# Comparison of the Densification and Properties of Stoichiometrically Modified Boron Carbide

Richard A. Haber
Steve Miller
M.Fatih Toksoy

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# Objectives

-Modify and synthesize clean, single phase, sub-micron boron carbide powder

-Densify commercial and stoichiometrically modified boron carbide

- Develop an improved understanding of the relations between microstructural characteristics and mechanical properties of varying boron carbide powder

# Methods

## Pre-Densification

- Commercial powders
- Stoichiometrically modified boron carbide (Graphite Transport Reactor )
- Powders characterization (XRD, FESEM, Particle Size, Chemical Analysis)

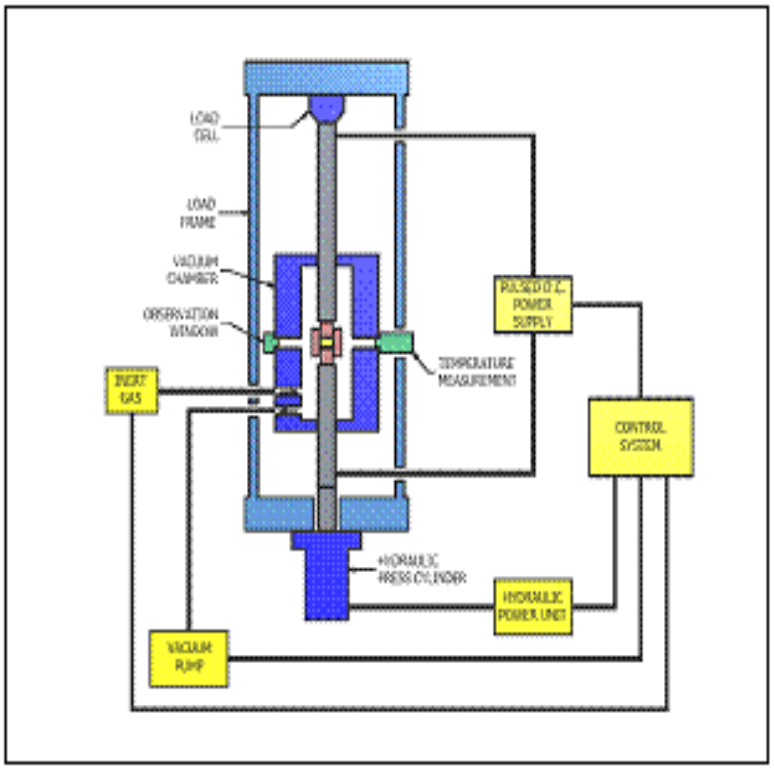
## Spark Plasma Sintering

- Rapid and uniform heating
- Full density and controllable porosity
- Fast cycle times
- Minimal grain growth

## Post Densification

- Hardness Test (Knoop Hardness Tests)
- Microstructural analysis (FESEM, Grain Size, Fracture Analysis )
- Chemical analysis (XRD, Titration, Carbon Analysis)

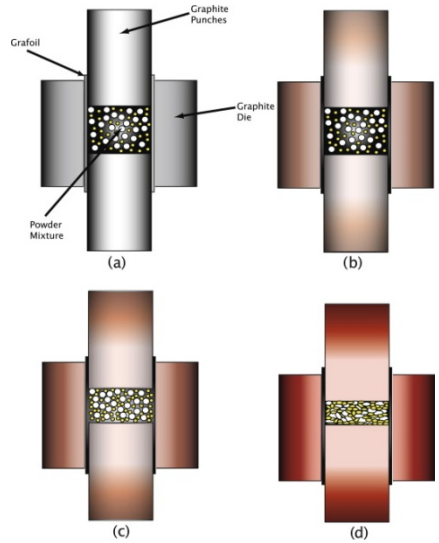
# Spark Plasma Sintering




Basic configuration of a

Spark Plasma Sintering (SPS) machine

- Rapid and uniform heat throughout the sample
- Full density and controllable porosity
- Pre-forming and binders not necessary
- Fast cycle times
- Vaporization of pre-existing contamination
- Minimal grain growth
- Minimal affect on microstructure




