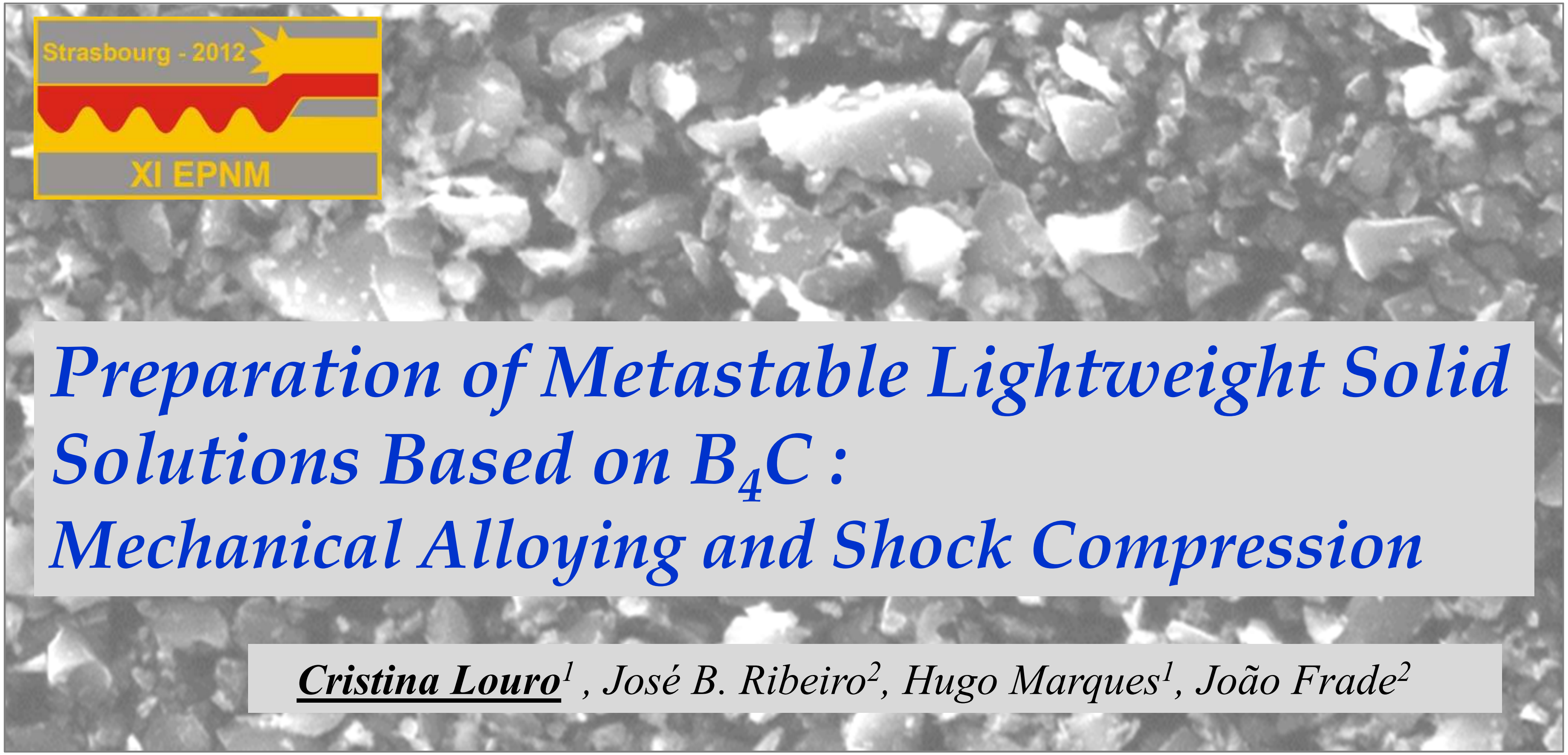
Strasbourg - 2012

XI EPNM



Preparation of Metastable Lightweight Solid Solutions Based on B_4C :
Mechanical Alloying and Shock Compression

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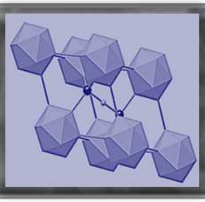


State-of-Art

Boron carbide, usually denoted as B_4C, stands apart from many advanced ceramics

Rather unique properties:

- **High hardness** (>30GPa)
- **High elastic modulus** (~460GPa)
- **High melting point** (2450 °C)
- **Hugniot elastic limit** (15-20GPa)
- **Fracture toughness** (2.5-3 $MPam^{1/2}$)
- **Low density** (2.52 gcm^{-3})
- **High erosion resistance**
- **High neutron absorption** (400-750 barn at 0.025eV)

Applications – Technical material:

- **Armour products (vest, vehicles)**
- Energy conversion
- Electron emission
- Thermal-neutron absorption
- Cutting tools and dies

☹ Sintering temperatures above 2000°C (close to T_m) and high pressure.
☹ Use of additives.

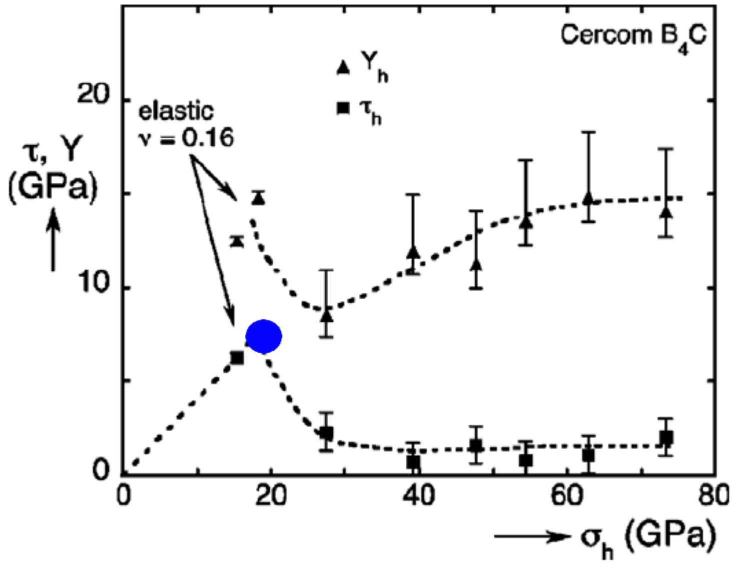
State-of-Art

Lightweight Armour Material

Key parameter for the potential of a ceramic as armour material:

HEL – Hugniot Elastic Limit

(the maximum uniaxial dynamic stress that a material can withstand elastically)



Shear stress and strength of Boron Carbide

In contrast to others ceramics, the shear stress of the B_4C falls rapidly above the HEL.

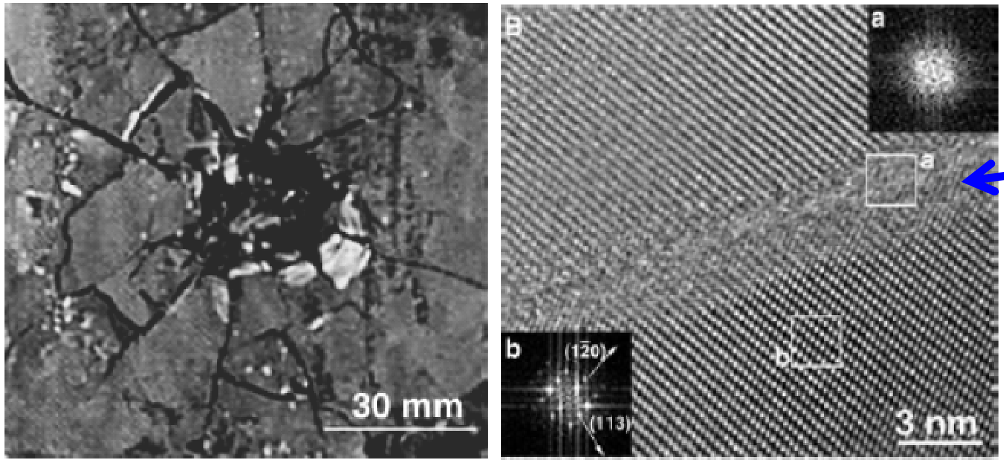
Premature failure as the shock stress reaches **20-25 GPa**

State-of-Art

Damage Mechanisms → **Solid State Amorphization**

Ballistic targets: localized amorphization

Subjected to supercritical impact velocities and pressures (> 23 GPa)



2-3 nm wide intragranular amorphous band

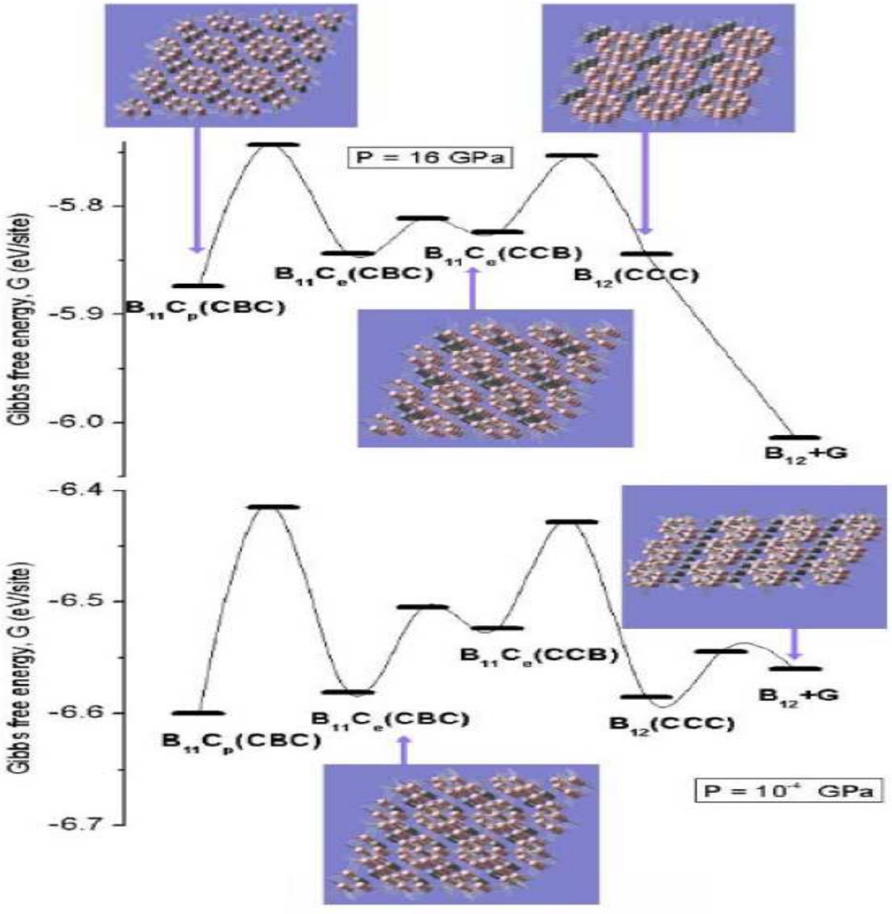
Chen MW, McCauley JW, Hemker KJ, Shock-induced localized amorphization in boron carbide**,** ***Science*** (**2003**) 299:1563.

