iron oxides and copper oxide, pure nickel and copper [2]. The method is based on the usage of highly exothermic self-sustained redox reactions between metal nitrates and organic "fuels", which are mixed on a molecular level in aqueous solution. Heating of reaction solution leads to water evaporation and formation of a homogeneous reactive mixture, followed by reaction initiation with rapid heat release. The intensive adiabatic self-heating of the environment and appearance of a great amount of gaseous products facilitates the formation of oxide or even pure metal nanocrystalline aggregates. The further development of the method requires to overcome aggregation of the resulted nanoparticles.



In present work, we have developed the solution combustion reaction in the individual micron-size droplets of ultrasoundic - generated aerosols using an oxidizer and fuel, namely iron, copper and nickel nitrate and glycine. An aqueous reaction solution was nebulized in a preheated to 450-750°C quartz tube furnace using ambient air or argon as a carrier gas to produce well dispersed powders (figure) with magnetic properties. Phase composition, morphology and optical properties of resulted powders were studied by XRD, SEM, TEM and BET techniques. All powders were found to contain metal or metal oxide phases depending on synthetic conditions and consisted of non-aggregated hollow micron - sized spheres with a complex internal structure. All oxide products demonstrated high values of specific surface area. Based on the obtained results, the possible reaction mechanism was proposed what could help to develop the synthetic conditions for a direct synthesis of another metal and oxide materials.

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Abstract No : 1128

THE SYNTHESIS OF NANOSIZED COBALT AND CERIUM OXIDES BY «SOLUTION COMBUSTION

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For today there is existing and expanding the variety of researches in the field of nano- and microparticles production. Method of combustion solutions has several advantages in comparison with classical methods: lower energy consumption, high purity of obtained product, high specific surface of the particles [1]. The methods that using the aqueous medium, in particular combustion of initial reagents, so-called "solution combustion" (liquid phase combustion) is a new direction in synthesis of nanomaterials [2].

The aim of this work is the production of nanosized metal oxide nanoparticles. As initial reagents there are cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), glycine ($\text{C}_2\text{H}_5\text{NO}_2$) as a reducing agent and nitric acid are used. The solid reagents were completely dissolved in distilled water. The solution was evaporated in a porcelain cup to volume of 5 - 7 ml. After evaporation, the reaction mixture was heated to 600 °C until ignition. The ignition is happened instantly and obtained product is deposited directly at walls of porcelain cup. The reaction product is an ultrafine black powder.

Table 1. The composition of initial and end products

| Initial reagents | Ignition temperature | End product |
|---|----------------------|-------------------------|
| $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\text{NO}_2$, HNO_3 | 600 °C | Co_3O_4 |
| $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\text{NO}_2$, NH_4NO_3 | 630 °C | CeO_2 |

For determination of characteristics the X-ray analysis (XRD) and scanning electron microscope studies (SEM) of obtained metal oxides were carried out (Fig. 1).

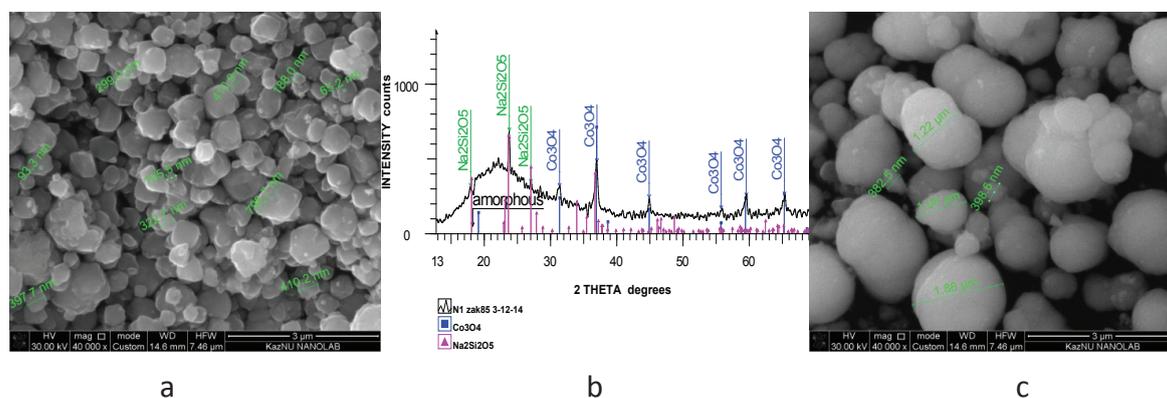


Figure 1. SEM images and diffraction patterns of metal oxide particles are obtained by solution combustion method: a, b) Co_3O_4 ; c) CeO_2