# Commercial Boron Carbide

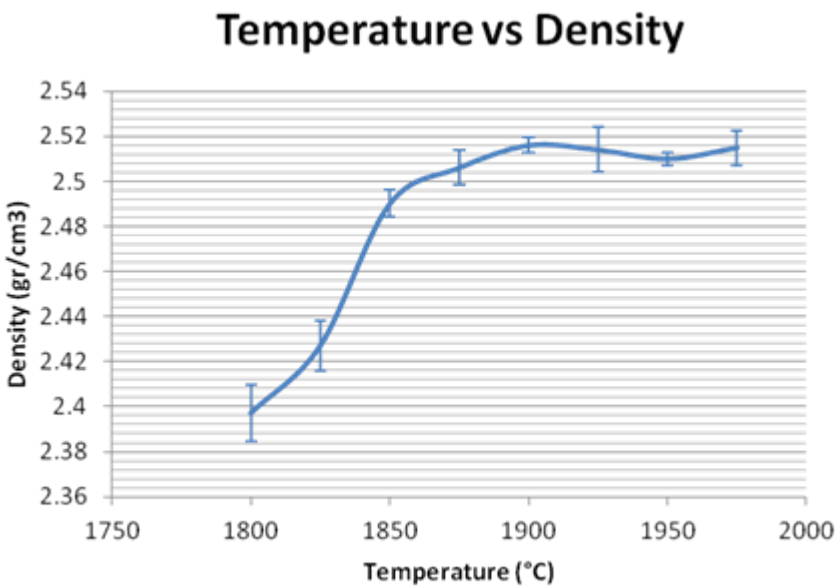
| Trial | Temperature (C) | Heating Rate | Pressure | Dwell |
|---|---|---|---|---|
| 1 | 1900 | 300C/min | 50 MPa | 20 min. |
| 2 | 1925 | 300C/min | 50 MPa | 20 min. |
| 3 | 1950 | 300C/min | 50 MPa | 20 min. |
| 4 | 1975 | 300C/min | 50 MPa | 20 min. |
| 5 | 1850 | 300C/min | 50 MPa | 20 min. |
| 6 | 1875 | 300C/min | 50 MPa | 20 min. |
| 7 | 1800 | 300C/min | 50 MPa | 20 min. |
| 8 | 1825 | 300C/min | 50 MPa | 20 min. |
| 9 | 1850 | 300C/min | 50 MPa | 0 min. |
| 10 | 1850 | 300C/min | 50 MPa | 10 min. |
| 11 | 1850 | 300C/min | 50 MPa | 30 min. |
| 12 | 1950 | 300C/min | 50 MPa | 0 min. |
| 13 | 1950 | 300C/min | 50 MPa | 10 min. |
| 14 | 1850 | 300C/min | 5 MPa | 20 min. |
| 15 | 1850 | 300C/min | 20 Mpa | 20 min. |
| 16 | 1850 | 300C/min | 35 MPa | 20 min. |
| 17 | 1850 | 300C/min | 60 MPa | 20 min. |
| 18 | 1850 | 100/min | 50 MPa | 10 min. |
| 19 | 1850 | 200/min | 50 MPa | 10 min. |
| 20 | 1850 | 400/min | 50 MPa | 10 min. |

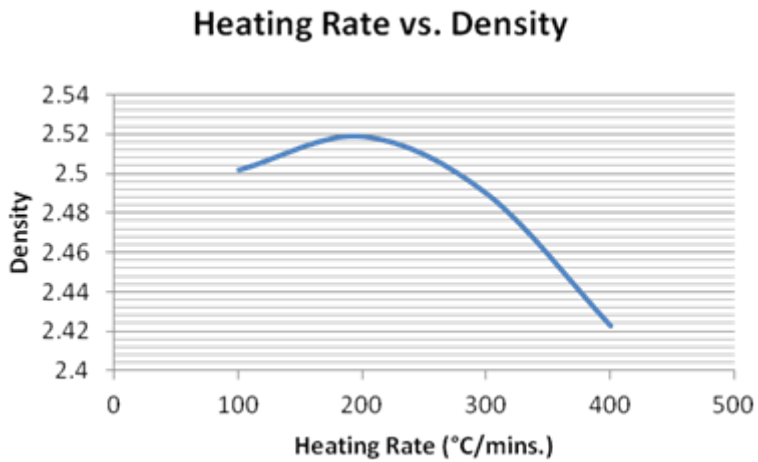
Commercial $B_4C$ are processed to determine optimum sintering cycle

