SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF CAST NANO-STRUCTURED 'HIGH-ENTROPY' ALLOYS BASED ON 3d AND 4d ELEMENTS

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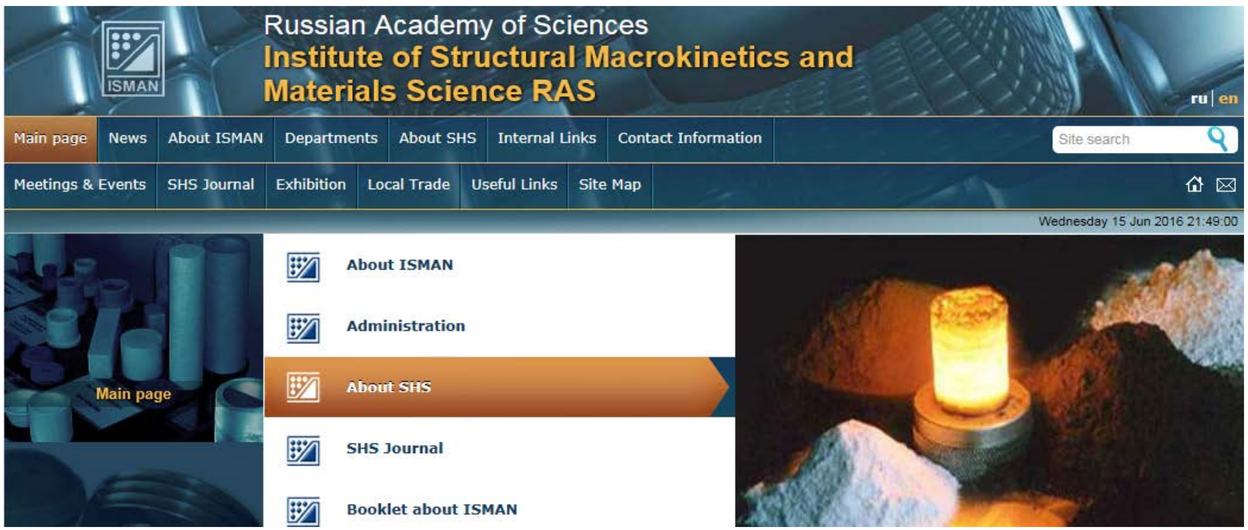

Development of practical alloy systems

- For many centuries, the conventional strategy for development of practical alloy systems has been based mainly on one principal element as the matrix, such as Fe-(steel), Cu–, Al–, Mg–, Ti–, Ni–, limiting the number of applicable alloy systems. The vast majority of the currently-used high-performance alloys had been developed by the 1970s, which is regarded by many as the period when traditional alloys had reached their maturity.

- Since this time, various routes have been taken to meet the continuous demand for materials with enhanced properties for advanced applications:
  - ✓ One approach has been to employ novel production routes, such as thermomechanical treatments, rapid solidification, mechanical alloying, spray forming, equal channel angular extrusion, high-strain-rate superplastic forming, stir friction welding, nanoscale material production etc.
  - ✓ Another method has been to manipulate the composition of the alloys, as is the case for the newly developed intermetallic compounds Ti-Al, Ni-Al, and Fe-Al and their alloys, metal matrix composites, amorphous multicomponent alloys prepared by melt spinning etc.

- However, as before the these new compounds typically based on one or, at most, two major elements.

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Development of multicomponent alloy systems

- **Multi-component alloying is widely used in the development of a variety of materials exploited in extreme conditions** (high temperatures and loads) **in particular, heat-resistant alloys of iron and nickel-based. In recent years, a multi-component alloys originated additional interest associated with the discovery of previously unexplored compositions of alloying elements and foundations that are in equiatomic concentration** *(Cantor, B. and others, A.J.B. Microstructural development in equiatomic multicomponent alloys. Mater. Sci. Eng. A 2004, 375, 213–218).*

- **Initially these new multi-principal-element alloys seemed very complex in composition and microstructure, and difficult to analyze, which was exacerbated by the lack of related literature. However, after previous research, it was soon discovered that their synthesis, processing, and analysis was feasible.** *(Yeh, J.W.; and others. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. Adv. Eng. Mater. 2004, 6, 299–303).*

- **The vast number of possible alloy combinations and the possibility of tailoring the constituent elements to tune the final properties of the multi-element alloys are the two major reasons for the increasing scientific attention in this field. The number of possible alloys combinations is further increased by the fact that the alloys may or may not be equimolar, and other minor elements could be added to modify their properties.***(J. W. Yeh. Recent progress in high-entropy alloys. European Journal of Control 31(6), 2006, pp.633-648).*

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The goal of the work

Up till now, more than 300 HEAs have been developed, forming a new frontier of metallic materials.

- Despite the growing interest in HEAs, most published works focus mainly on the thermodynamic aspects of HEAs, the resulting microstructure and limited mechanical properties.
- Less attention was paid to study processing route and developing new methods of HEA's preparation. Although a formation of the homogenous metallic multi-component alloys is complicated science and application task.

In this work, we for the first time attempted to fabricate cast HEAs by SHS-metallurgy and find process parameters that would be favorable for deposition of protective coatings of the HEAs *in-situ* SHS (SHS surfacing).

Background and motivation

- Our many years positive experience in production of cast multicomponent metallic materials in combustion mode (based on Co–, Ni –, Ti – and composites based on them.
- SHS-metallurgy (one of scientific direction into SHS) don't require additional energy, based on use relatively cheap materials (oxides) and can be regard as method to obtain these HEAs with a cheaper, easier and faster way.

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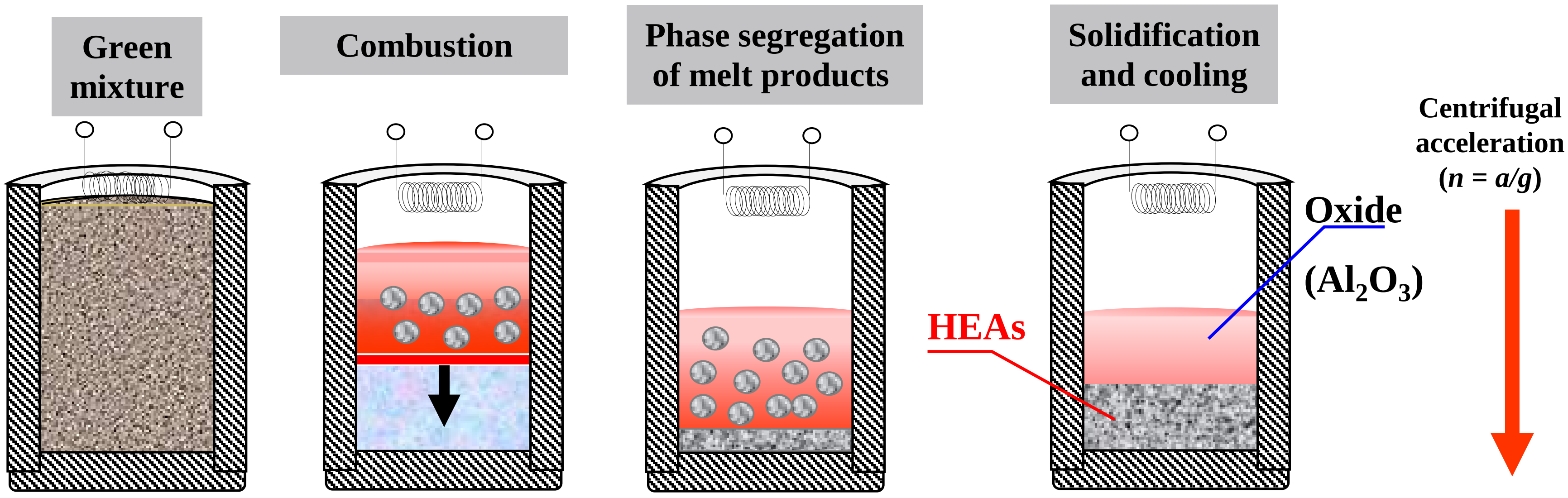
Synthesis of as cast HEAs by SHS metallurgy

Overall chemical scheme of synthesis

$$(Ox_1 + Ox_2 + Ox_3 + \ldots Ox_n) + Al(Ti, Mg) \rightarrow (Ni, Co, Ti, Fe, W, Cr, Al \text{ etc.}) + R_kO_l$$

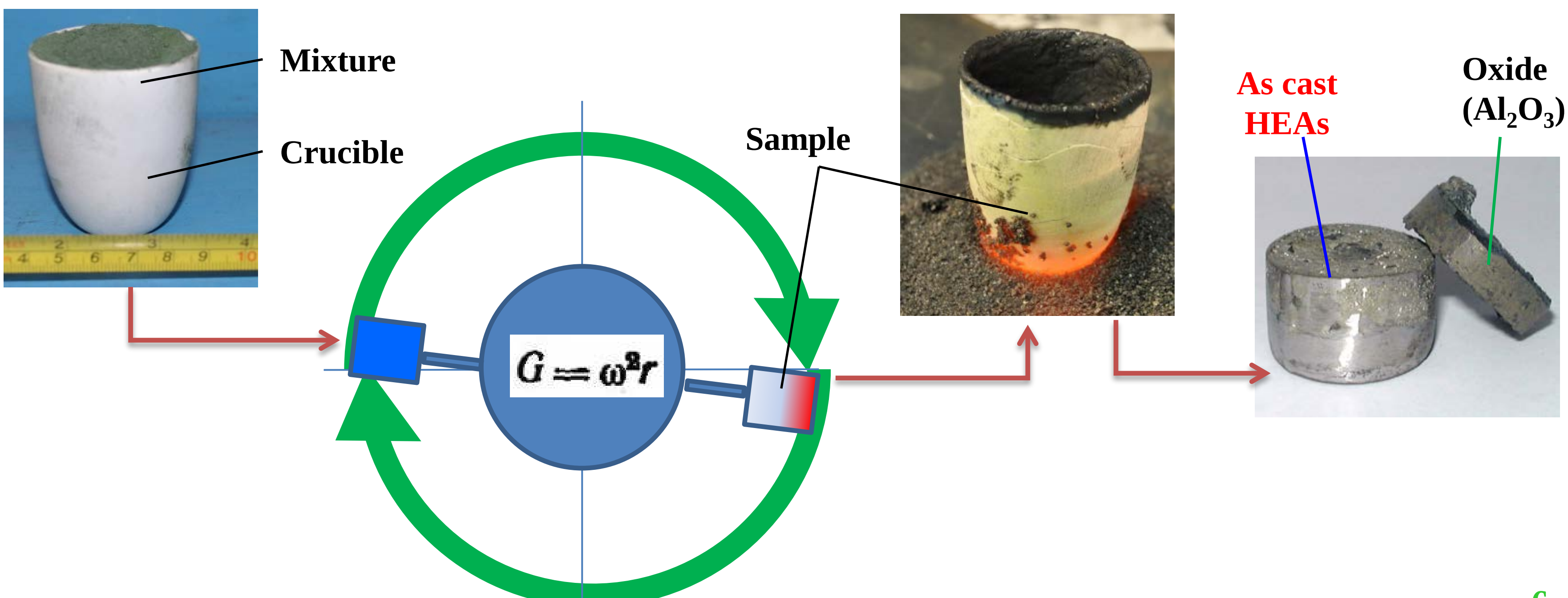
where Ox_i is oxides of Ni, Co, Fe, Ti, W, Cr, V, Mo, Nb etc.,
Al(Ti, Mg) – reducing agent