State-of-Art

Validations

Theorical investigation: hydrostatic pressure at RT

Fanchini G, McCauley JW, Chhowalla M, Behavior of disordered boron carbide under stress, Physical Review Letters (**2006**) 97,035502.



16 GPa

$B_{11}C_p$ (C-B-C) → B_{12} + G/a-C

6-7 GPa

B_{12}(C-C-C) → B_{12} + G/a-C

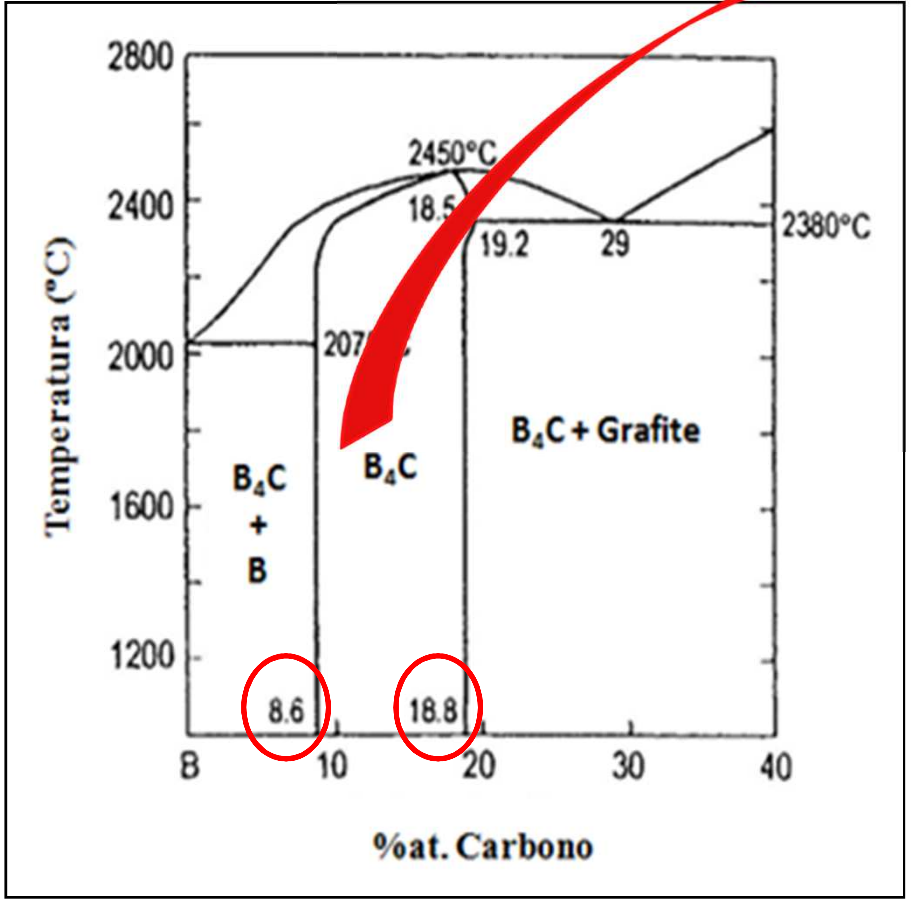
The failure threshold depends on the B_{12} (CCC) polytype concentration

↓

How to avoid?

State-of-Art

Phase Diagram B-C



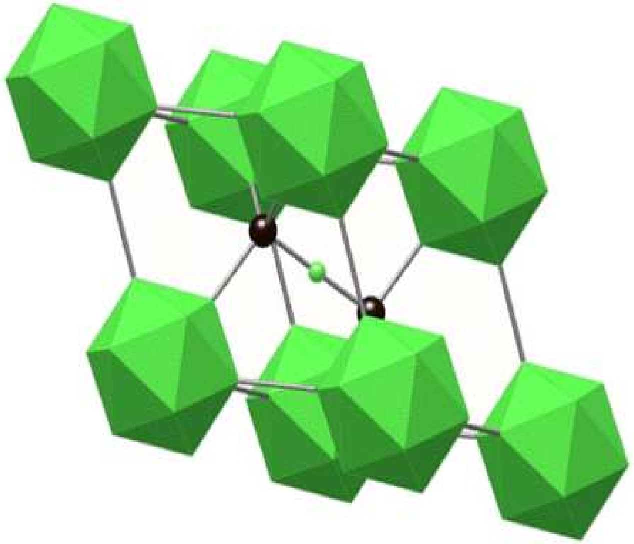
Riedel, R., "Handbook of hard ceramic materials", Wiley-VHC, Wienheim, Germany (2000).

Solid Solution:

$B_{11}C$ – rich boron side

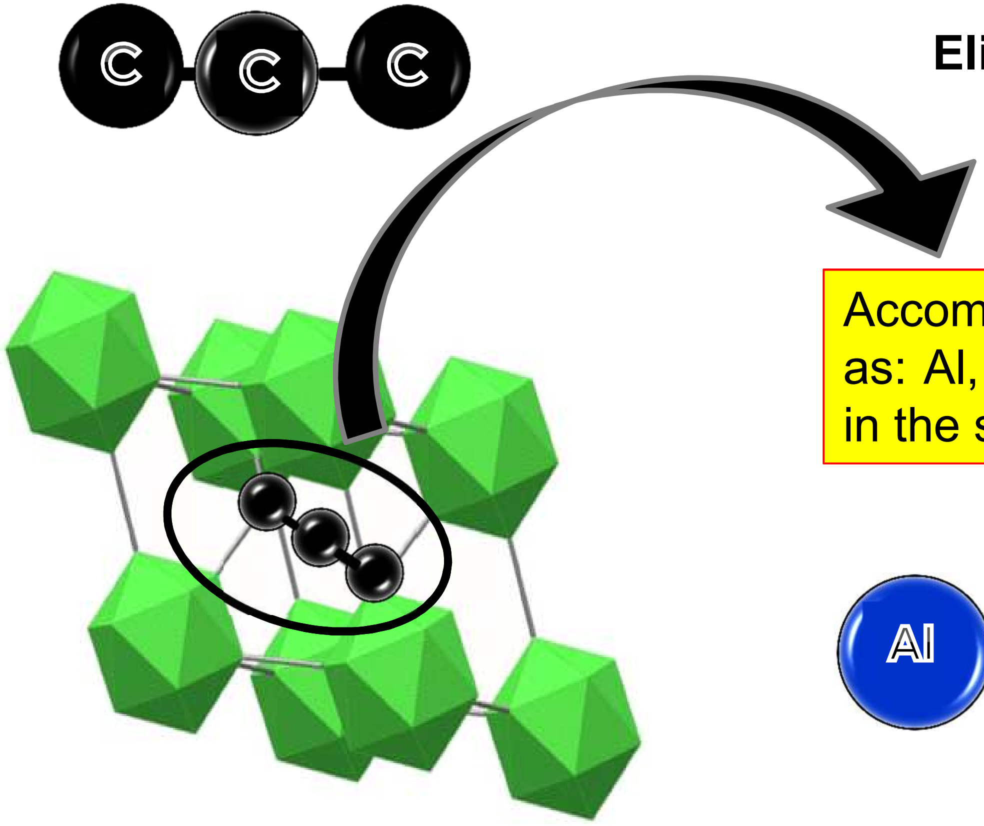
$B_{4.3}C$ – rich carbon side

Rhombohedral Bravais Lattice



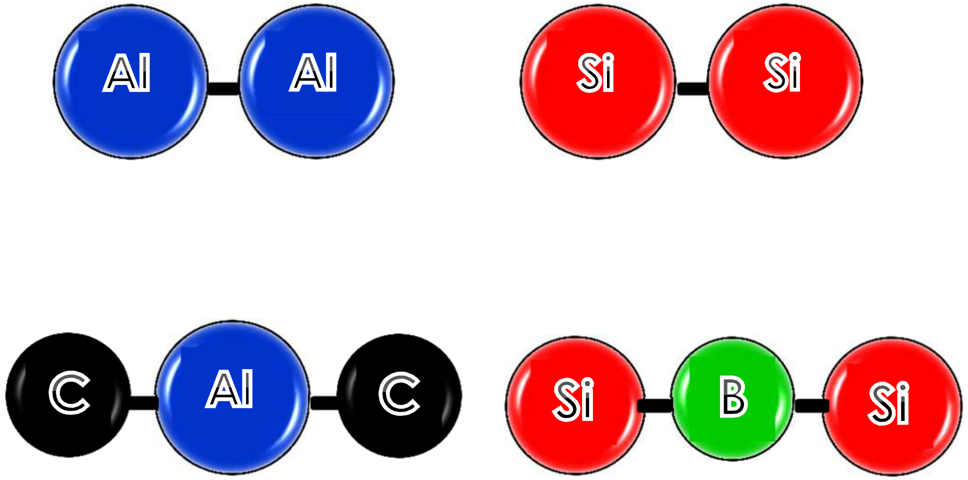
Arrangement of boron icosahedra cross-linked by 3-atoms chain along the (111) axis

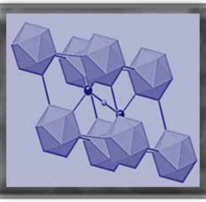
Motivation



Elimination of C-C-C main chain

Accommodation of other elements, such as: Al, Si, P, As and O, without a change in the structure: **solid solutions**