Average particles size of raw material is 1.9µm

High Density Samples were taken to further evaluation

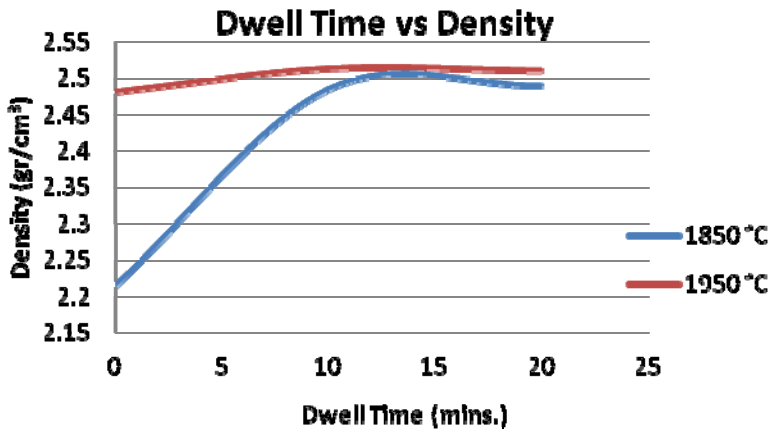
# Commercial Boron Carbide



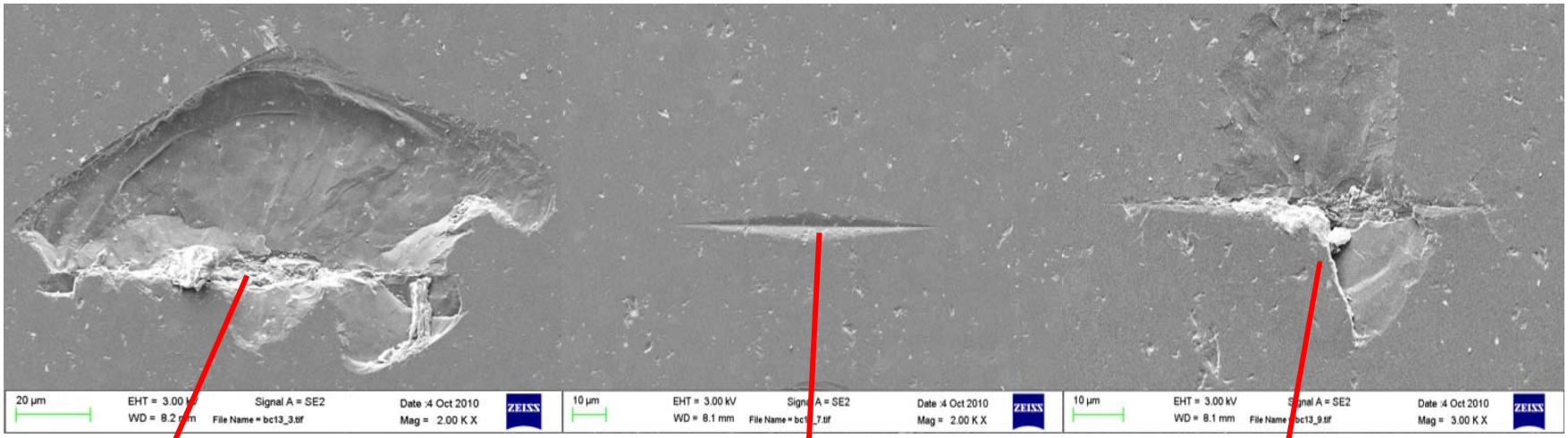




- Commercial boron carbide powders are processed and fully densified by Spark Plasma Sintering
- Variables are examined

(Temperature, Pressure, Dwell Time, Heating Rate)