Maine stages of the SHS for as cast materials

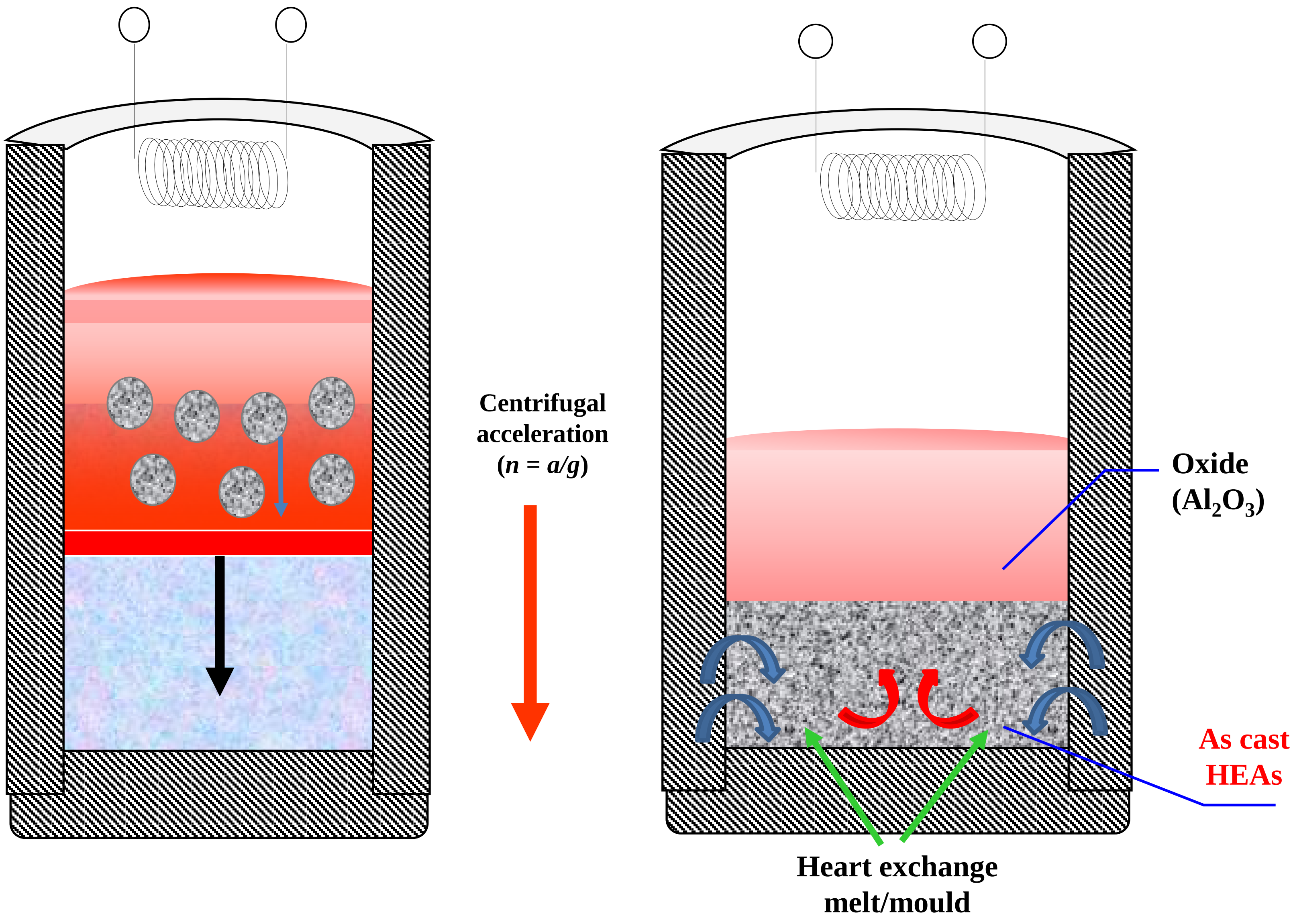


SHS- centrifuges

Common flowsheet for preparation of as cast HEAs by centrifugal casting –SHS process



Common effect of high gravity on phase segregation of final product during centrifugal casting –SHS process and formation HEAs fine structure



The compositions synthesized by centrifugal casting –SHS process

Nominal composition

Composite, weigh. %	Ni	Cr	Co	Fe	Al	Cu
(HEA-I) – NiCrCoFeAl	23.3	20.6	23.3	22.1	10.7	-
(HEA-II) – NiCrCoFeAlCu	18.6	16.5	18.6	17.7	8.5	20.1

Composite, weigh. %	Ni	Cr	Co	Fe	Mn	Al
(HEA-III) – $NiCrCoFeMnAl_{0,2}$	20.6	18.2	20.7	19.6	19.3	1.6
– $NiCrCoFeMnAl_{0,6}$	19.9	17.6	20.0	18.9	18,6	5.0
– $NiCrCoFeMnAl_{1,0}$	19.0	17.3	19.1	18.1	17.8	8.7
– $NiCrCoFeMnAl_{1,2}$	18.7	16,5	18.8	17.8	17.5	10.7
– $NiCrCoFeMnAl_{1,6}$	17.8	15.8	17.9	17.0	16.7	14.8
– $NiCrCoFeMnAl_{2,0}$	16.9	15.0	17.0	16.0	15.8	19.3

Composite, weigh. %	Nb	Ti	Mo	Zr	Cr	Al	Si
(HEA-IV) – $NbTiMoZrCrAl_{0,5}Si_{0,1}$	23.5	12.1	24.2	23.0	13.1	3.4	0.7
$NbTiMoZrCrAl_{0,5}Si_{0,4}$	23.0	11.8	23.7	22.6	12.8	3.3	2.8
$NbTiMoZrCrAl_{0,5}Si_{1,0}$	22.0	11.6	22.7	21.6	12.3	3.2	6.6
$NbTiMoZrCrAl_{0,5}Si_{1,3}$	21.6	11.1	22.3	21.2	12.1	3.2	8.5
$NbTiMoZrCrAl_{0,5}Si_{1,6}$	21.2	10.9	21.9	20.8	11.9	3.1	10.2
$NbTiMoZrCrAl_{0,5}Si_{2,0}$	20.7	10.7	21.3	20.3	11.5	3.0	12.5

Composite, weigh. %	Nb	Mo	Zr	Cr	W	Hf	Ta
(HEA-V) NbMoZrWHfTa	11,3	11,6	11,1	0	22,3	21,7	22
$NbMoZrWHfTaCr_{0,25}$	11,1	11,5	10,9	1,6	22,0	21,3	21,6
$NbMoZrWHfTaCr_{0,5}$	10,9	11,3	10,7	3,1	21,6	21,0	21,3
$NbMoZrWHfTaCr_{0,75}$	10,8	11,1	10,6	4,5	21,3	20,7	21,0
$NbMoZrWHfTaCr_{1.0}$	10,6	11,0	10,4	5,9	21,0	20,4	20,7

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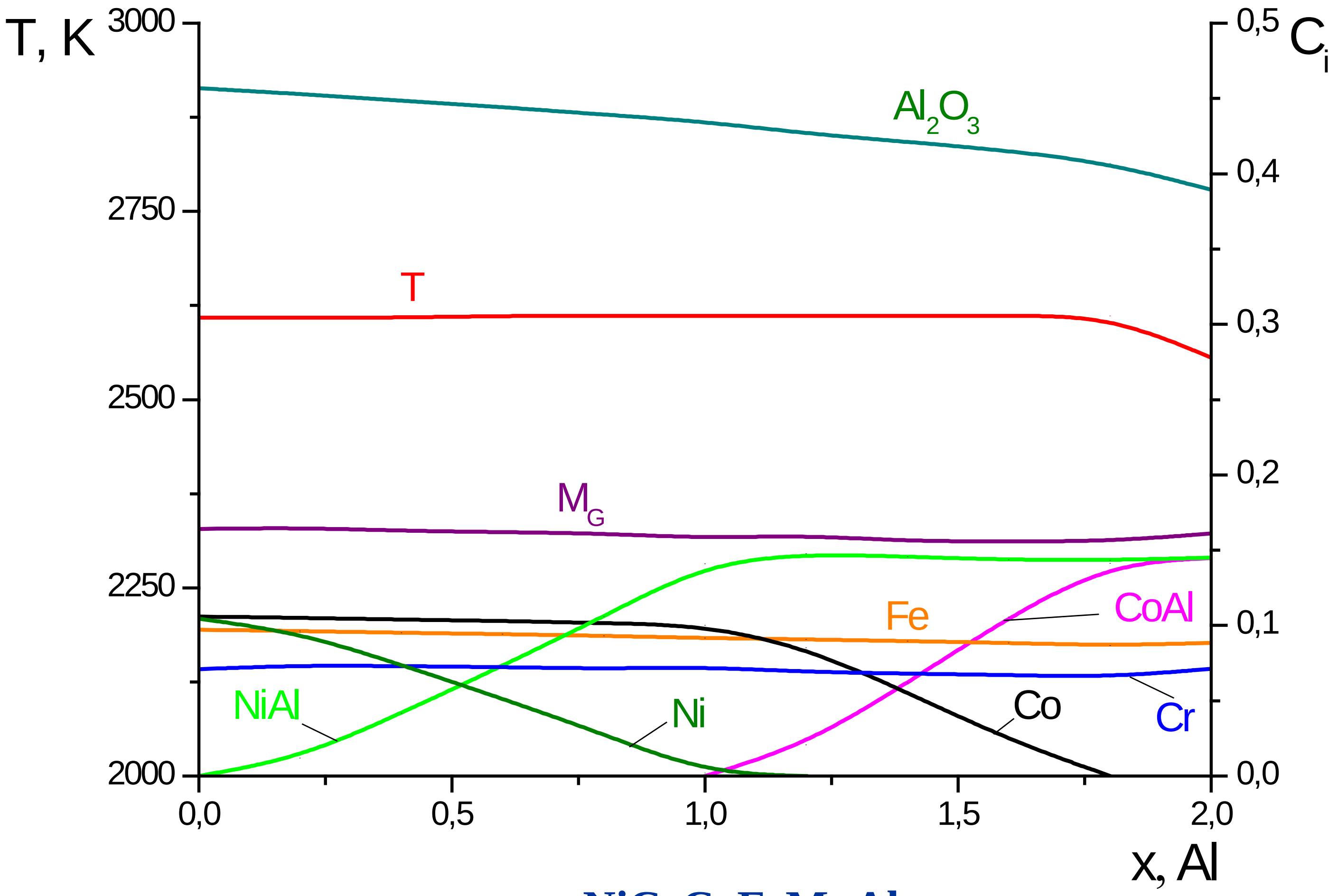
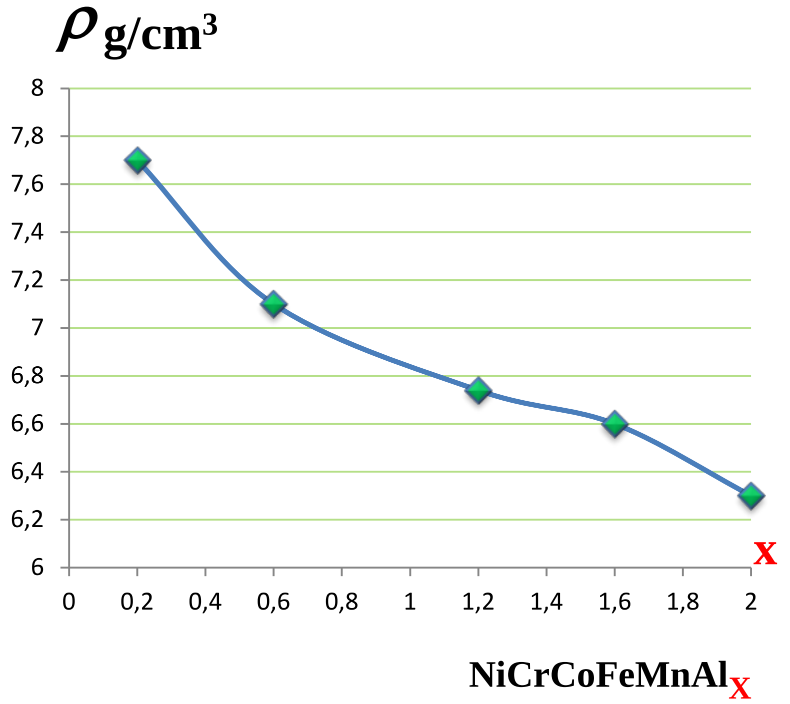
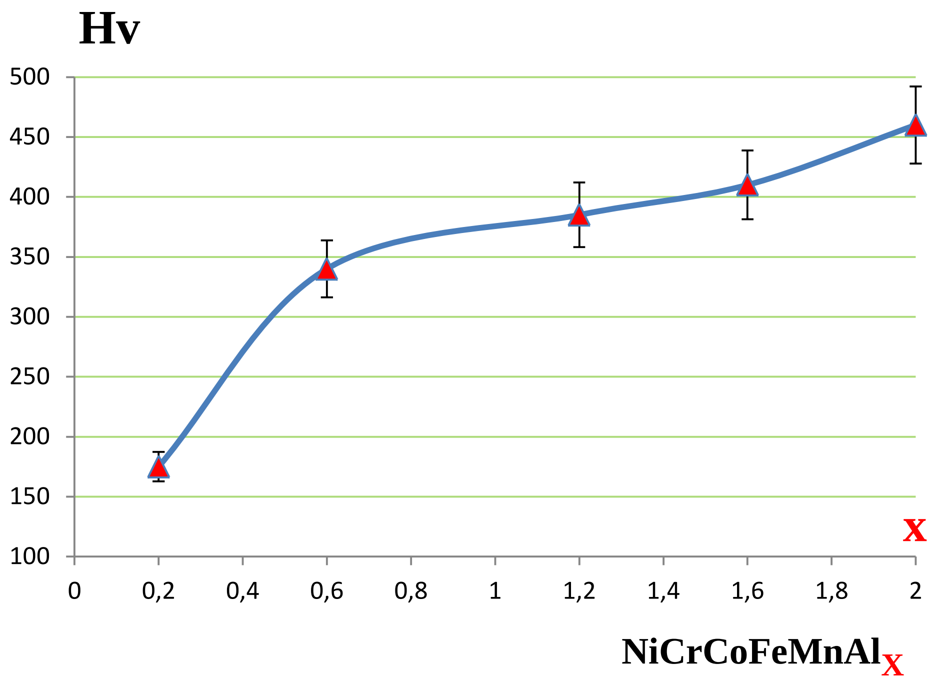
Thermodynamic analysis of $NiCrCoFeMnAl_x$ alloy composition