As can be seen from the results of SEM images for Co_3O_4 the particle sizes lies in the range from 65 to 800 nm, and have significant crystalline structure. SEM analysis for CeO_2 have shown that the particle size range from 380 nm to 2 microns, at that the particles have a spherical shape.

Nanoparticles of metal oxides are obtained by solution combustion method were used for synthesis of carbon nanotubes. Synthesis was carried out in a tubular reactor at the temperature of 770 -780 ° C, the flow rate of propane-butane mixture is - 55 cm^3 / min, argon - 80 cm^3 / min, the synthesis time is - 40 min. For synthesis the cobalt oxide with mass of 0,079 g was taken, a mass of CNTs are obtained at this mass of 0.2577 g

The investigation results have shown the high efficiency of solution combustion method for producing of ultrafine metal oxides particles.

Among a large number of different methods for obtaining of metal oxides nanoparticles, the liquid phase combustion method take special place because its high efficiency of this method, low cost, availability of various metal oxide nanoparticles

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Abstract No : 1136

SYNTHESIS OF NANOCRYSTALLINE ALPHA-HEMATITE (α -Fe₂O₃) MICROSPHERES BY SOLUTION COMBUSTION IN ULTRASOUNIC - GENERATED AQUEOUS AEROSOLS

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Iron oxide is one of the most used metal oxides in many scientific and industrial applications. For example, α -Fe₂O₃ (hematite) is widely utilized as a pigment, as well as a catalyst for oxidation of alcohols to aldehydes and ketones, while magnetite (Fe₃O₄) is a catalyst for various reactions such as ammonia synthesis [1]. Although many different approaches are developed to obtain iron oxides with required properties, any new technique allowing a direct synthesis of single-phase nanomaterials still attracts a significant attention.

As it has been shown, a "solution combustion" technique is one of the most promising candidate for different iron oxides production with controllable properties [2]. The method is based on the usage of highly exothermic self-sustained redox reactions between metal nitrates and organic "fuels", which are mixed on a molecular level in aqueous solution. Heating of reaction solution leads to water evaporation and formation of a homogeneous reactive mixture, followed by reaction initiation with rapid heat release. The intensive adiabatic self-heating of the environment and appearance of a great amount of gaseous products facilitates the formation of oxide nanocrystalline aggregates. The further development of the method requires to overcome aggregation of the resulted nanoparticles.

In present work, we have developed the solution combustion reaction in the individual micron-size droplets of ultrasonic - generated aerosols using an oxidizer and fuel, namely iron nitrate and glycine. An aqueous reaction solution was nebulized in a preheated to 650-750°C quartz tube furnace to produce brown or red powder depending on preparation temperature and aerosol flow velocity. Phase composition, morphology and optical properties of resulted powders were studied by XRD, SEM, TEM and BET techniques. The brown product obtained at mild thermal treatment conditions was found to be an amorphous dried mixture of initial reagents which reacts after the initiation by a hot wire and produces a mixture of alpha and gamma Fe₂O₃. The red magnetic powder obtained at high temperatures at low flow velocity was found to be a well crystalline single phase hematite. Both powders consisted of non-aggregated hollow micron - sized spheres with a complex internal structure. All oxide products demonstrated high values of specific surface area. Based on the obtained results, the possible reaction mechanism was proposed what could help to develop the synthetic conditions for a direct synthesis of another oxide materials.