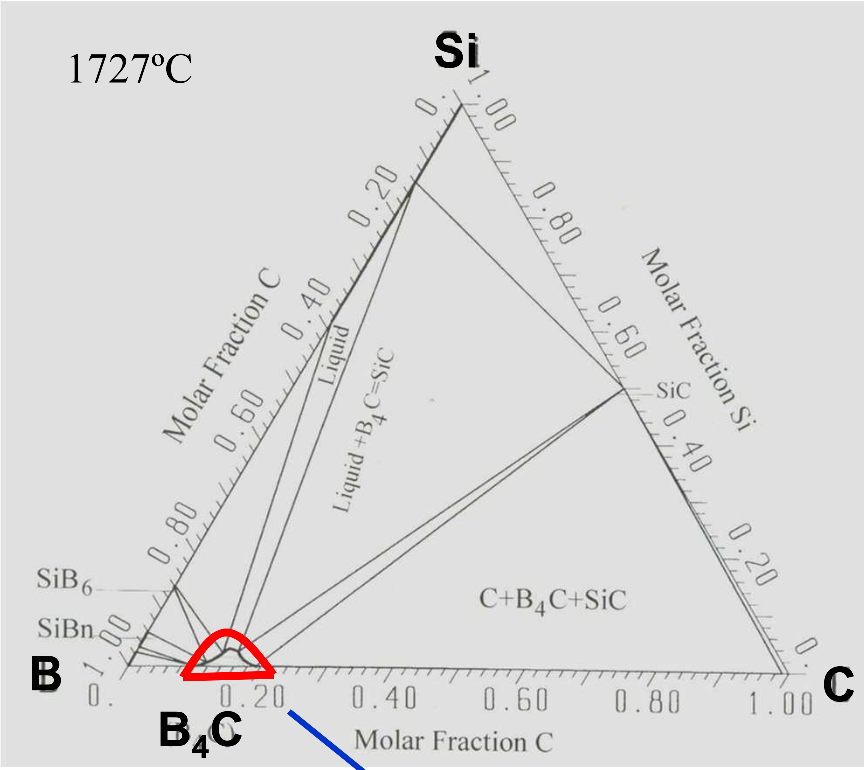


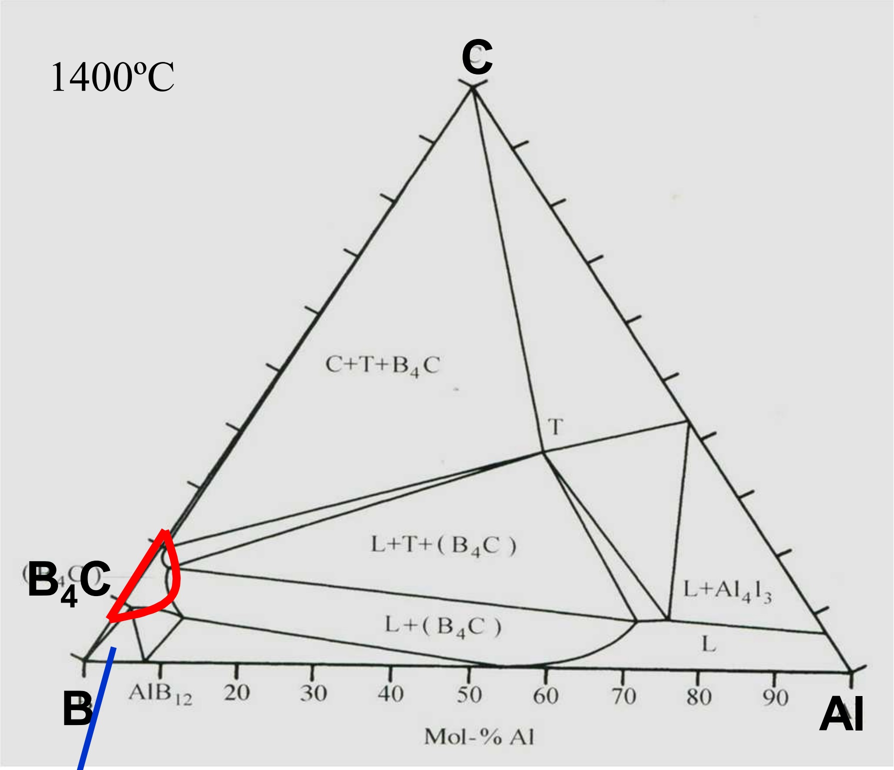


State-of-Art

Ternary Phase Diagram

Very low solid equilibrium solubility





Maximum limit content of 2.5 at.%

- Atomic size
- Melting point

≠

Goals

Modify the chemistry of hard boron carbide ceramic with light elements: **Al**, **Mg** and **Si.**

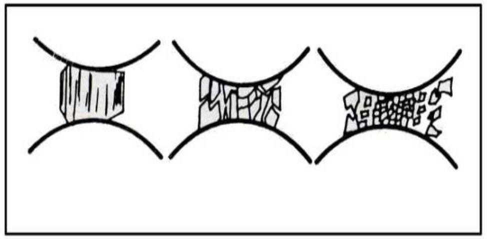
The aim of the present investigation was twofold:

- Produce nanocrystalline grain size solid solutions, by **Mechanical Alloying** of commercially available powders.
- Compact, by non-conventional sintering method, the MA mixtures, using **Shock-Wave Compaction**.

***Far-From-Equilibrium* Processes**

Experimental: powder mixtures

Planetary Ball Mil (Pulverisete 6 – Fritsch)



6-7 at.% Si incorporation leads to a theoretical material with possibly the highest ever HEL.

7at.% of elemental powders:

Al, Mg, Si

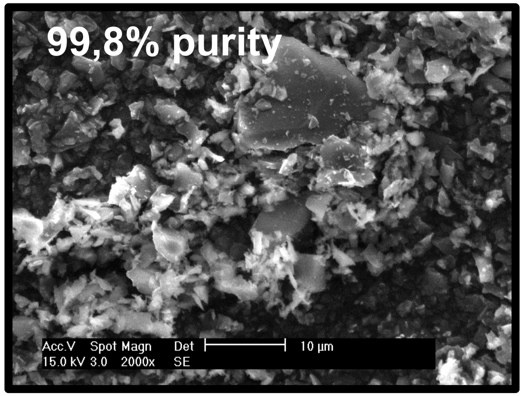
for feed quantity of 21 g

G. Fanchini and M. Chhowalla, to be published
Rutgers University, Piscataway, NJ (USA)

Experimental: powder mixtures

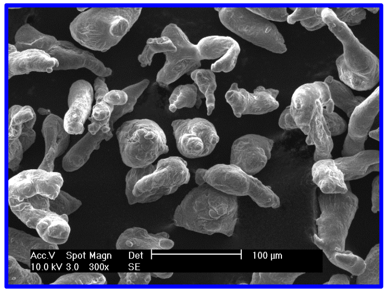
B_4C

Neyco


99,8% purity

Al

0,26g



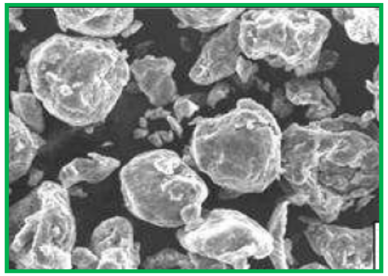
Cerac

B_4C:7Al system

49h milling

Mg

0,67g



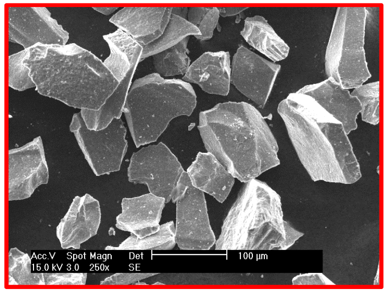
Cerac

B_4C:7Mg system

49h milling

Si

0,77g



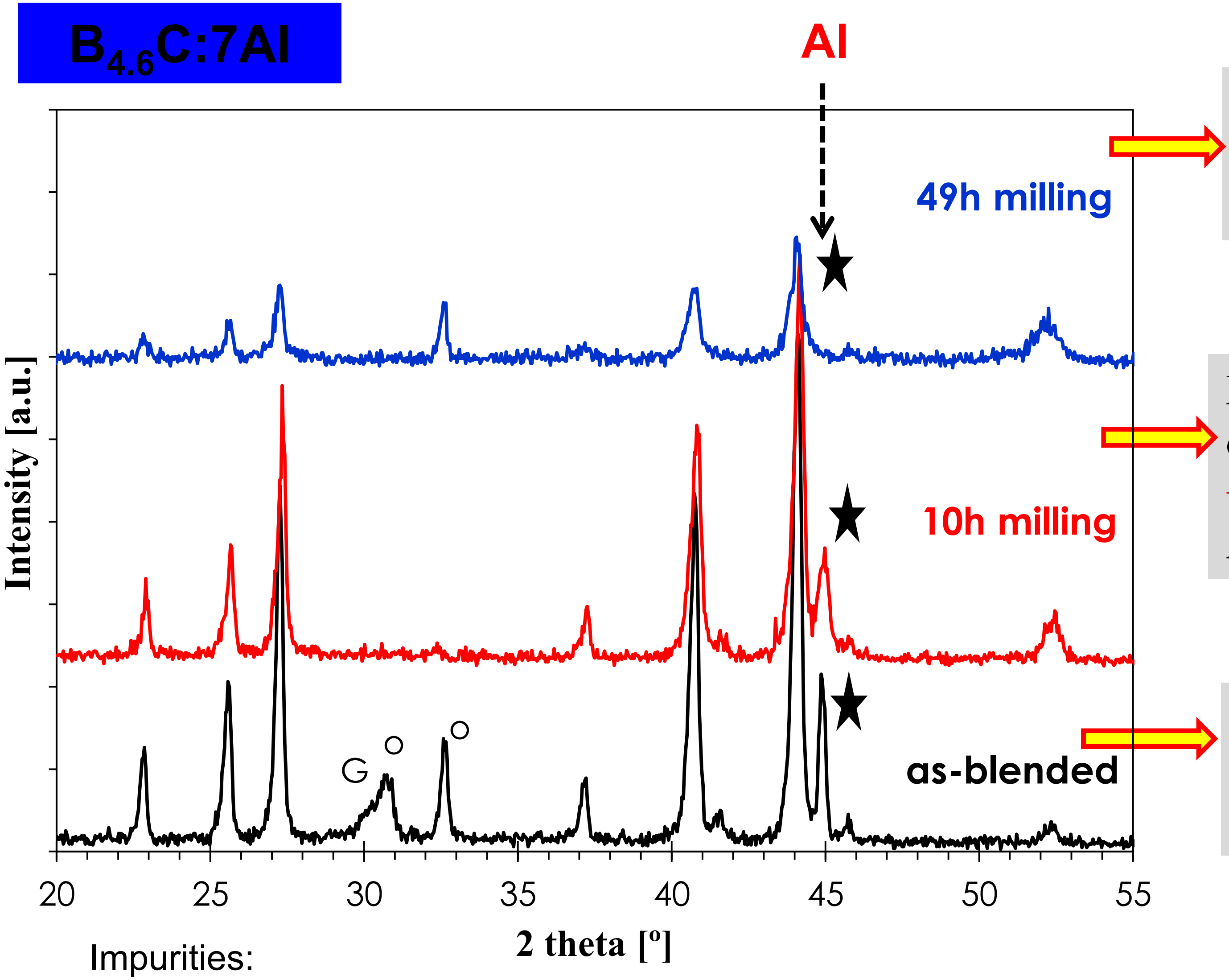
Cerac

B_4C:7Si system

73h milling

Results: evolution during milling

$B_{4.6}C$:7Al



Rhombohedral
Solid solution
B_4 (C, Al)