$NiCrCoFeMnAl_x$

Density and micro hardness *vs.* Al content in cast $NiCrCoFeMnAl_x$ HEA



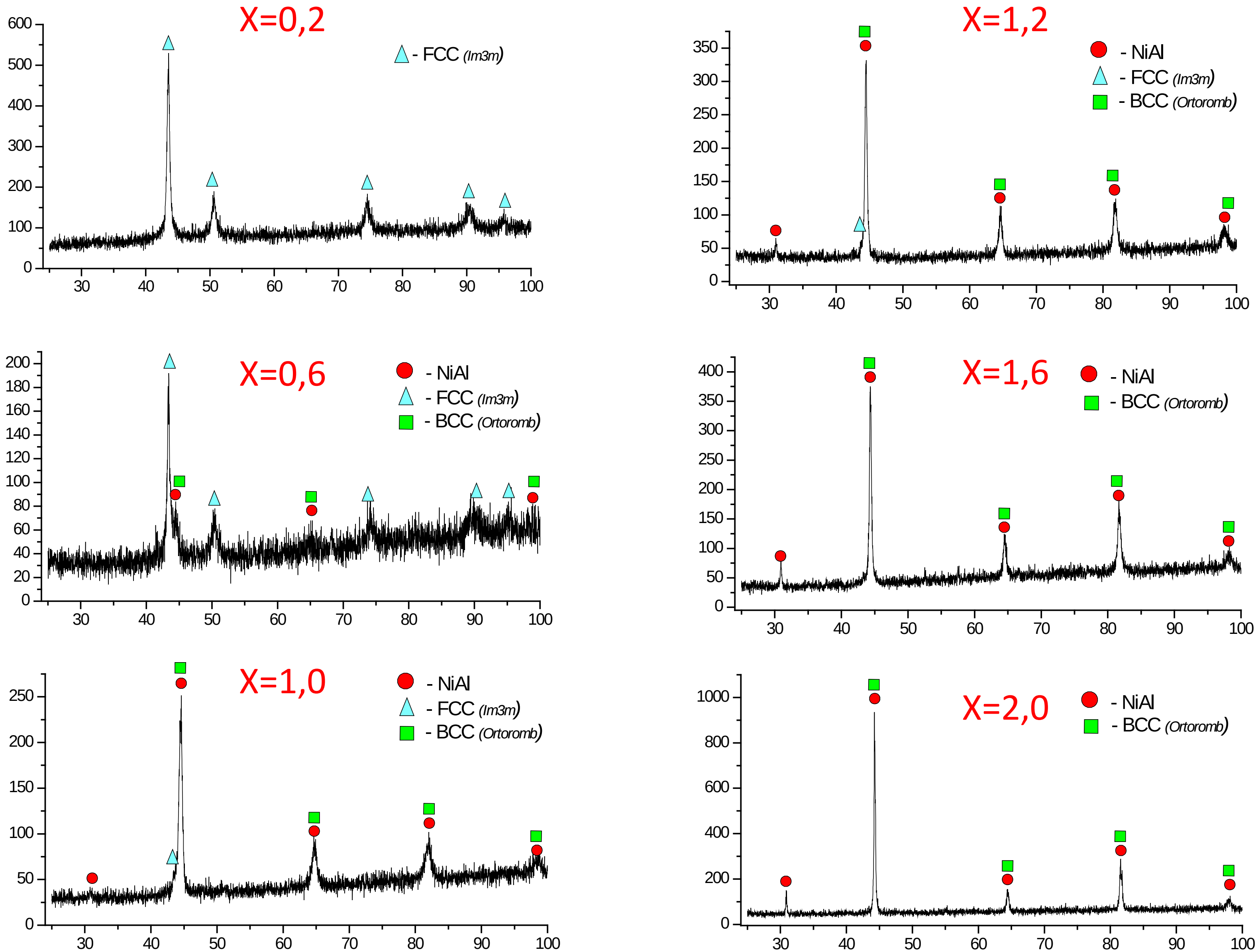


Outward appearance of cast $NiCrCoFeMnAl_x$ HEAs

HEAs

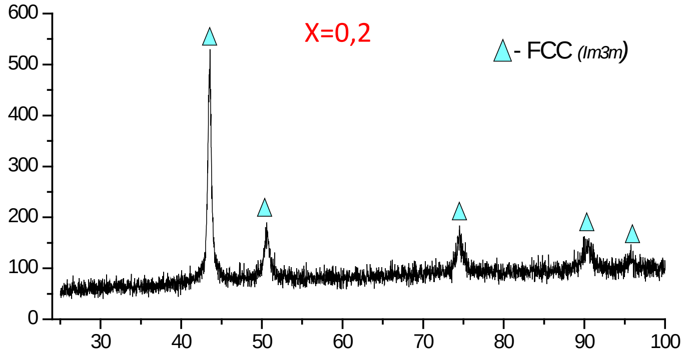
Al oxide

X-ray diffraction patterns of NiCrCoFeMnAl$_X$ HEA

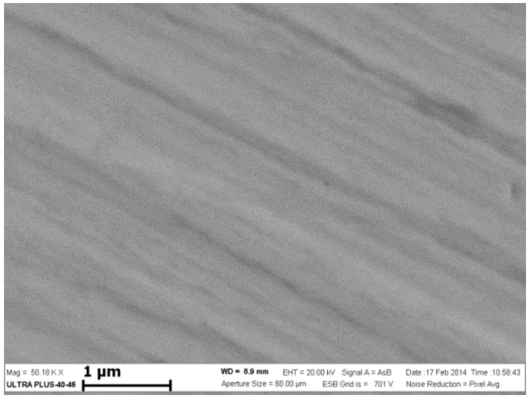


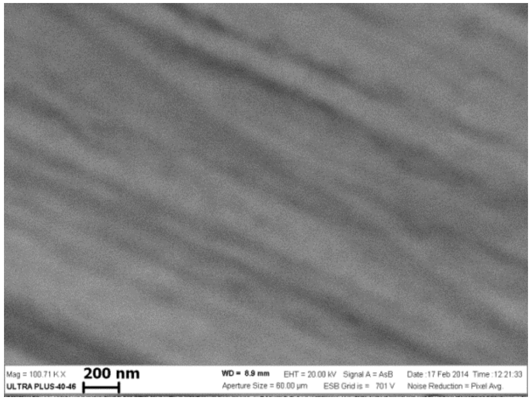
XRD and microstructure of cast $NiCrCoFeMnAl_{0,2}$ HEA

XRD date

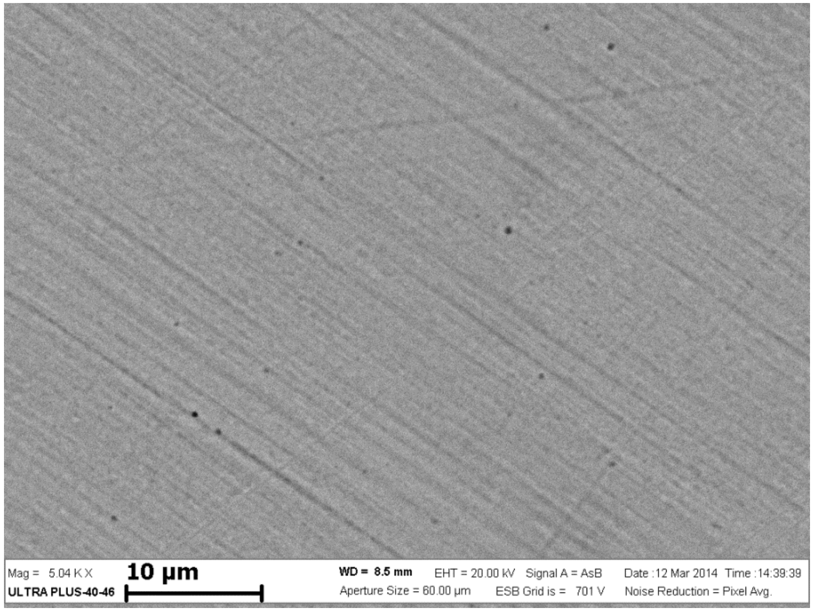


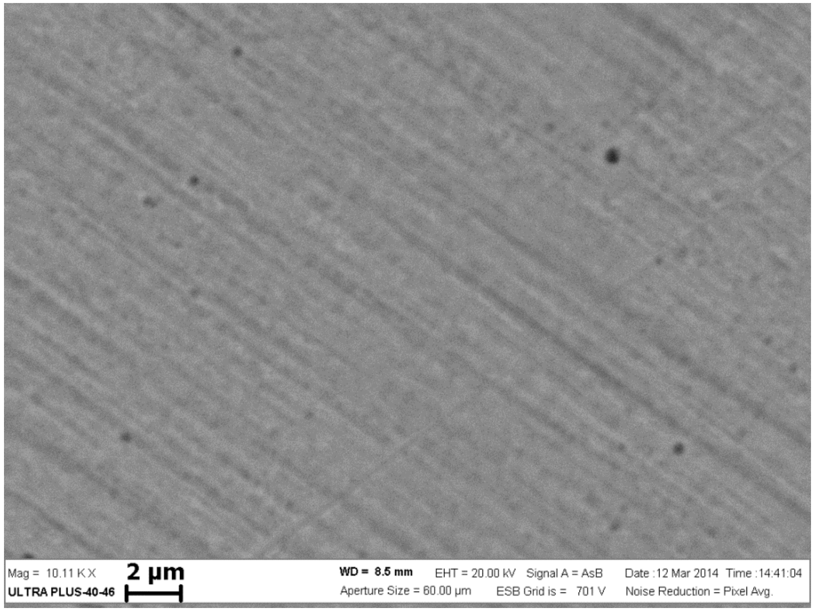
Polished sample (SEM)