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Abstract No : 1137

ONE-STEP SYNTHESIS OF NICKEL-BASED CATALYSTS COMPOSITIONS BY SOLUTION COMBUSTION METHOD IN ULTRASOUNIC - GENERATED AQUEOUS AEROSOLS

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Numerous of metal based catalysts have been studied for catalytic oxidation of CO in flowing reactor, such as Ni, Ru, Rh and Co on various supports (Al_2O_3 , SiO_2 [1], ZrO_2 , TiO_2). Among these, Ni-based catalysts, especially supported on Al_2O_3 , have been investigated extensively for industrial purposes because nickel is inexpensive and readily available, as well as it is highly active and selective for methane formation [2]. Despite these advantages, the traditional Ni-based catalysts are easily deactivated in flowing reactor as a result of being prone to sintering and/or carbon deposition at high temperatures. In addition, the Ni/ Al_2O_3 catalyst exhibited good catalytic activity for CO methanation in flowing reactor. In present work, Ni/($\text{Al}_2\text{O}_3/\text{SiO}_2$) catalyst were prepared by the solution combustion synthesis impregnation method using $\text{Al}_2\text{O}_3/\text{SiO}_2$ support. The method is based on the usage of highly exothermic self-sustained redox reactions between metal nitrates and organic "fuels" using $\text{Al}_2\text{O}_3/\text{SiO}_2$ support, which are mixed on a molecular level in aqueous solution. Heating of reaction solution leads to water evaporation and formation of a homogeneous reactive mixture, followed by reaction initiation with rapid heat release. The intensive adiabatic self-heating of the environment and appearance of a great amount of gaseous products facilitates the formation of nanocrystalline particles of metal Ni on the surface of oxides. The further development of the method requires to overcome aggregation of the resulted nanoparticles. An aqueous reaction solution was nebulized in a preheated to 650-1000°C quartz tube furnace to produce micron-size powder depending on preparation temperature and aerosol flow velocity. Phase composition, morphology and optical properties of resulted powders were studied by XRD, SEM, TEM and BET techniques. Combined with catalyst characterizations, the structures and catalytic behaviors of Ni-based catalysts were studied in detail so as to optimally design a highly active catalyst for the application of CO methanation in a flowing reactor.

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Abstract No : 1160

OBTAINING CERMET MATERIALS IN Ti-Si-C SYSTEM

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MAX phase Ti_3SiC_2 is one of the most perspective compounds in the system Ti-Si-C. It is known that this material has a high hardness and Young's modulus, well machined and exhibits metallic properties such as ductility, impact resistance, and high electrical and thermal conductivity (better than that for pure Ti). At the same time, it combines the properties of ceramic materials, such as high temperature resistance, chemical resistance and durability, a low friction coefficient. It has found its application in different areas of technics such as electronic industry [1], chemical industry [2], space industry [3] also it is suitable for production of many corrosion resistant products.

This work has been devoted to the study of regularities in the formation of the MAX-phase in system obtained by means of self-propagating high temperature synthesis (SHS).

A high-energy ball milling (1,2,3,4,5,6 min) in planetary ball mill «Activator 2S» was carried out for the preparation of reactive mixtures. For stoichiometric mixtures has been determined critical time of activation. In the range of 5-6 minutes it's found that reaction occurred in the milling jar. In addition, it has been investigated how the change of activation modes affects on the MAX-phase content in synthesized material.

X-ray analysis showed that the pre-activation of the mixtures allows achieving more Ti_3SiC_2 content in the product after SHS. Furthermore, the results of X-ray diffraction analysis revealed optimal activation time, which was 2 minutes. Parameters of SHS in $3Ti + Si + 2C$ system such as wave propagation velocity and initiation temperature of the reaction were established.

In order to increase the density of the synthesized material spark plasma-sintering method was applied to MAX-phase samples. The obtained relative density achieved more than 90% of theoretical. Investigation of the compound structure using images obtained by scanning electron microscopy allowed us to study the mechanism of the MAX-phase and other phase's formation during the synthesis (TiC, TiSi).

At the final stage, optimal parameters for producing magnetron-sputtering targets using the SHS-method in order to obtain coatings for electrocontact materials have been established.