# Commercial Boron Carbide



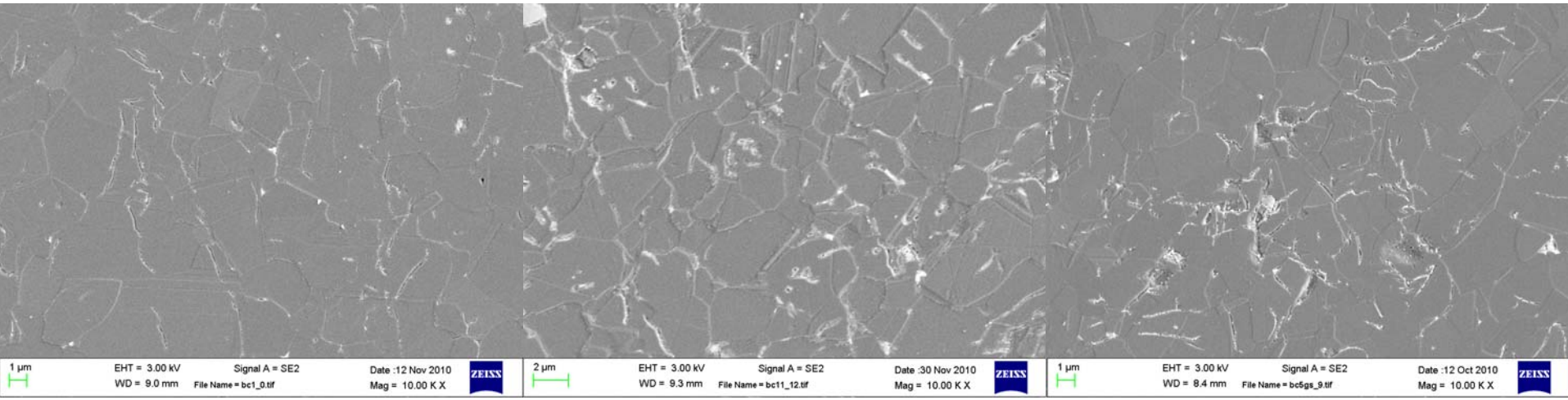

-Massive crack growth at 2kg load and clear indent at 1kg load.

-Most of the samples can't resist to 2kg load and exhibit massive crack growth at 2kg.

- Massive crack growth at carbon rich area at 1kg load

- Unlikely to have massive results at 1kg load

# Commercial Boron Carbide



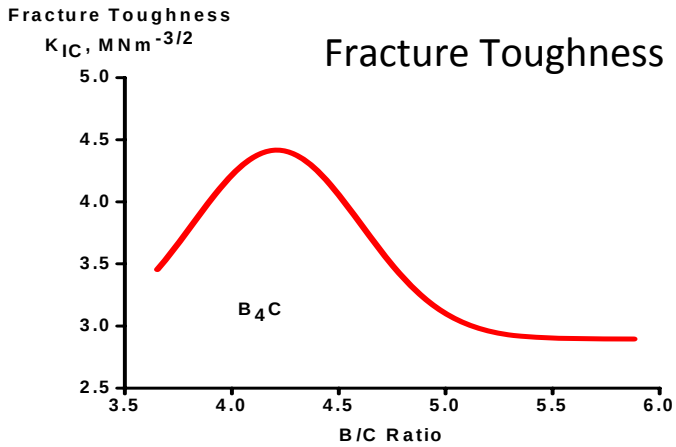

- Average grain size is above 3.0 µm
- Hardness result were taken at Knoop Hardness with 1kg. load
- Average of 2200-2250 HK hardness results above 2.49gr/cm $^3$
- 2050-2150 HK hardness results below 2/49gr/cm $^3$
- Abnormal grain growth in some areas
- A lot of pullouts and inclusions

# Mechanical Properties and B/C Ratio

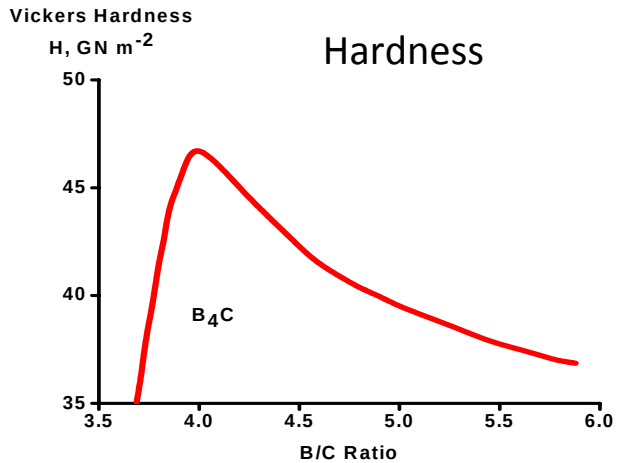
- Stoichiometry affects the hardness and fracture toughness of $B_4C$.
- Composition and residual carbon affects hardness and toughness
- Grain size is also affects properties according to Hall-Petch eqution.