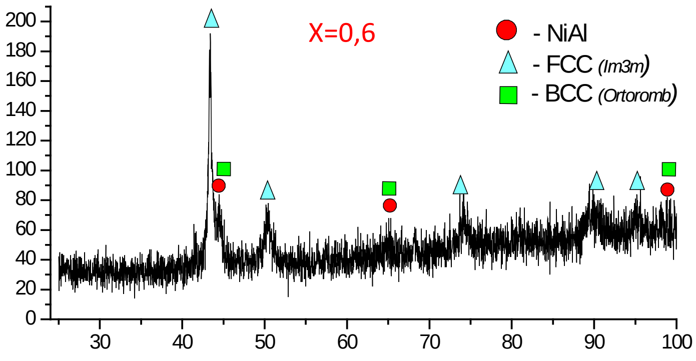
After light etching (SEM)



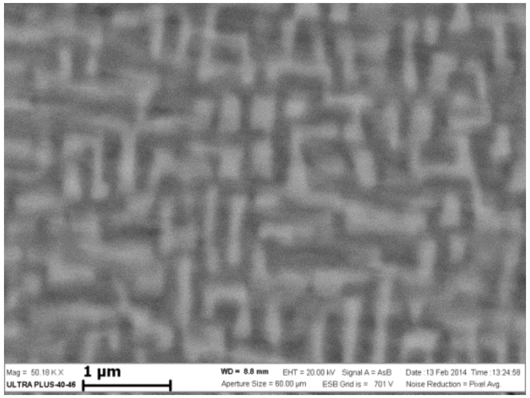


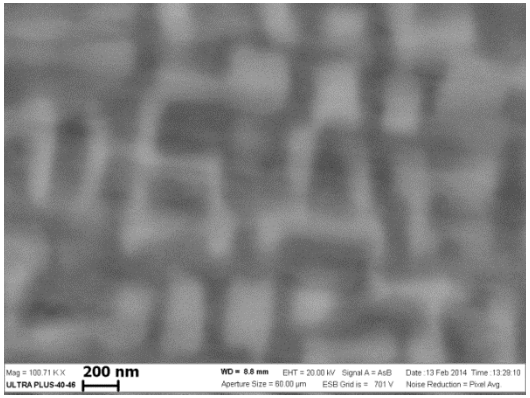
XRD and microstructure of cast NiCrCoFeMnAl$_{0,6}$ HEA

XRD date

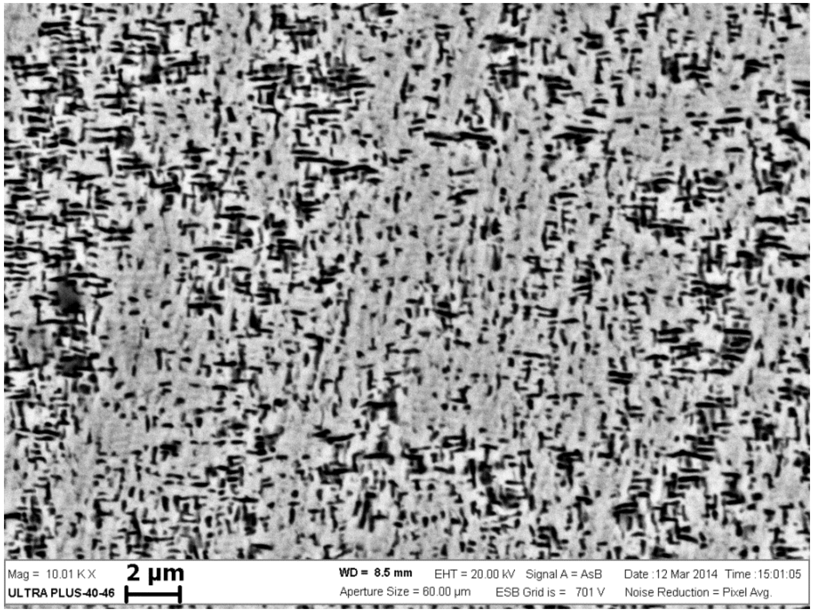


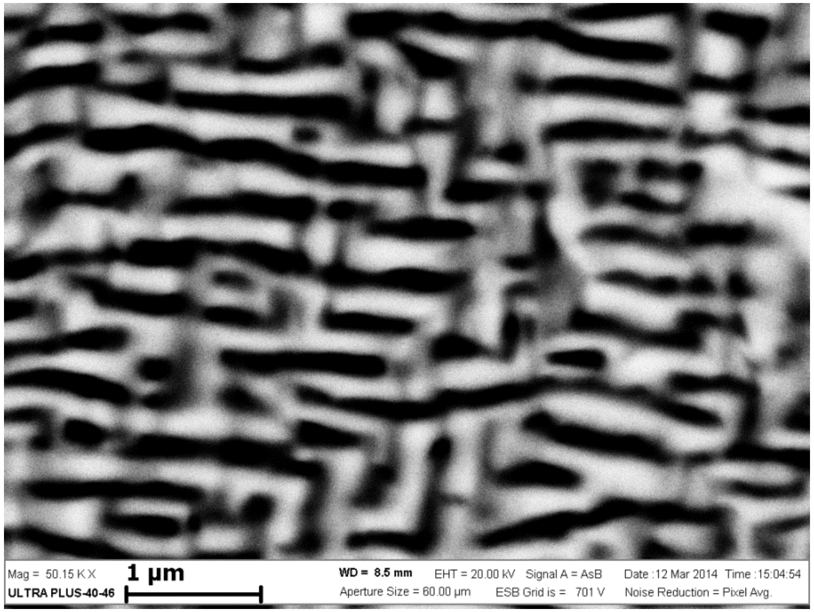
Polished sample (SEM)





After light etching (SEM)





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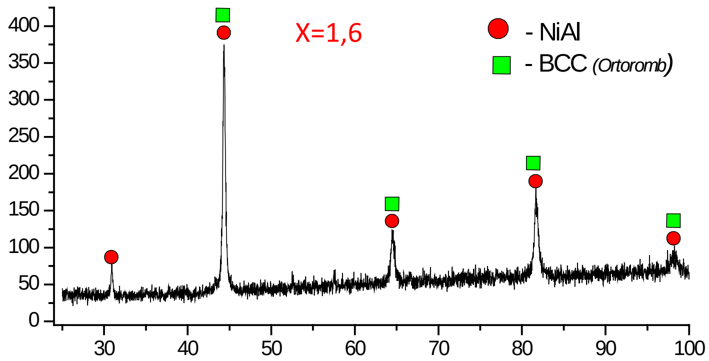
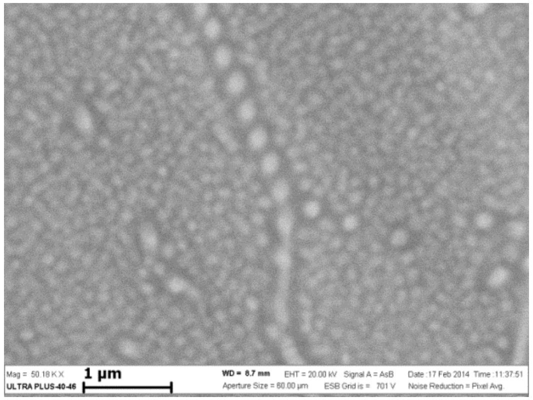
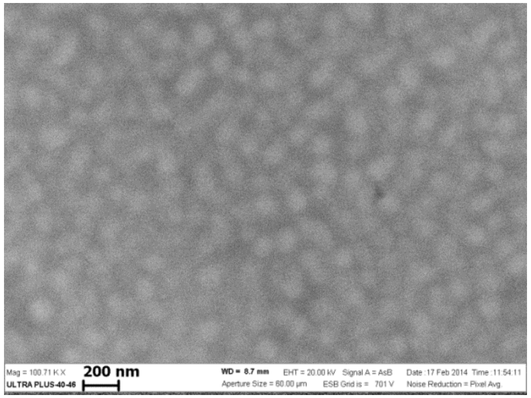
XRD and microstructure of cast NiCrCoFeMnAl$_{1,6}$ HEA

XRD date

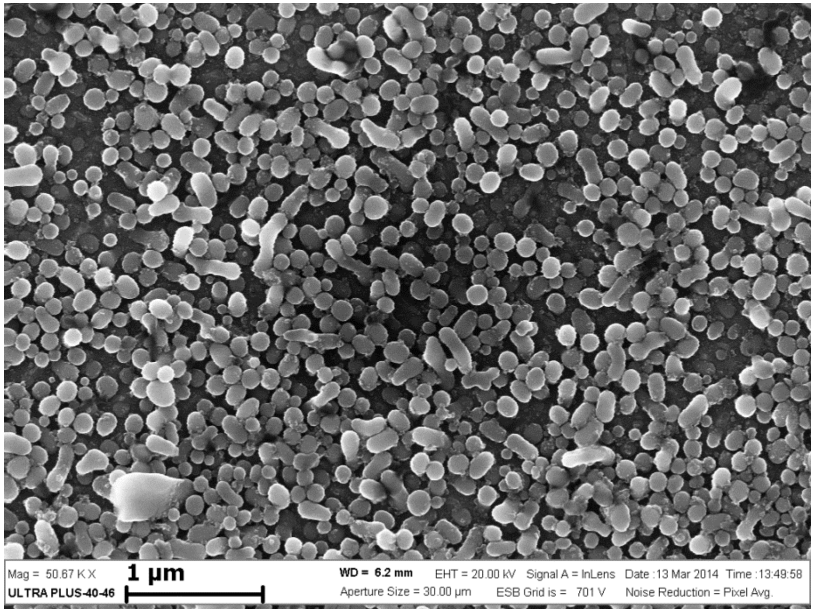


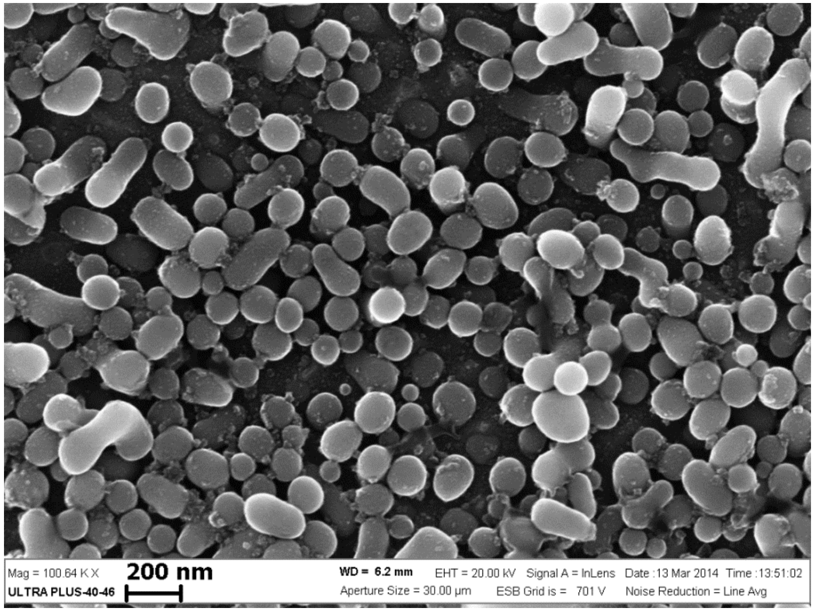
Polished sample (SEM)