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7. Application and Industrialization

Abstract No : 1030

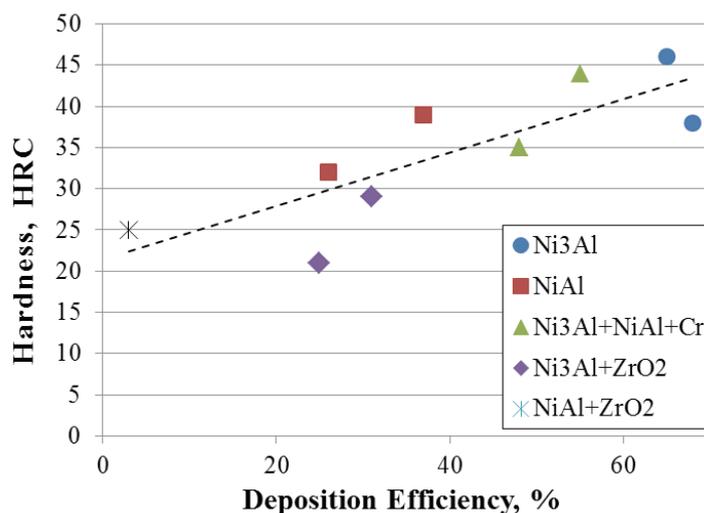
PLASMA SPRAY OF METAL AND CERMET COATINGS FROM Ni-Al ALLOYS PREPARED BY SHS PROCESS

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Metal alloys based on Ni-Al system are widely used for production of heat-resistant and wear-resistant coatings. The system Ni-Al forms four phases: NiAl₃ (β), Ni₂Al₃ (γ), NiAl (δ) and Ni₃Al (ε). Among them, the greatest interest for the application of protective coatings are phase NiAl (melting point 1638 °C) and Ni₃Al (melting point 1380 °C). Importantly, the SHS reaction products in the mixture of Ni and Al, corresponding to the stoichiometric composition of Ni₃Al, besides the main Ni₃Al phase almost always contain NiAl and Ni. This is due to a narrow homogeneity zone of Ni₃Al on the binary state diagram [1]. Functional characteristics of produced plasma coatings can be improved by introducing additives into the material, in particular metals Cr, Ti, Mo or oxides Al₂O₃, ZrO₂. The aim of this work is to study the possibility of obtaining metal and cermet coatings based powders produced by SHS in the Ni-Al [2].

By means of SHS process NiAl and Ni₃Al materials were prepared, which were crushed to produce 40-80 micron powders for plasma spraying. Spraying on steel substrates was carried out in Ar/N₂ (30/30 slpm) plasma jet at a current of 150-200 A [3]. The following composition of the powder were investigated: NiAl, Ni₃Al, NiAl + Ni₃Al + Cr, NiAl + ZrO₂, Ni₃Al + ZrO₂. The phase composition of all the materials was examined by means of XRD before and after spraying, the structure of coatings cross section was studied, the microhardness of coatings by Rockwell was measurements.



It was found that the plasma spraying does not lead to noticeable changes in the phase composition of the deposited materials. Regimes of plasma spraying, providing high quality coatings for composite materials based on NiAl and Ni₃Al are sufficiently different, which is due to the higher melting point of NiAl phase. A Ni₃Al coating with a hardness of 46 HRC at a deposition efficiency (DE) of 68% was obtained. A linear relationship between the hardness of the coating and deposition efficiency was revealed, which can be explained by strong dependence of both these parameters on the presence in the coating of unmelted particles. Spraying of the mechanical mixture of powders (Ni₃Al, NiAl) + ZrO₂ was found to be impossible due to high melting temperature of the oxide.

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Abstract No : 1064

THE METALLURGICAL SHS PROCESS

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The report provides results of the research and commercial development of a new technology designed for production of nitrogen-bearing addition alloys without using furnace equipment, id est the self-propagating high-temperature synthesis (SHS).

Ferroalloys are normally produced by carbon or silicon reduction of beneficiated ore in electric furnaces. Sometimes, the aluminothermic process is used. To produce nitrogen alloys the raw material is processed at high temperature in vacuum furnaces in a nitrogen-bearing atmosphere. In a traditional SH-synthesis, the mixture of powders is ignited by local heating, which induces an exothermic reaction for generating inorganic compounds. Later, nitrogen and hydrogen were used as reagents to synthesise nitrides and hydrides.