XRD peaks intensity decreases
+
Al, FCC

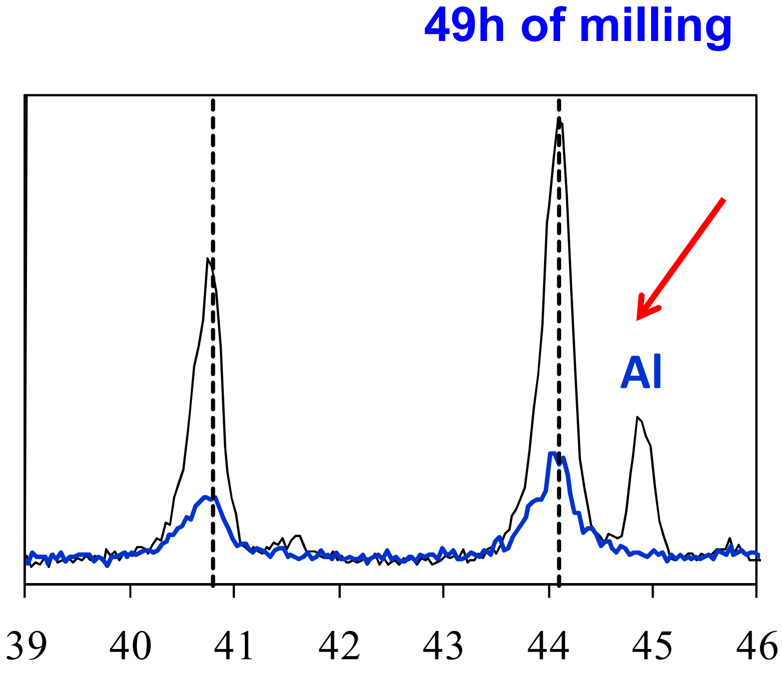
B_4C, Rhombohedral
+
Al, FCC

Impurities:
graphite + boron oxides

Philips X´Pert (Co-Kα) , **X-Ray Diffraction**

Results: evolution during milling

$B_{4.6}C$:7Al

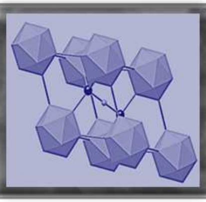


- No new phases are formed.

- Chemical and structural stability after 49h of MA

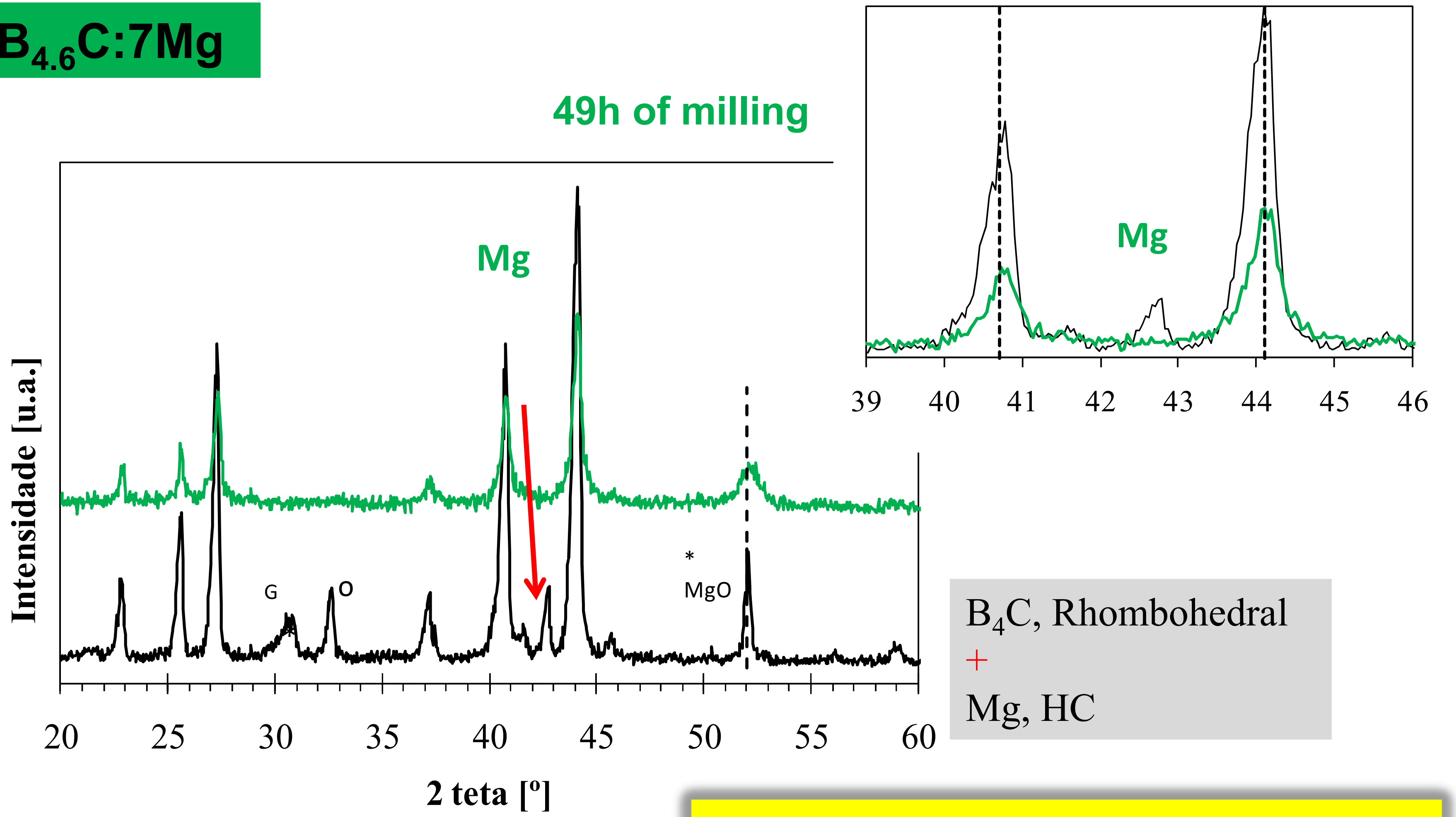
The rhombohedral structure is preserved → **Metastable Structure**

- The broadness of the XRD peaks with milling time is due to the distortion of the crystal lattice and to the reduction in crystallite size.



Results: evolution during milling

$B_{4.6}C$:7Mg



B_4C, Rhombohedral
+
Mg, HC

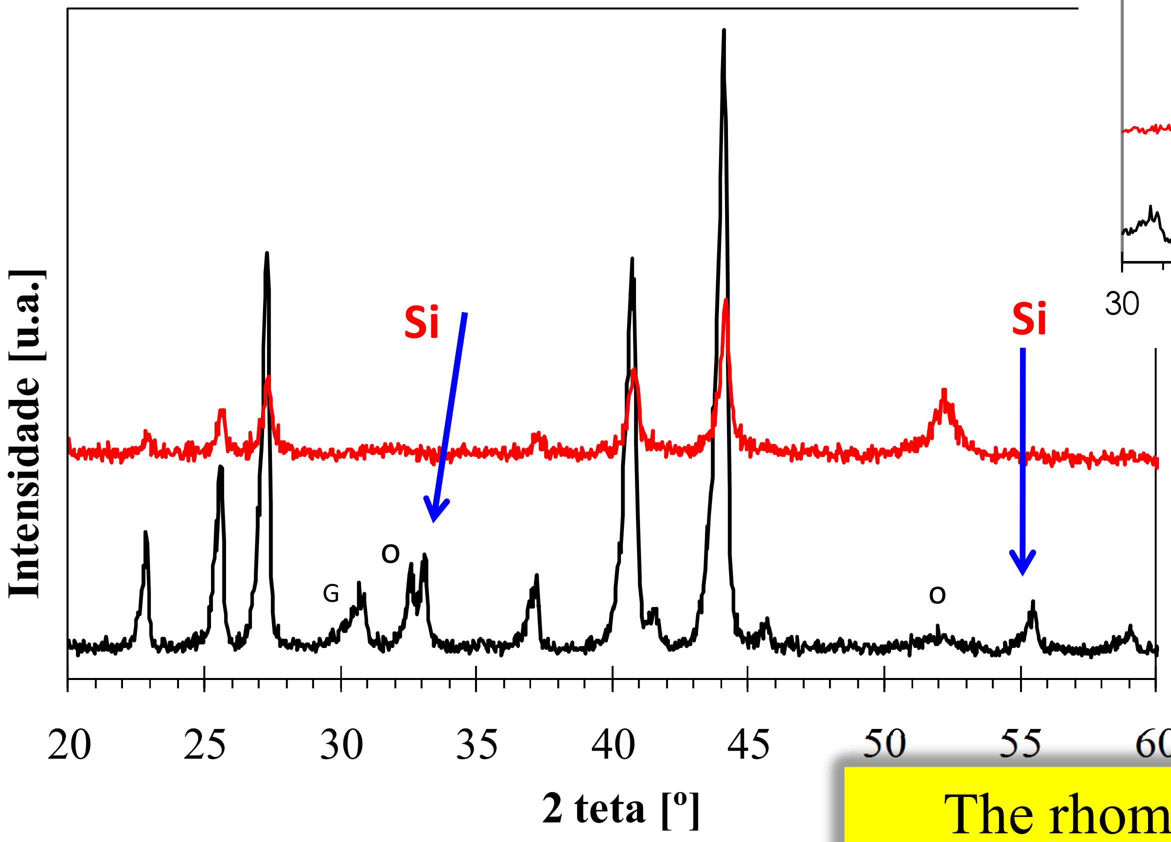
The rhombohedral structure is preserved → **Metastable Structure**

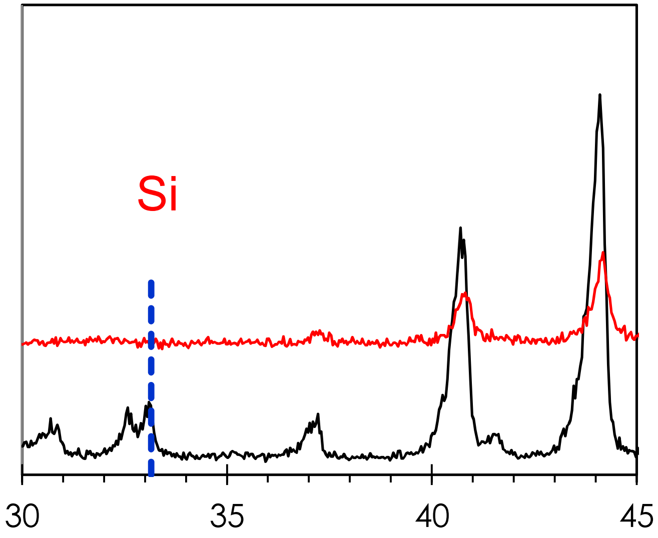
Philips X´Pert (Co-Kα) , **X-Ray Diffraction**