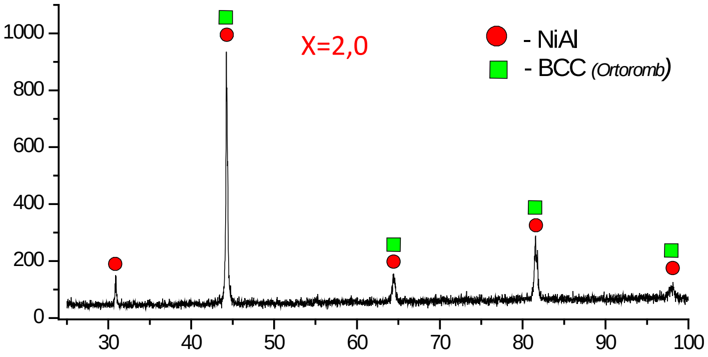
After light etching (SEM)



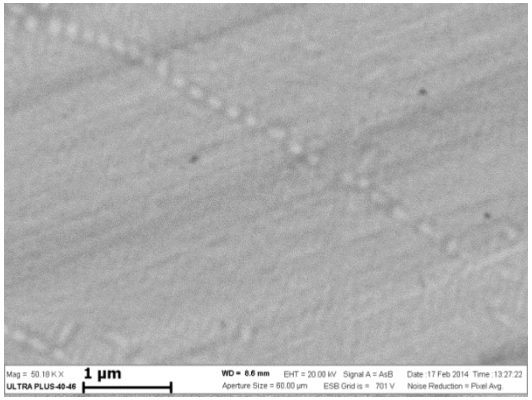


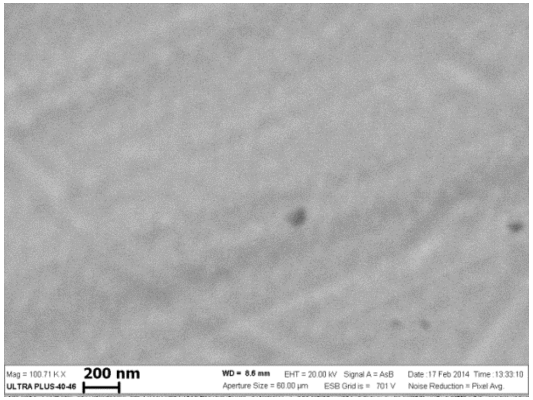
XRD and microstructure of cast $NiCrCoFeMnAl_{2,0}$ HEA

XRD date

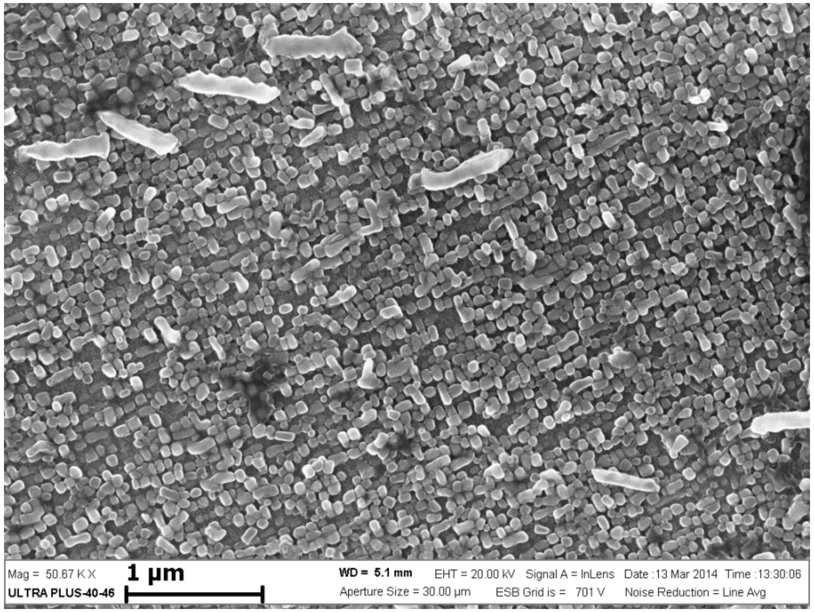


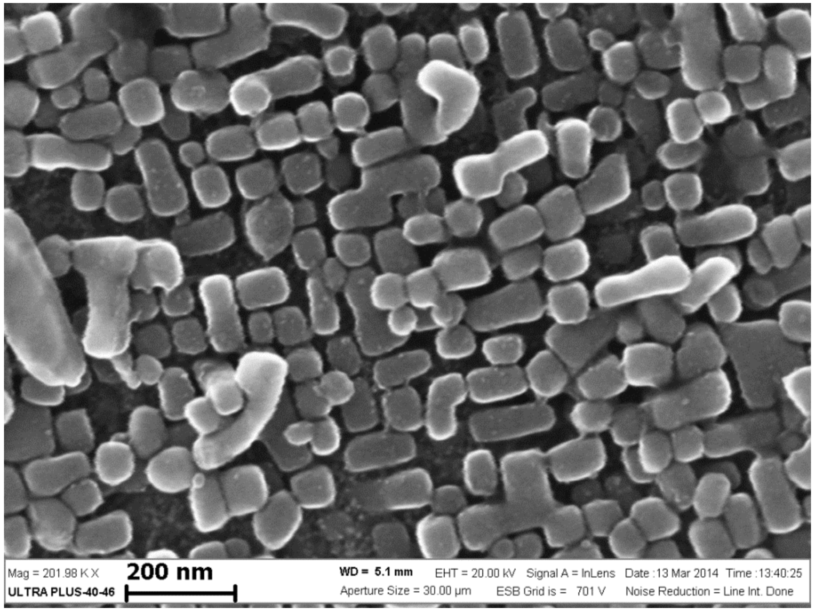
Polished sample (SEM)





After light etching (SEM)





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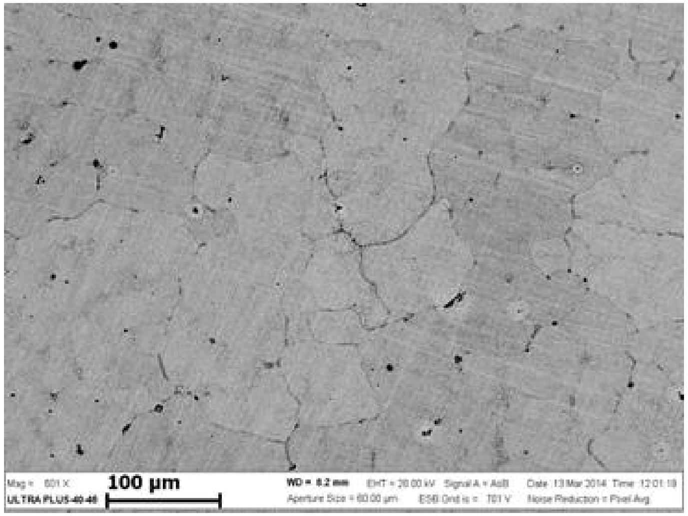
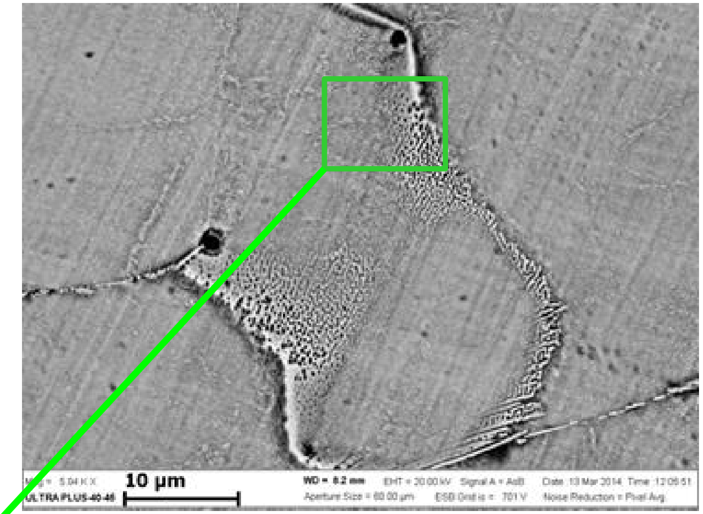
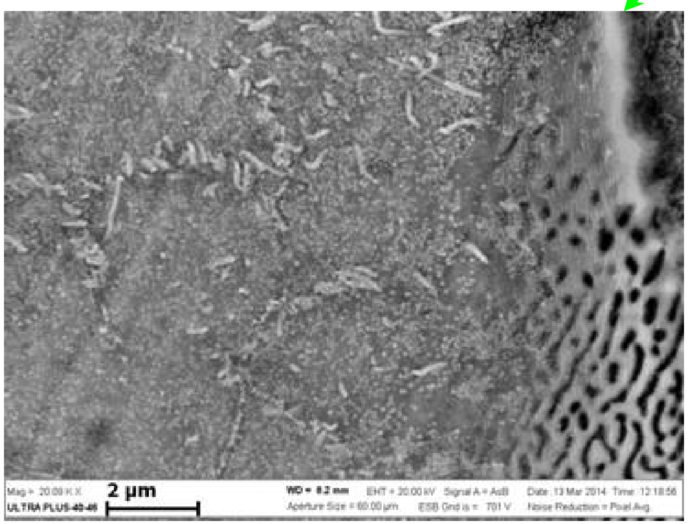
Bimodal structure of cast NiCrCoFeMnAl$_{2,0}$ HEA

After light etching (SEM)

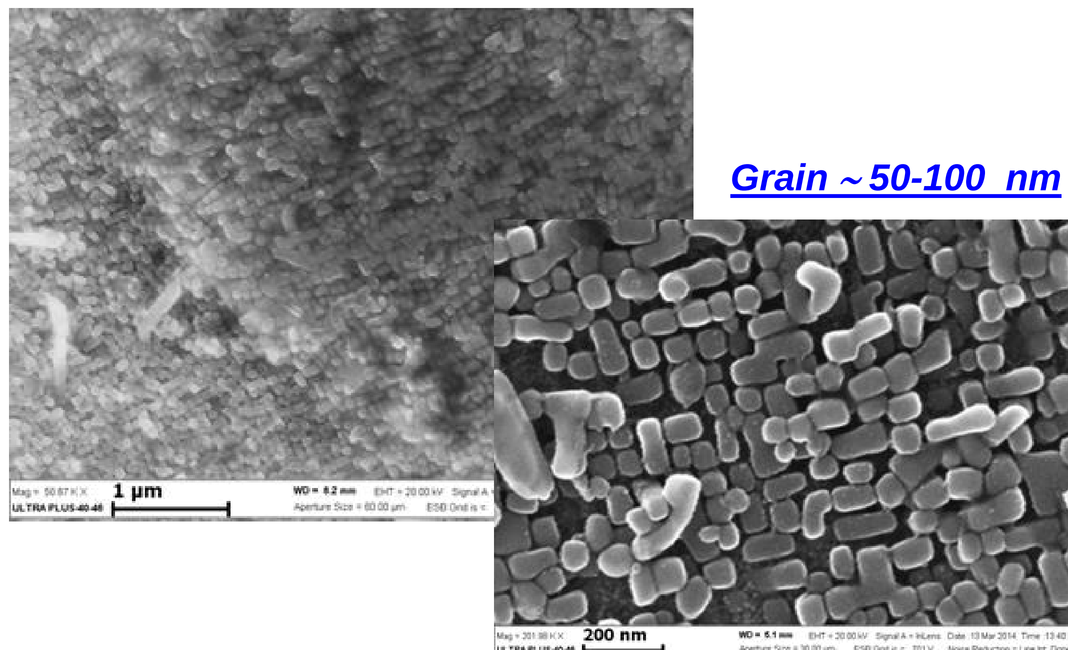




Grain ~ 50-100 µm



Grain ~ 50-100 nm



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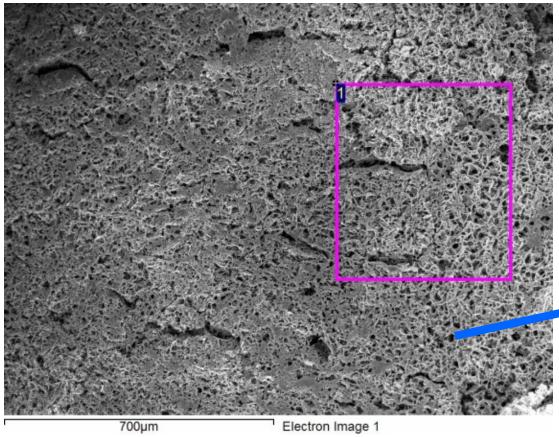
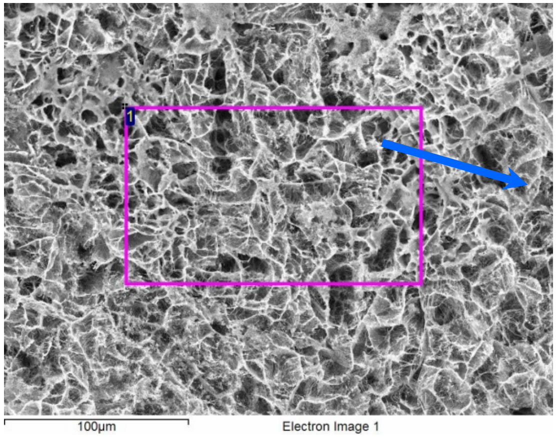
Composition of NiCrCoFeMnAl$_X$ HEA after etching