SHS is similar to metallothermy in many respects. Both processes are based on exothermic reactions and effected without electric power. The main difference between the SHS and metallothermy is the type of chemical reaction. In metallothermy, the reactions are oxidation-reduction, whereas in the SHS they are direct synthesis reactions. The SHS-process does not need oxygen, and combustion products have no slag. In the traditional SHS-method, the mixture of metal and non-metal powders is used as the green materials. Most such powders are quite expensive and it is not economically sound to apply them in metallurgy. Therefore, ferroalloys are suggested to be used as initial materials for the SHS-production in metallurgy. We were called this kind of the SHS - method the metallurgical one.

| Usual SHS reactions | Metallothermic reactions | Metallurgical SHS reactions |
|---------------------------|---|--|
| Ti + B → TiB ₂ | Fe ₂ O ₃ + Al → Fe + Al ₂ O ₃ | FeB + Ti → TiB ₂ + Fe |
| Zr + N ₂ → ZrN | B ₂ O ₃ + Mg → B + MgO | FeV + N ₂ → VN + Fe |
| Mo + S → MoS ₂ | Cr ₂ O ₃ + Ca → Cr + CaO | FeTi + C → TiC + Fe |
| Ni + Al → NiAl | V ₂ O ₅ + Al → V + Al ₂ O ₃ | FeS + Mn → MnS + Fe |
| Ta + C → TaC | MoO ₃ + Si → Mo + SiO ₂ | FeSi ₂ + N ₂ → Si ₃ N ₄ + Fe |
| | | FeB + N ₂ → BN + Fe |

According to their phase composition, most ferroalloys are represented by various compounds: silicides, carbides, borides and others. Thus, in a metallurgical SHS-process, some interchange exothermic reactions normally take place and they seem very similar to metallothermic ones. However, in the metallurgical SHS-process, in contrast to these reactions, there is no slagging and oxygen is not required for the reactions to proceed. Combustion products are composite alloys based on refractory inorganic compounds with a binder of iron or iron-base alloy. Let us consider the metallurgical SHS-process by the example of producing nitrogen-bearing addition alloys. The base for this synthesis is high exothermicity of nitride formation reactions.

When ferroalloys are used as reagents, the exothermicity of reactions decreases as no heat is caused by iron nitride formation. So, the higher the concentration of iron in ferroalloy, the lower the temperature can be during its nitriding. Nitride synthesis takes place in the filtration mode of combustion. That is why, to sustain combustion, nitrogen is supplied to the reaction zone by means of filtration. As a result of the continuous consumption of nitrogen, the pressure difference

is maintained. Thus, the combustion zone acts as a pump for chemical reactions. Such a chemical pump operates until a complete termination of combustion. The main distinctive property of filtration combustion is its dramatic effect on the intensity of the nitrogen pressure process.

As evident from calculations, to produce low-porosity compositions during combustion, the volume fraction of liquid in the combustion zone is to be more than ~40%. Then, the merging mechanism of solid-liquid droplet particles induces the composite product being formed with a minimum porosity.

The results of laboratory research have been used for the development of industrial technology. The commercial SHS-reactor is a thick-walled metal vessel equipped with ignition and cooling systems. This reactor can operate at a pressure of up to 15 MPa. It should be noted that the simultaneous influence of high pressure and maximum temperature allows forming alloys with a unique set of performance properties.

This can be clearly seen from the example of ferrovandium nitride synthesis.

The combination of high density with maximum nitrogen content was first possible in this alloy. In addition to nitrogen alloys, the metallurgical SHS-process can be used to produce composite alloys for boron- and sulfur-alloying of steel. In particular, the synthesis of iron - titanium boride composition is affected in vacuum. For synthesis used the mixture of titanium powder with ferrobore. Such type of the SHS-process is called gas-free. Unlike filtration combustion, in gas-free synthesis the pressure does not influence the process intensity. Moreover, mixture weight does not change in the course of combustion.

Therefore, the SHS-technology provides addition alloy production with a combination of properties which is impossible for using in the traditional furnace method. It is important that the new technology does not consume electric power. Besides, the heat caused by combustion is used for heating production premises.

Abstract No : 1131

REFRACTORY AND HEAT INSULATING SHS-MATERIALS

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Refractory linings used in heating aggregates are often subjected not only to high temperature effects but abrasive wear or aggressive media. As a result of such conjugated action of crushible factors the lining refractory materials used are destroyed thus creating the necessity of a considerable outlay to the basic repair.