Results: evolution during milling

$B_{4.6}C$:7Si

73h of milling





B_4C, Rhombohedral
+
Si, FCC

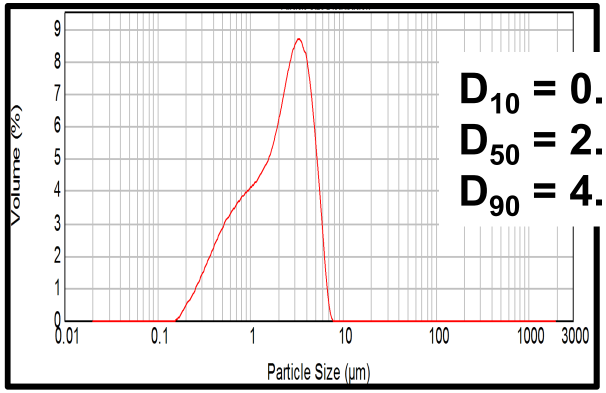
The rhombohedral structure is preserved → **Metastable Structure**

Philips X´Pert (Co-Kα) , **X-Ray Diffraction**

Results: particle distribution

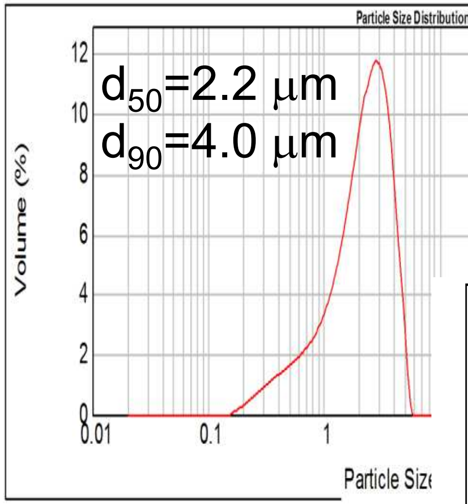
Malver Mastersizer 2000

$B_{82}C_{18}$ (B/C=4.6)



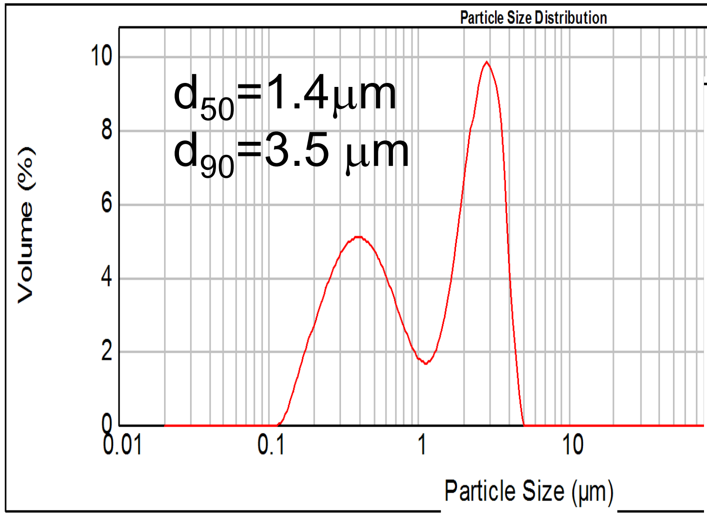
D_{10} = 0.5µm
D_{50} = 2.2µm
D_{90} = 4.6µm

$B_{4.6}C$:7Al



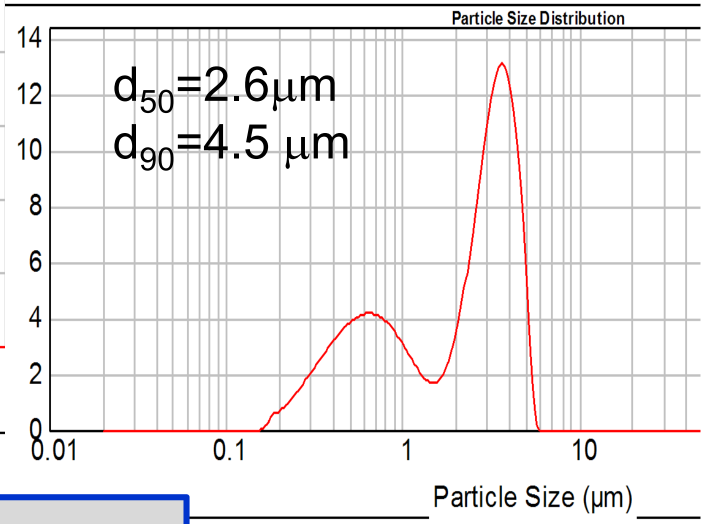
d_{50}=2.2 µm
d_{90}=4.0 µm

$B_{4.6}C$:7Mg



d_{50}=1.4µm
d_{90}=3.5 µm

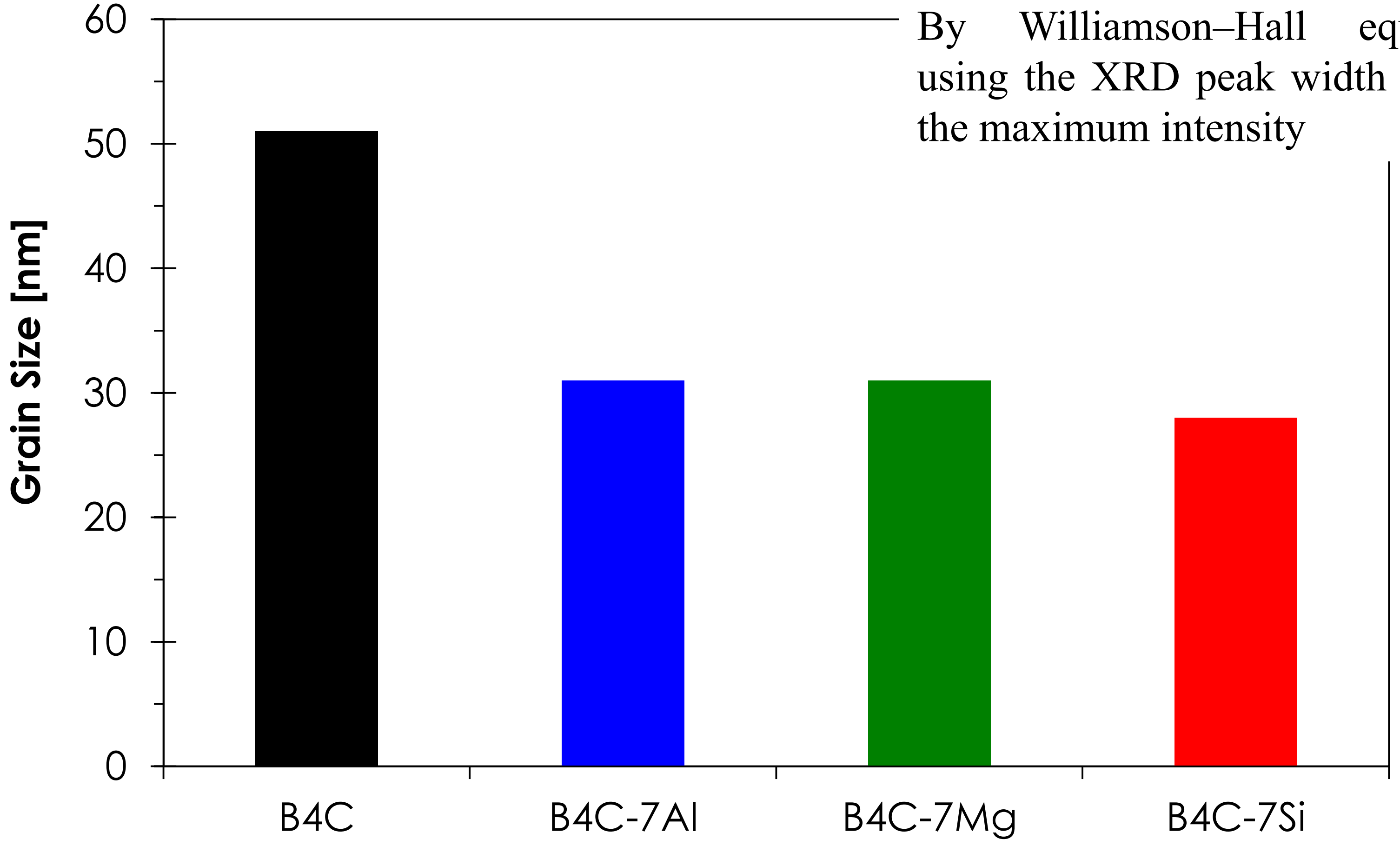
$B_{4.6}C$:7Si



d_{50}=2.6µm
d_{90}=4.5 µm

- Particles agglomeration coexisting with small size ones

Results: grain size

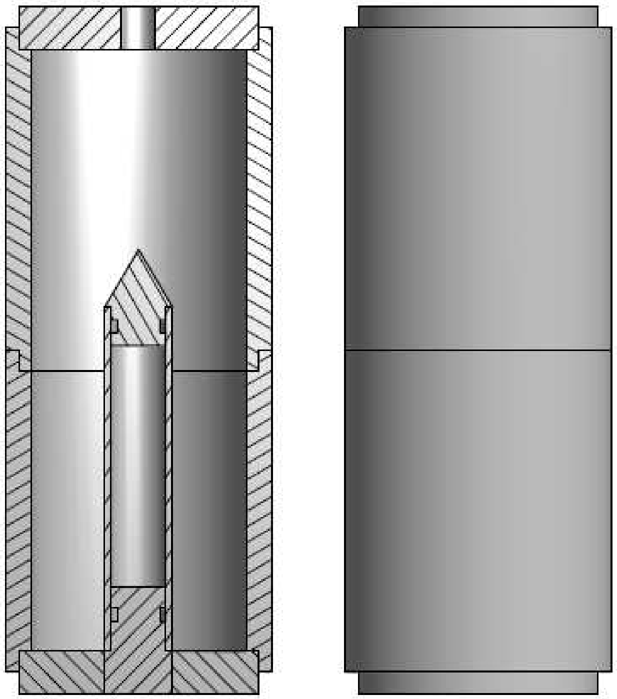


By Williamson–Hall equation, using the XRD peak width at half the maximum intensity