After strong etching (SEM)



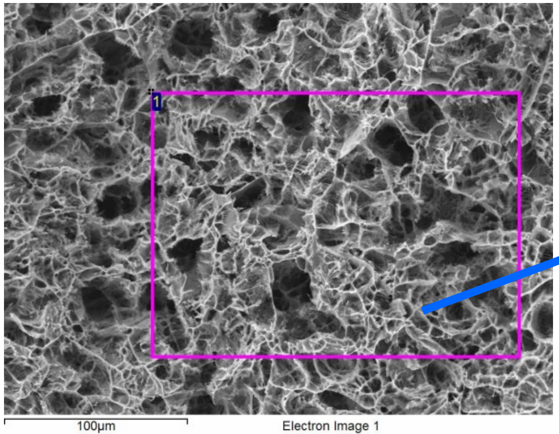
NiCrCoFeMnAl$_{0,6}$

Spectrum	Al	Cr	Mn	Fe	Co	Total
1	1.1	48.7	11.3	31.4	7.5	100.0



NiCrCoFeMnAl$_{1,6}$

Spectrum	Al	Cr	Mn	Fe	Co	Total
1	2.6	50.1	12.2	30.9	4.2	100.0

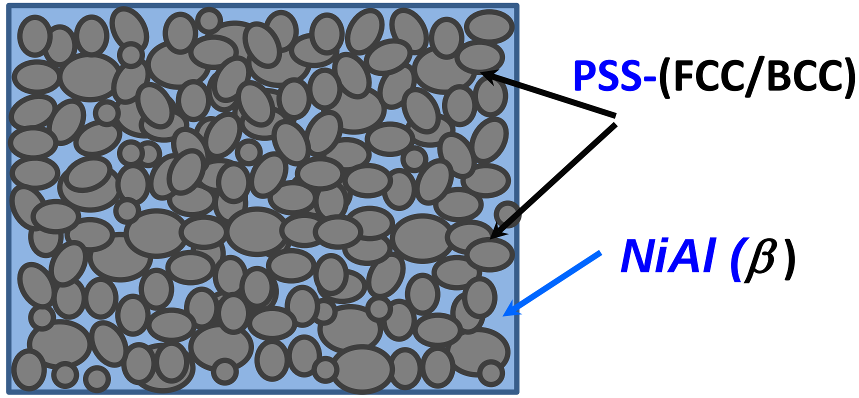


NiCrCoFeMnAl$_{2,0}$

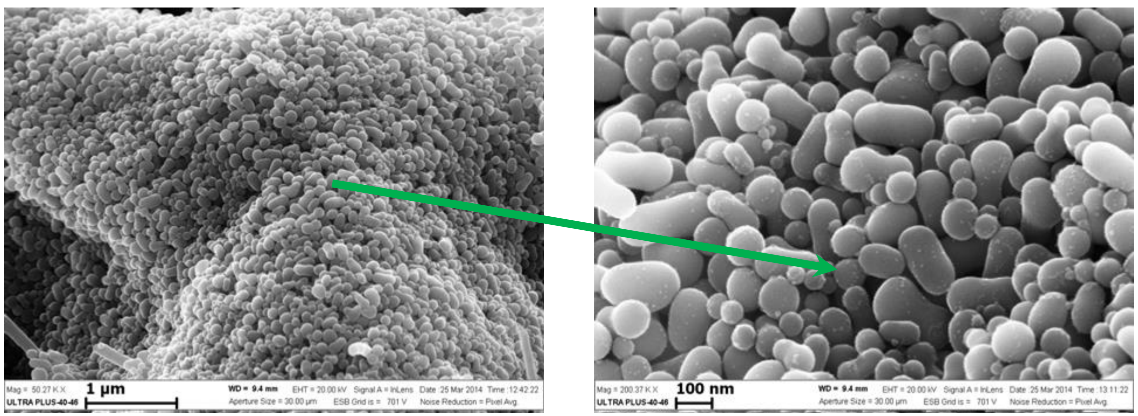
Spectrum	Al	Cr	Mn	Fe	Co	Total
1	2.8	52.8	10.6	30.2	3.6	100.0

Nanoscale composite structure of synthesized $NiCrCoFeMnAl_{2,0}$ HEA

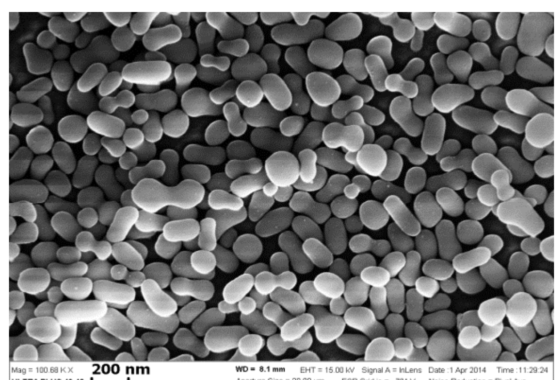
Structural sketch



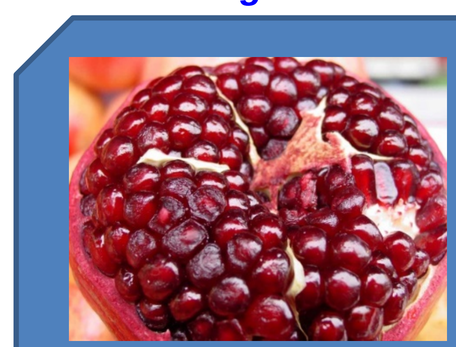
Pomegranate structure (SEM of surface after strong etching)



Extracted powder



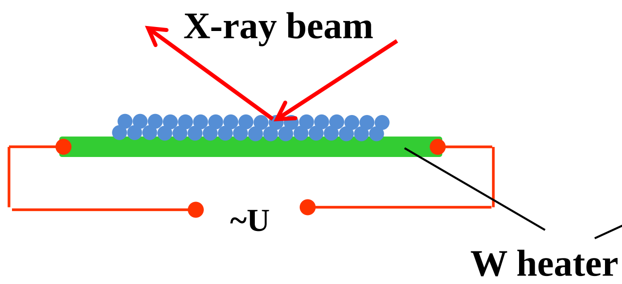
Pomegranate

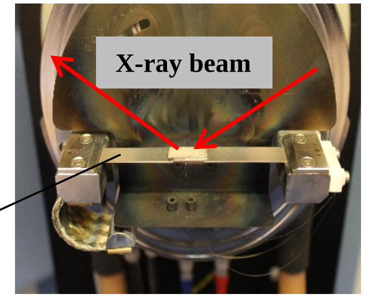


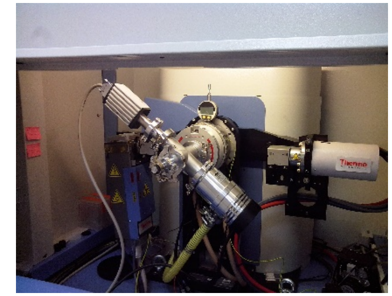
Effect of temperature on phase stability for NiCrCoFeMnAl$_{1,6}$ HEA