At present, protecting refractory coatings, masonry mortars and porous solid materials have been developed with the use of advanced technology of self-propagating high-temperature synthesis (SHS). Such materials expand range of thermal application, lead to significant reduction of physicochemical and mechanical erosion, increase heat-resistance (up to 200°C) under conditions of static and dynamic aggressive media forces, high-temperature gas and dust currents. However, the application of such materials is limited because of insufficient knowledge of the processes taking place during SHS and impossibility of reliable forecast of their final physicomechanical and operation properties.

The purpose of the investigation was to study synthesis of mullite and corundum structures in SHS aluminosilicate (AS-materials) and improve technologies for their production. The materials based on SHS mixtures were investigated:

1. Refractory masonry mixture brand KR-1, which is designed for furnaces, boilers, reactors and other units as mortar. After passing the SHS in the joints of masonry bonding occurs in the monolith of fireclay, high-alumina and other refractory bricks.

2. Material brand M-1 is intended to be applied to the surface of the aluminosilicate materials and products used in the lining of engineering and metallurgical furnaces. The refractory protective coating extends application temperature region of refractory lining and greatly reduces the physical- chemical and mechanical erosion of its surface.

3. Refractory, including porous insulating materials based on dry technology blends brand VBF density from 400 to 1700 kg / m³.

The work was supported by RFBR №14-08-00866/14

Abstract No : 1163

ANTIMONY PRODUCTION BY USING NIEDERSCHLAG PROCESS

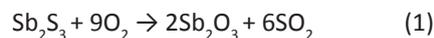
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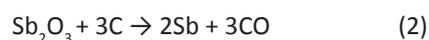
Antimony is a semimetal with symbol Sb and atomic number 51. This metalloid is found in nature mainly as sulfide mineral stibnite (Sb₂S₃), the second main antimony mineral is its oxide form, valentinite (Sb₂O₃). Antimony is a poor conductor of heat and electricity, it is stable in dry air and is not attacked by dilute acids or alkalis. Pure antimony is too soft it has a MohsScale hardness of 3. Antimony has four allotropes; one stable metallic form and three metastable forms (explosive, black and yellow). Metallic antimony is shiny grey and also brittle. When molten antimony cooled slowly it crystallizes in trigonal cell [1, 2].

Stibnite, is the most important source of metallic antimony. It is a soft grey material which crystalizes in an orthorhombic space group. It contains 71.7% antimony. Stibnite has a quite low melting point which is 546 °C.

There are several methods to produce metallic antimony from stibnite. Gasification is a reduction process which is one of the most important metallic antimony production methods. At the first step stibnite is oxidized under air atmosphere between 350 - 400 °C [3].



Sb_2O_3 would sublime under these conditions and to prevent the loss, the product is collected in condensation chambers. Afterwards collected Sb_2O_3 is mixed with coal and the reduction takes place in a reverberatory type furnace. Reduction process takes approx. 10-12 hours [3].



Electrolytic production is another method of producing metallic antimony. The antimony is recovered from the alkaline solution by electrolysis. Antimonite is digested in hot sodium sulfide solution. Sodium thioantimonate solution is obtained. Electrolysis is applied for this solution via anodes and cathodes made of mild steel. This method is also applicable for gaining copper or silver from stibnite [1].

Niederschlag process is a metallothermic process which is conducted in one step for metallic antimony production. Using this method Sb_2S_3 is mixed with coal and metallic iron and subjected to reduction. During heating antimony sulfide, decomposition occurs and sulphur combines with iron to form the matte phase. Metallic antimony is collected at the bottom of the crucible. Scrap iron is preferred as reductant for the process generally [2, 3].



Rich sulfide ore or liquated antimony sulfide is used as raw material in the process. The amount of used scrap iron is slightly more than the theoretical amount. It depends on the ability of iron to displace antimony from molten antimony sulfide [2].

In the present study, evaluation of Sb_2S_3 concentrate, which was mined in Halıköy - Turkey, was investigated by using Niederschlag process. Examined main parameters were reductant stoichiometry, process temperature and duration. Metallization ratios and purities were determined for reduced metallic antimony nuggets. Chemical analysis methods, atomic absorption spectrometry (AAS) and X-ray diffraction spectrometry (XRD) were used for the characterization of the concentrate, metallic nuggets and matte phases.

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