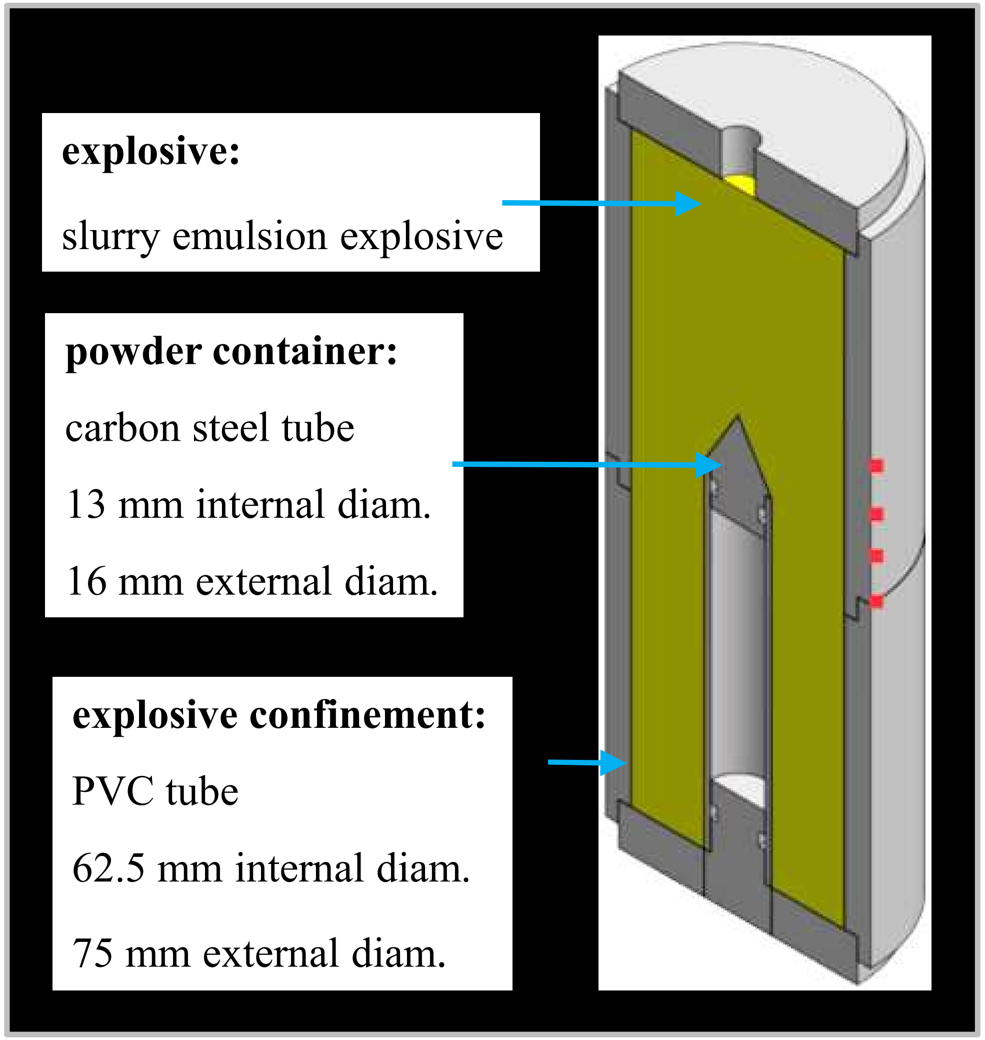
- Reduction of ~40% of the initial grain size

Experimental: powder compaction

Cylindrical configuration



By AUTODESK Educational Product



explosive:

slurry emulsion explosive

powder container:

carbon steel tube

13 mm internal diam.

16 mm external diam.

explosive confinement:

PVC tube

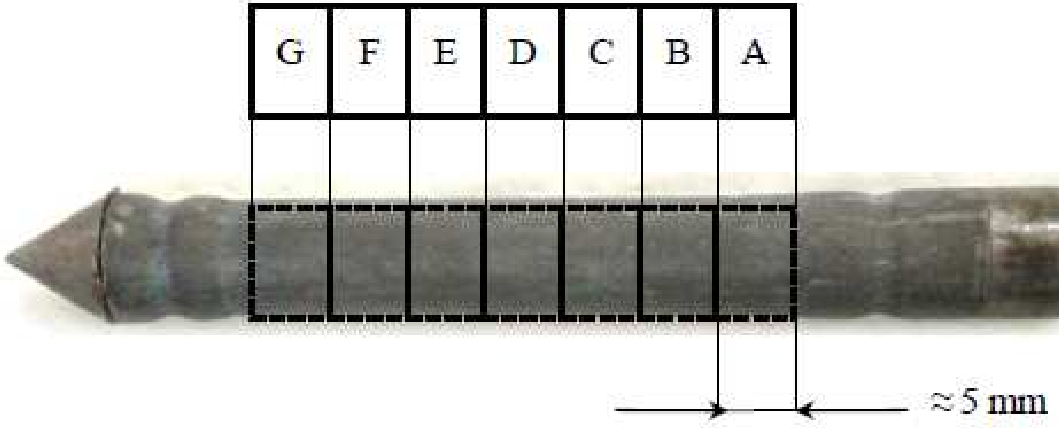
62.5 mm internal diam.

75 mm external diam.

Experimental: powder compaction

Results: commercial B4C

Experimental: samples preparation

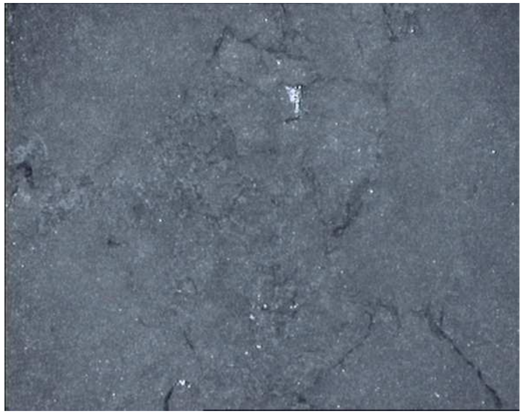


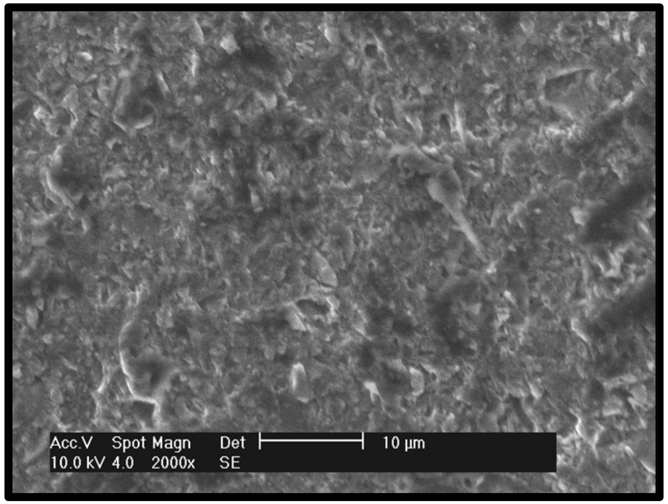
Results: commercial B4C

$B_{4.6}C$

38% TMD
D = 4.8 Km/s

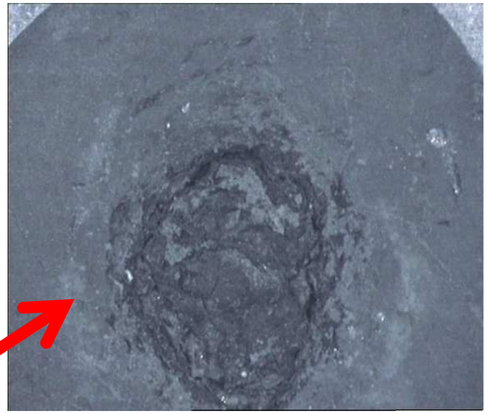
G



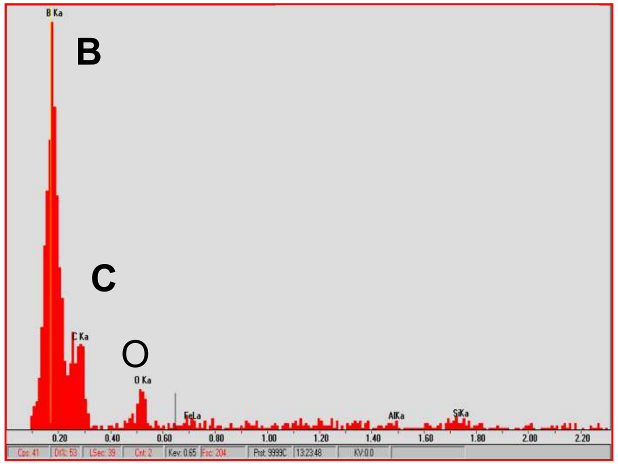


Open-pore microstructure

A



Mach defect



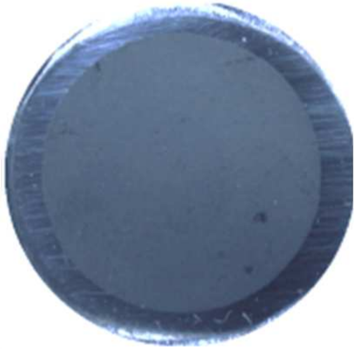
Philips XL30-Series, SEM/EDS **Microscopy**