Furnace HTK 2000 “Anton Paar” and diffractometer ARL`XTRA

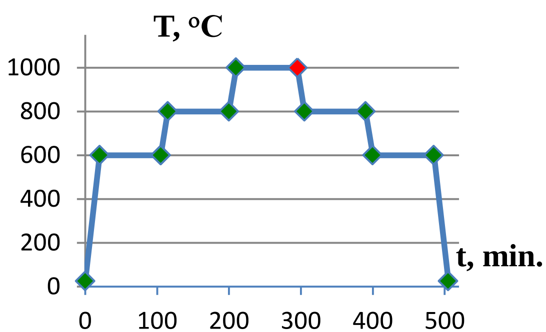
The sketch of high temperature XRD



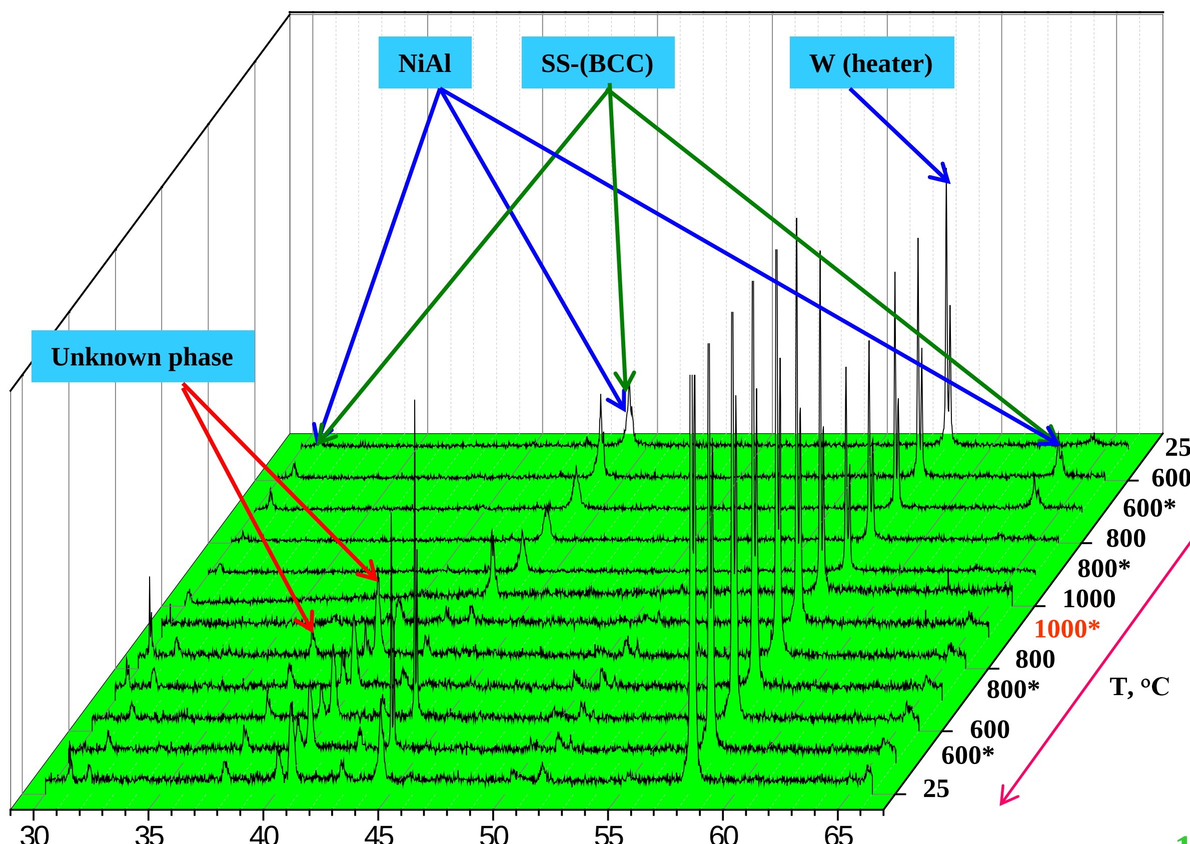




The temperature profile of heat treatment

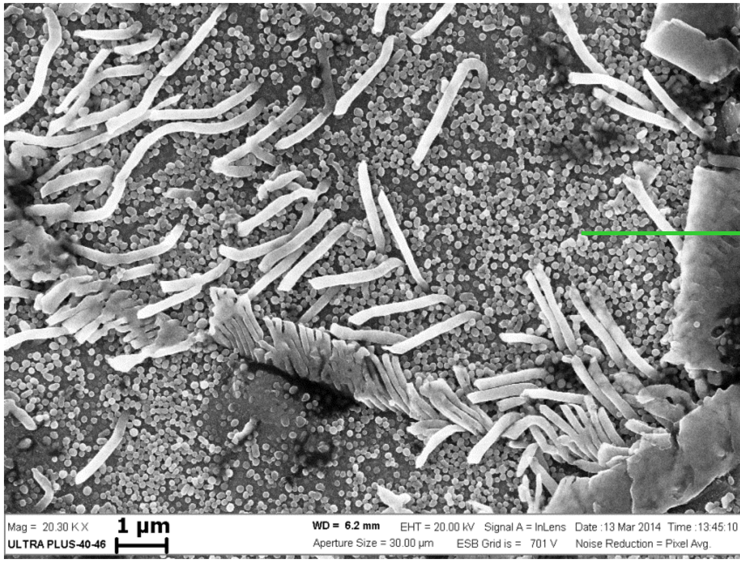


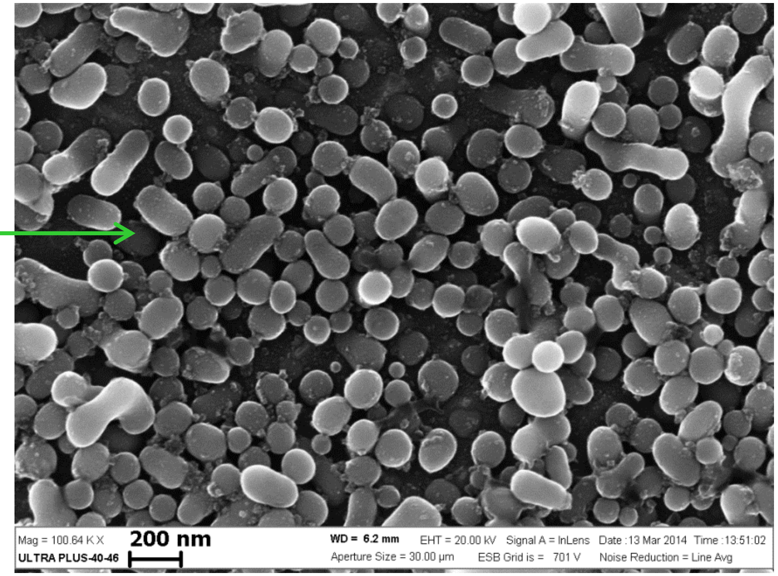
3D XRD patterns vs. temperature



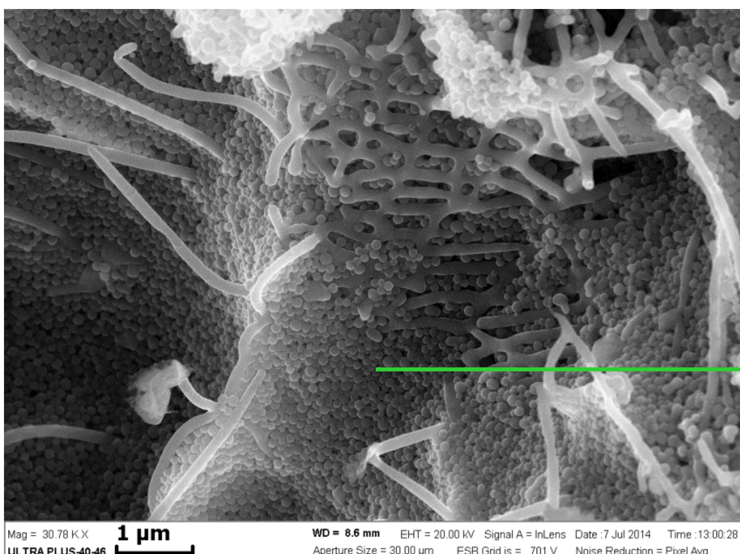
X-ray diffraction patterns of NiCrCoFeMnAl$_x$ HEA

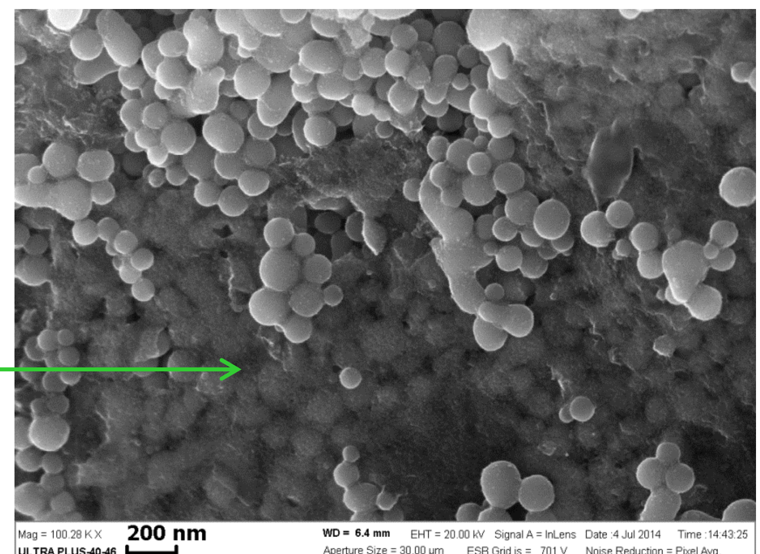
SHS





After temperature treatment





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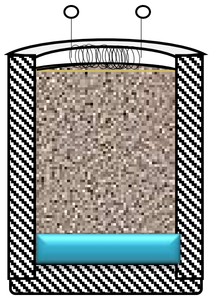
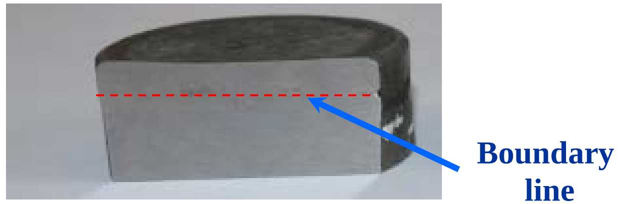
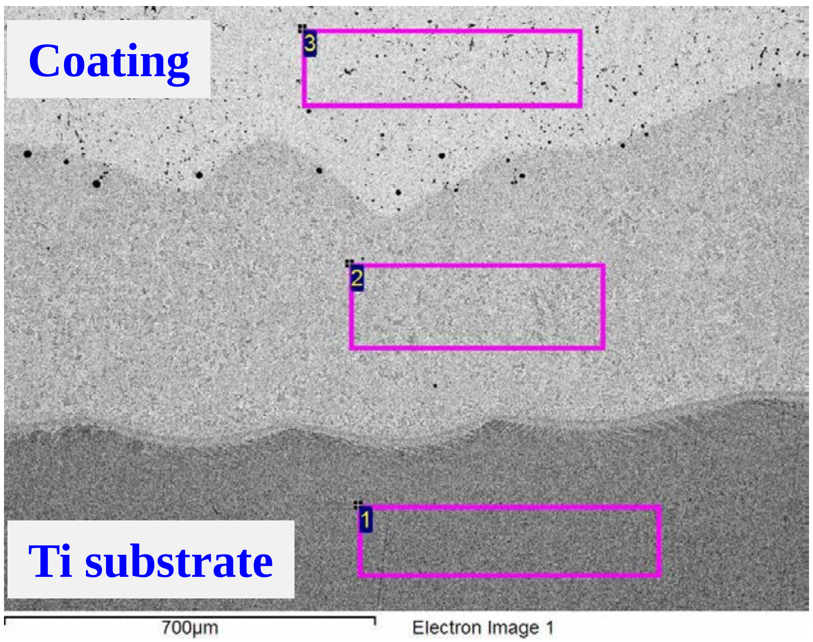
SHS surfacing of $Ti_{substrate}$ / $NiCrCoFeMnAl_{1.6}$



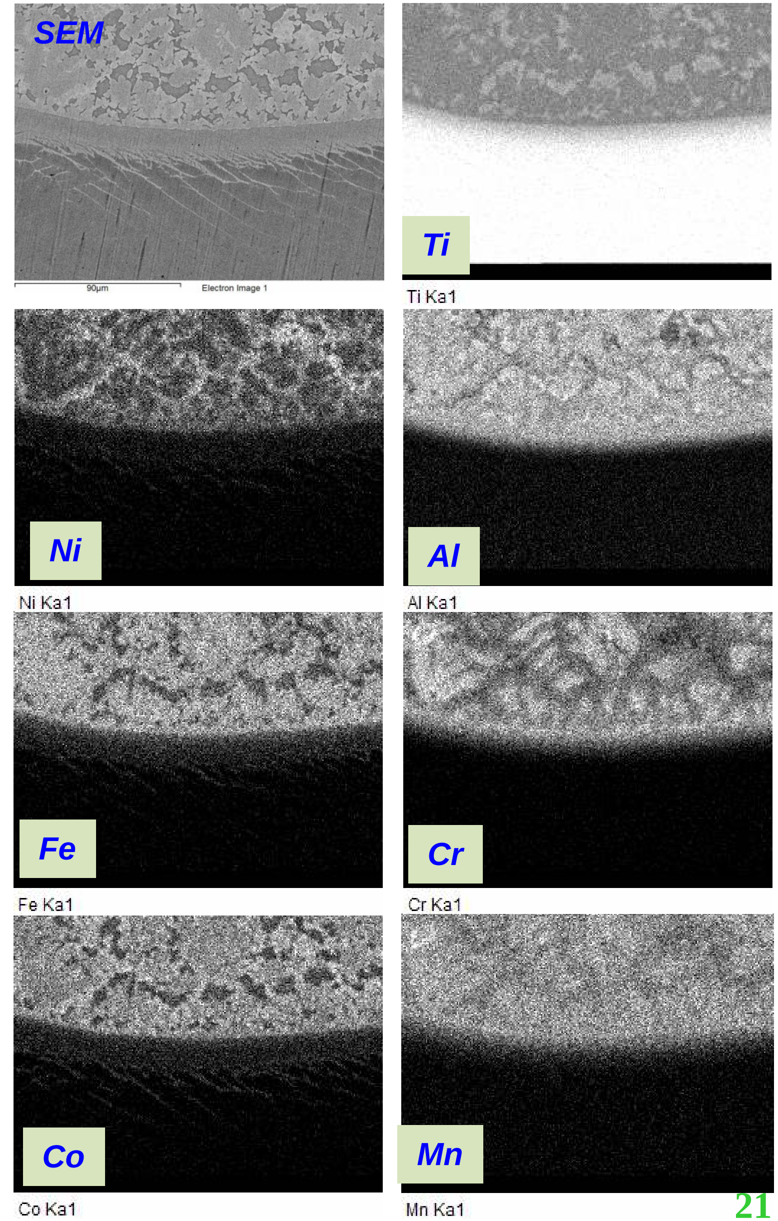
Outward appearance
(cross cutting)