**To improve properties:**

- Highly pure, single phase
- Submicron, narrow size distribution
- Stoichometric $B_4C$ powder
- with Rapid Carbothermal Reduction??



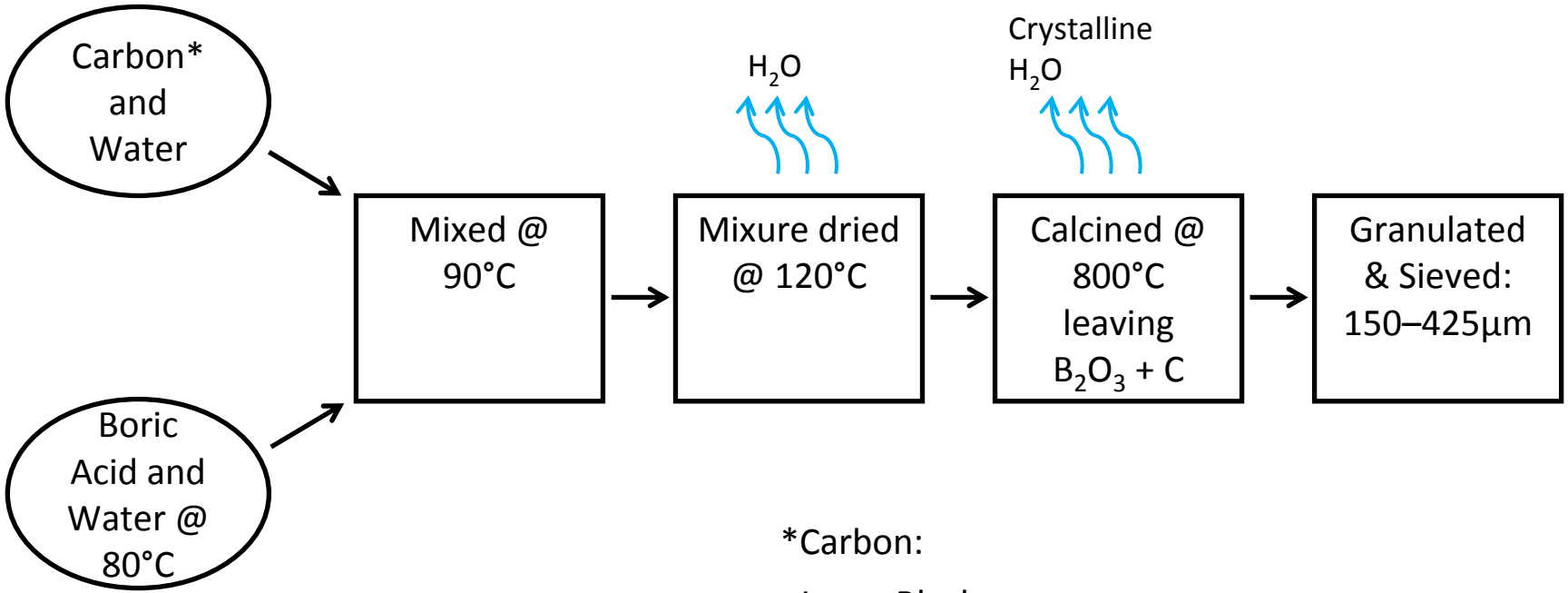

Fracture Toughness




Hardness