Results: milled powders

$B_{4.6}C$:Al

55% TMD
D = 5.3 Km/s

G



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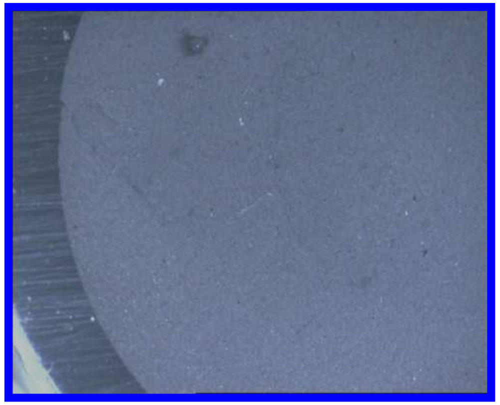
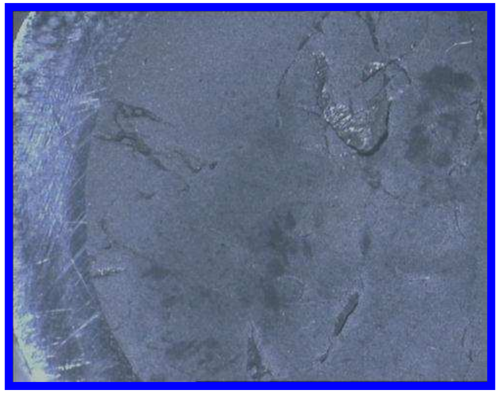
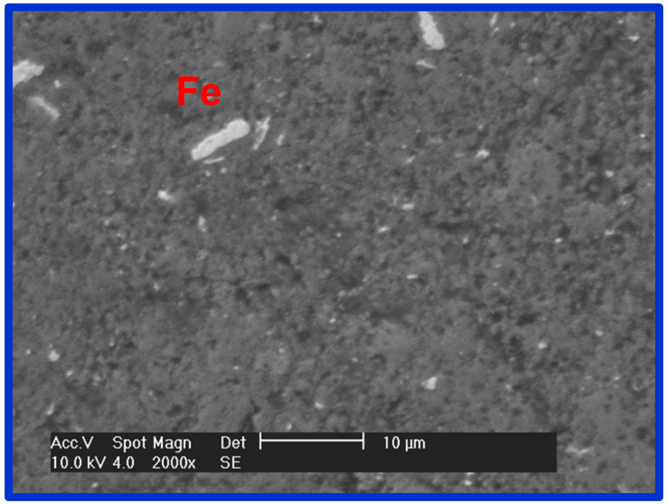
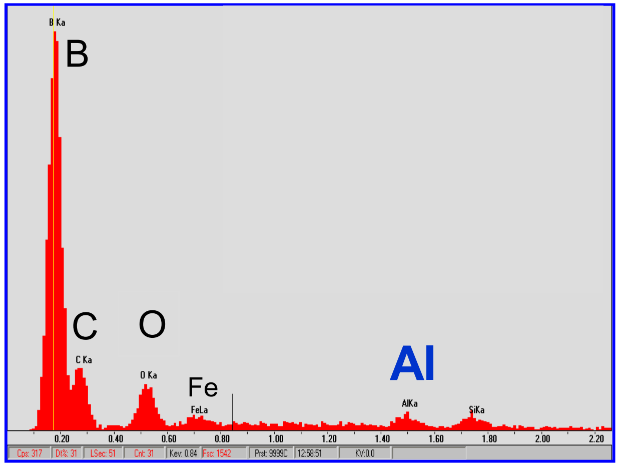




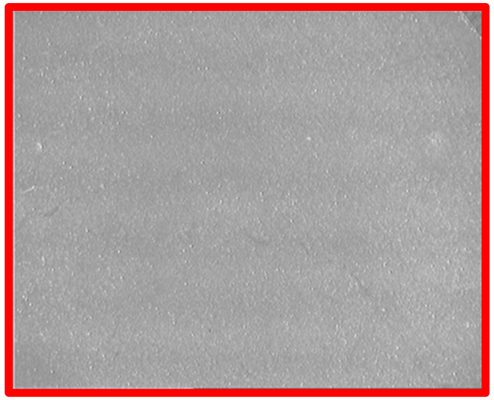


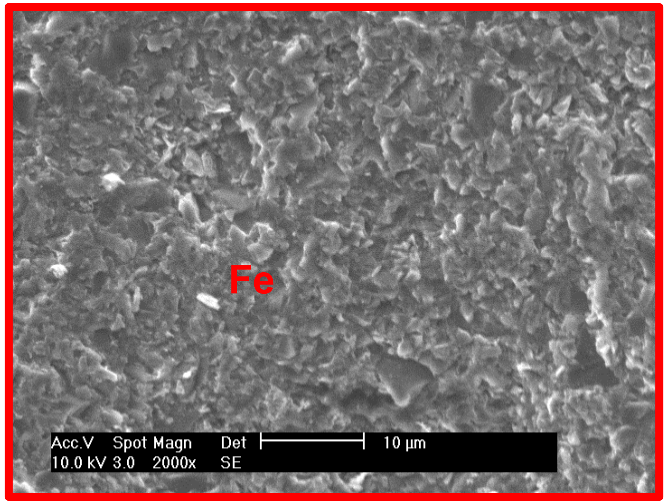


Results: milled powders

$B_{4.6}C$:Si

G





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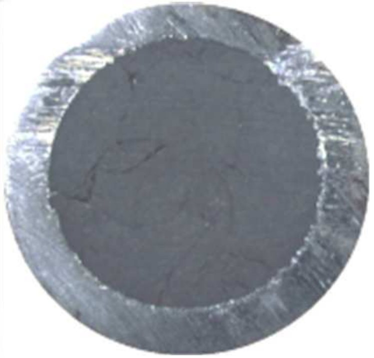
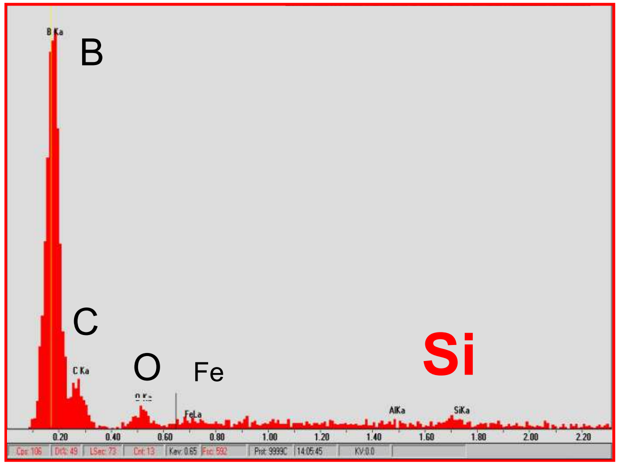
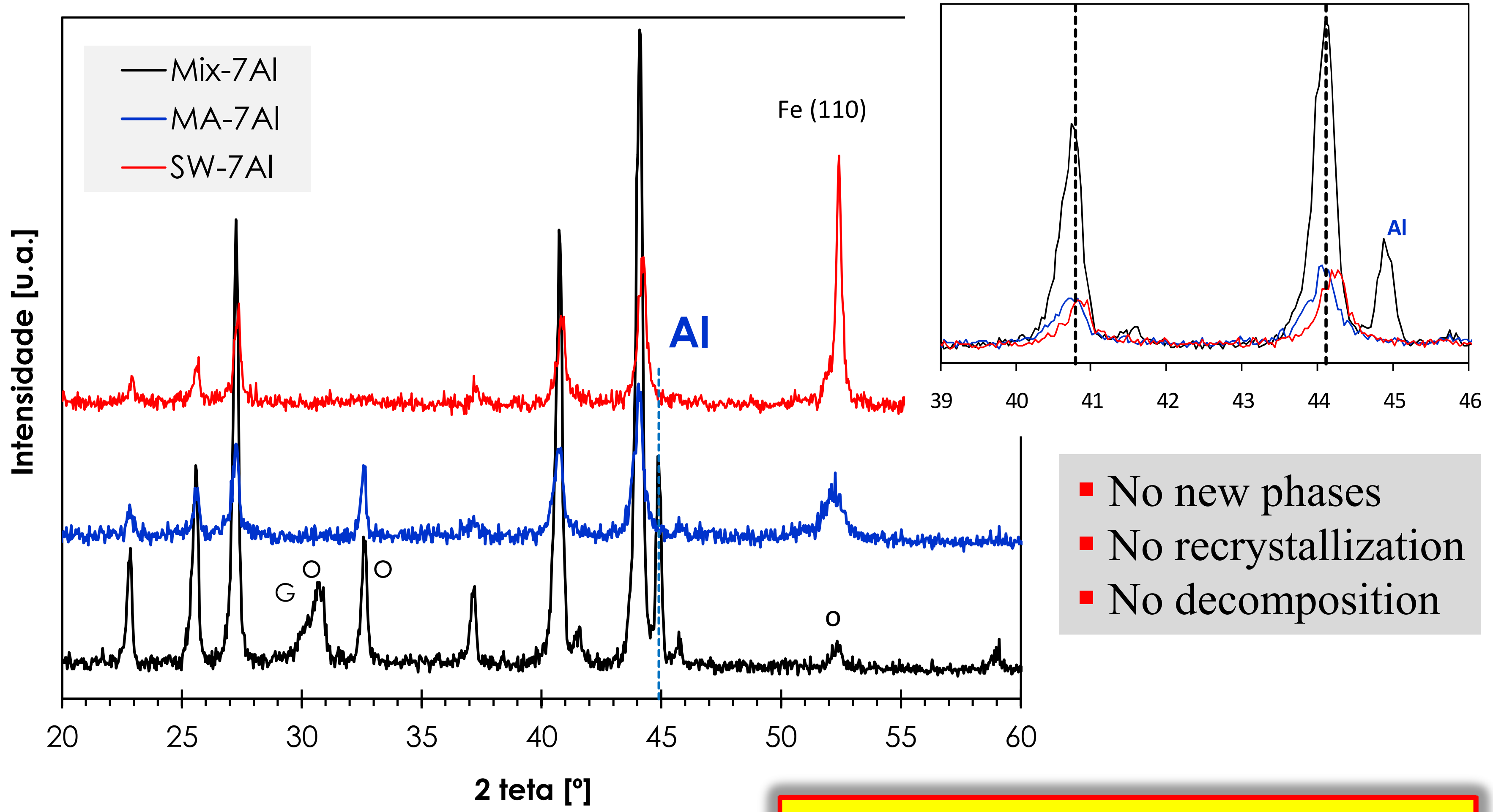




66% TMD
D = 5.3 Km/s

The best compact !