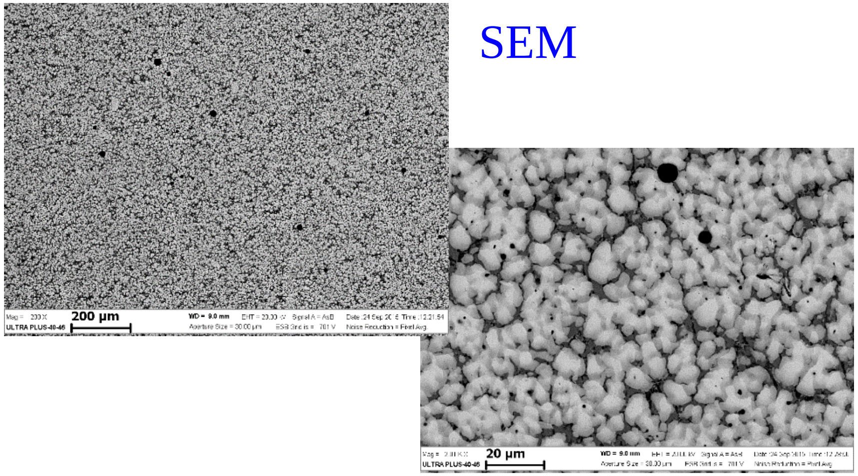
Spectrum	Al	Ti	Cr	Mn	Fe	Co	Ni	Total
1	1,1	98,9						100
2	8,3	55,5	7,2	4,7	8,1	8,6	7,6	100
3	13,7	24,4	11,9	7,9	13,7	14,9	13,5	100

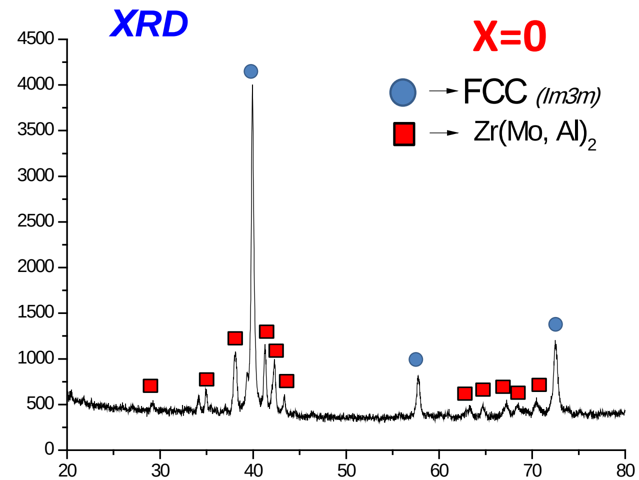
EDX maps of boundary layer



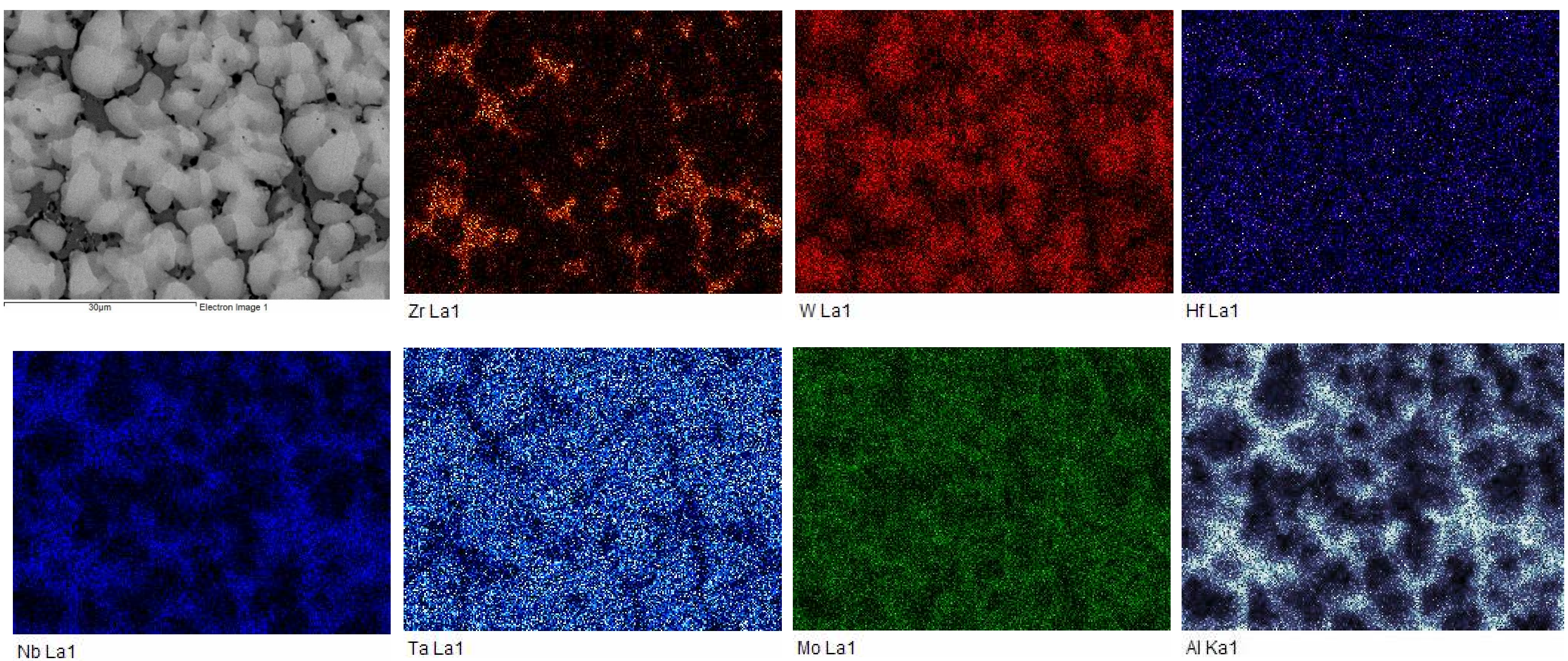
SEM image and XRD date of $NbMoZrWHfTaCr_{0.5}$ HEAs

SEM



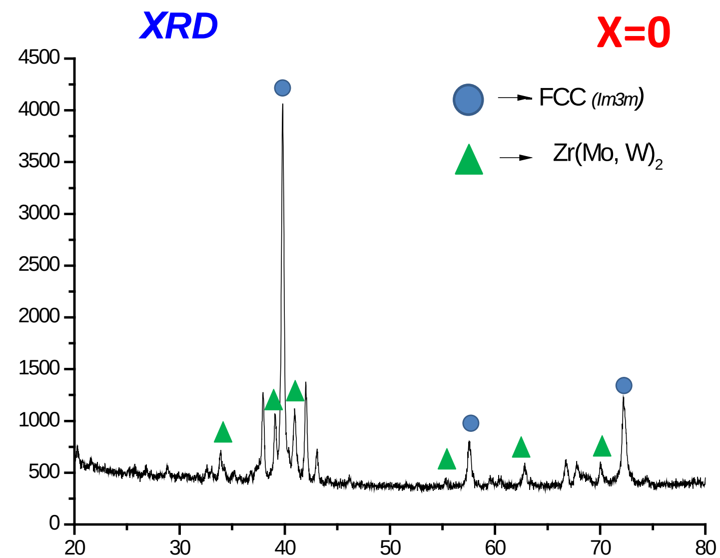


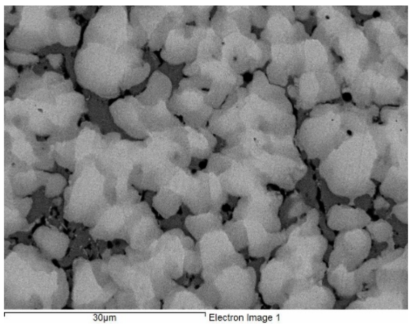
SEM image and EDS results for
distribution of the elements in the alloy

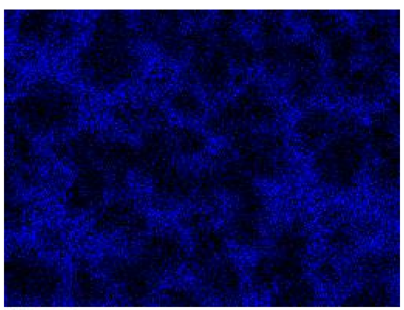


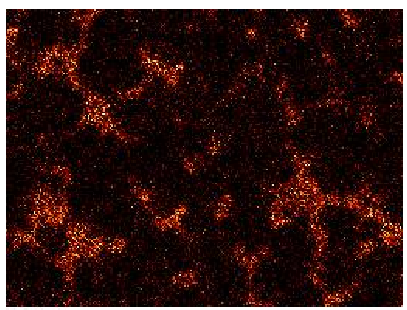
XRD date of NbMoZrWHfTaCr$_X$ HEAs

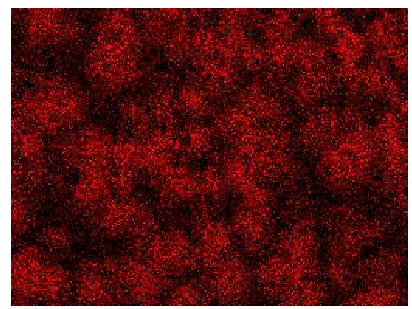
SEM image and EDS results for distribution of the elements in the alloy

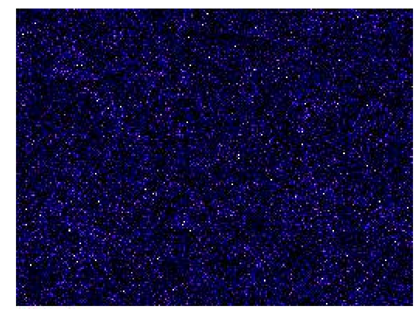


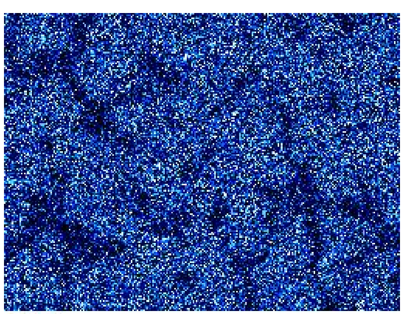


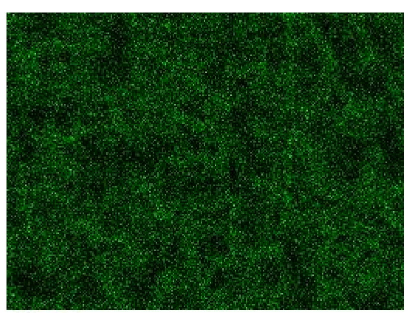

Nb La1

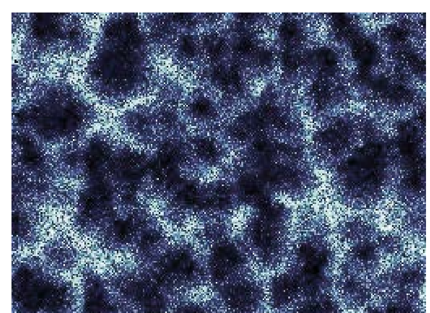

Zr La1


W La1


Hf La1


Ta La1


Mo La1


Al Ka1

Conclusion

- **It was shown great ability centrifugal SHS techniques to production of cast HEAs. Synthesized alloys $NiCrCoFeMnAl_x$ with high Al (up to 15 wt. %) had unique nano-sized composite structure which consist of NiAl as body phase and nano-sized (rounded shape) precipitates formed of polymetallic solid solution (FCC/BCC).**
- **Analysis of obtained data leads to the conclusion about the promising use the polymetallic alloys (HEAs) and production method (SHS) for formation of cast bulk nano-structural materials.**
- **The construction of new metallic materials based on the new concept (polymetallic solid solution) can significantly broaden the base for creation of new advanced materials and production of new items running under extreme conditions.**
- **This work can be regarded as the first positive experience of SHS surfacing by cast HEAs on Ti alloy substrate.**

The present results can be expected to make engineering background for industrial-scale manufacturing of new cost-effective process for fabricating HEAs with valued properties and protective coatings based on them.

ISMAN

Thank you for your attention !

The scientist - is not the one who gives the correct answer, and the one who puts the right questions.

Claude Levi-Strauss