Results: compacted powders

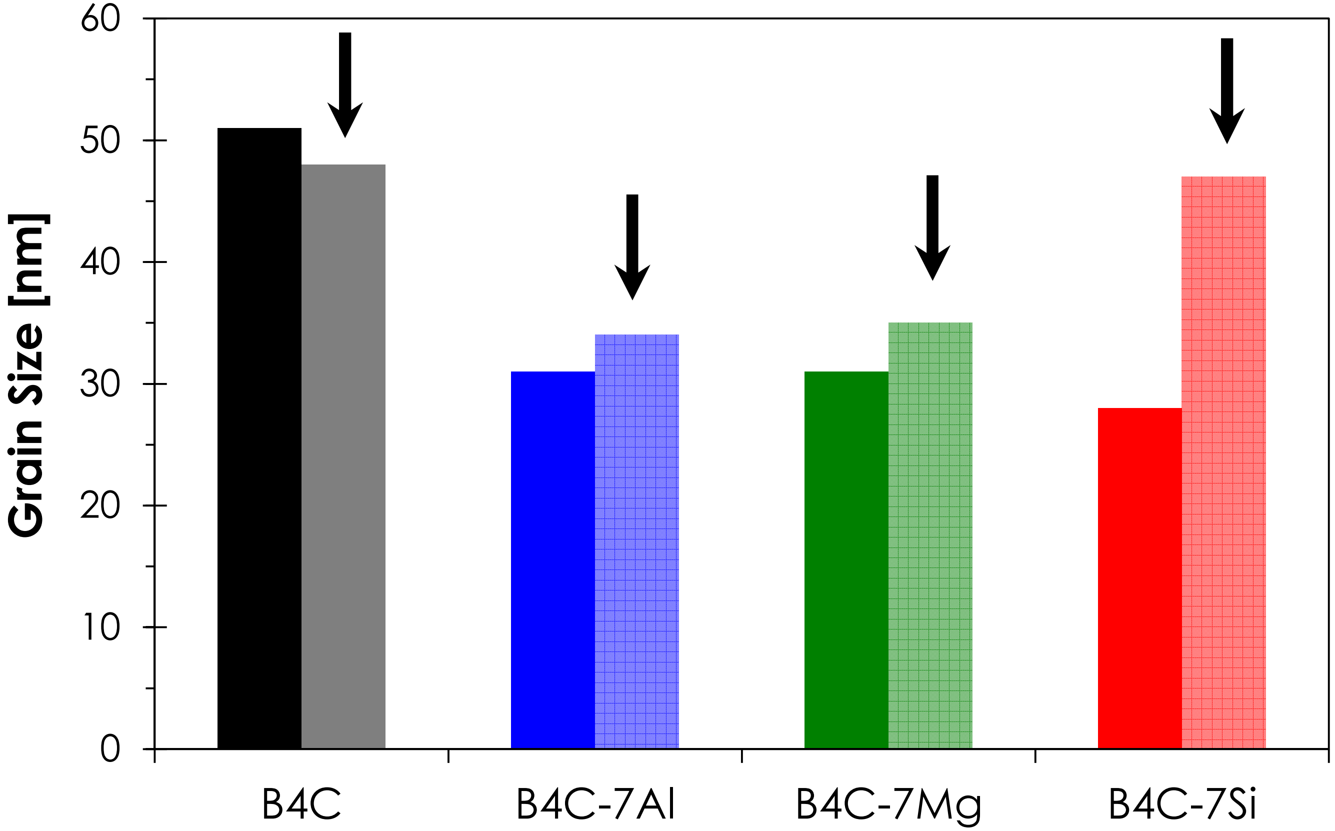


- No new phases
- No recrystallization
- No decomposition

The metastable structure attained by milling is preserved after detonation

Philips X´Pert (Co-Kα) , **X-Ray Diffraction**

Results: compacted powders

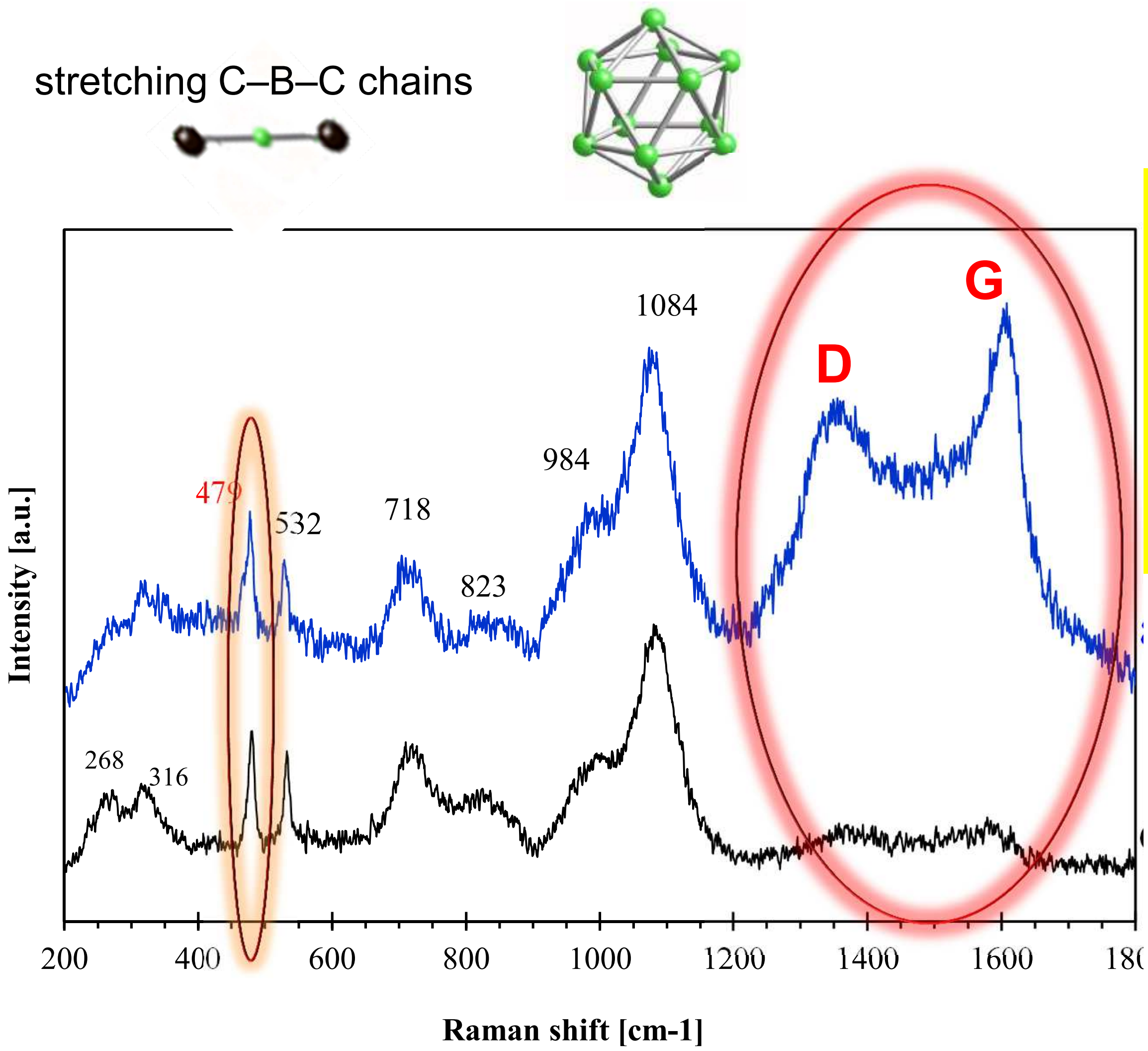


- Grain size remains almost constant after shock wave compaction.
- The exception was only found for the B_4C-Si system.

Results: powder vs bulk

$B_{4.6}C$

stretching C–B–C chains



Two broad Raman bands at ~1300 and ~ 1600 cm^{-1}

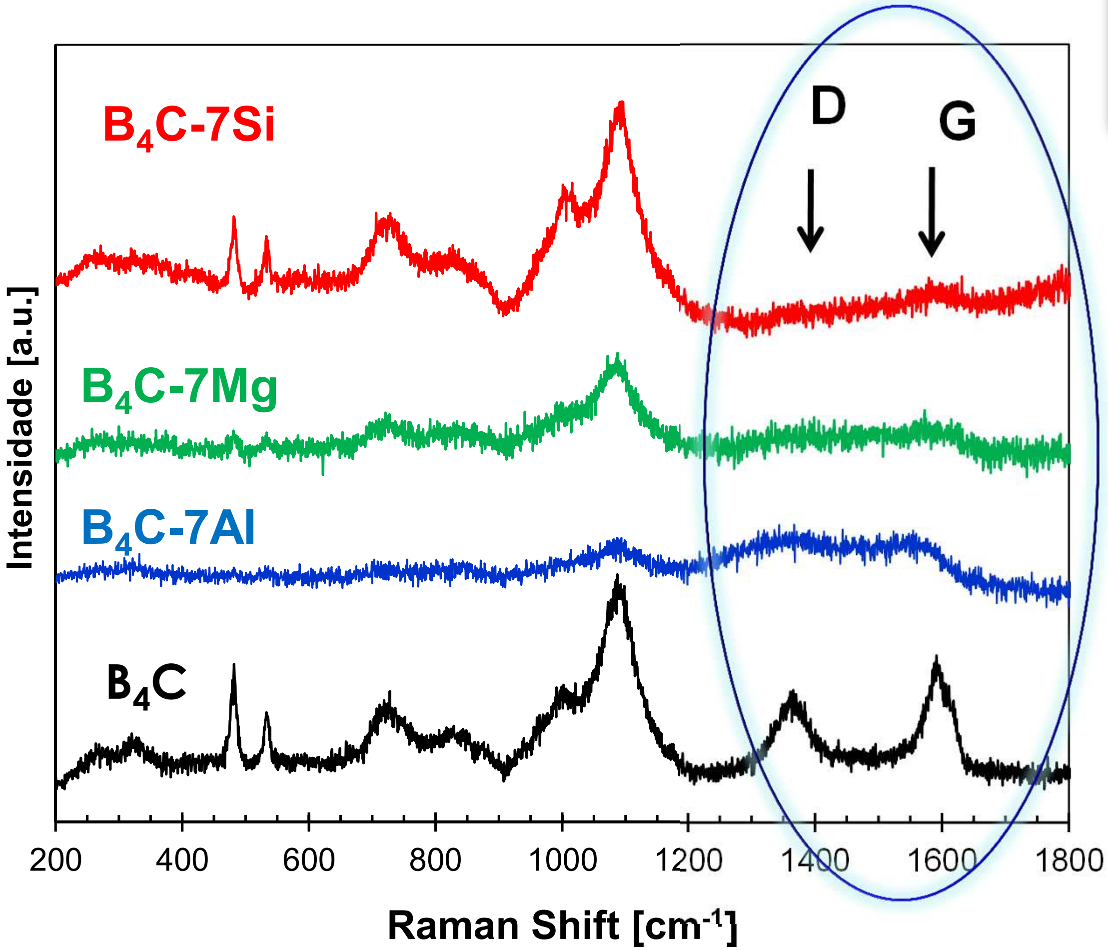
↓

sp^2-sp^3 bonding

Disordered Carbon

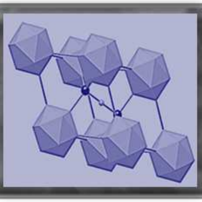
Hariba Jobin-Yvon (50mWAr$^+$ ion laser power, 514.5nm), **Raman Spectroscopy**

Results: compacted powders



An additional positive effect

No amorphous carbon



Conclusions

✓Applying Mechanical Alloying technique, metastable solid solutions were successfully obtained. Besides the good reinforcement homogeneity, also particle powder refinement were obtained, being important approaches to improve density and brittle fracture during the subsequent consolidation.

✓Shock Compression has different features from static compression: short duration and shear stress, which can be used as a consolidation method of non-equilibrium materials without recrystallization or decomposition.

✓Further studies are currently in progress to determine the exact Si, Al and Mg atoms position in the rhombohedral B_4C structure.

Tank you for listening !