K. Nihara et. al., *Comm. Am. Cer. Soc.*, Jan. 1984.

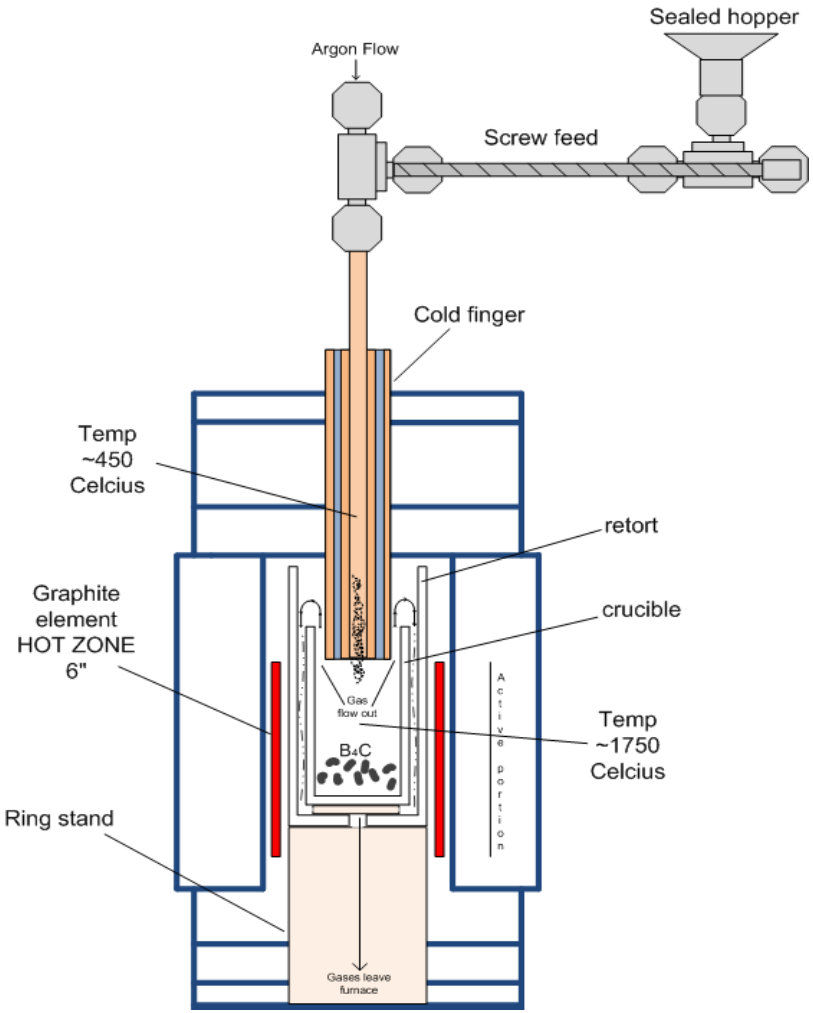
# Precursor Preparation




*Carbon:

- Lamp Black
- Vulcan XC-70
- Cornstarch

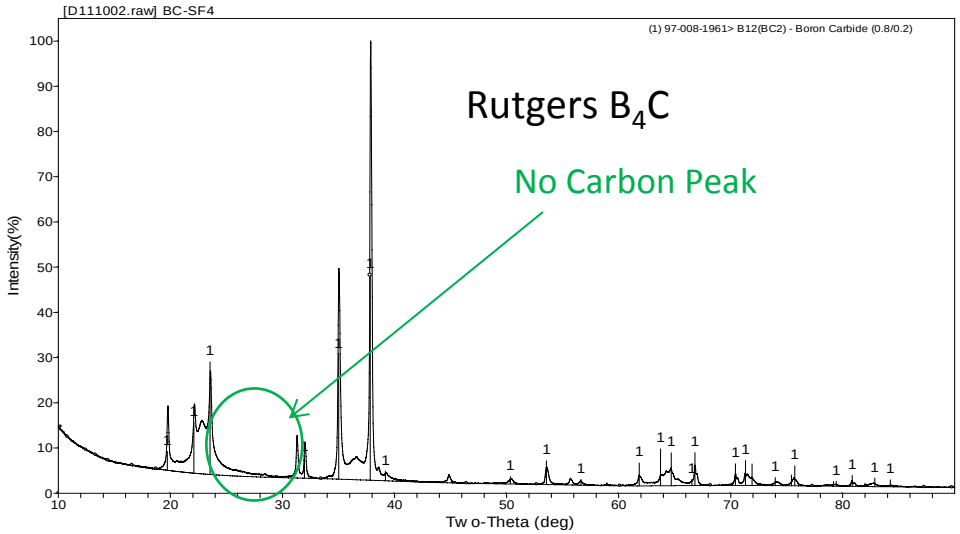
# Rutgers Rapid Carbothermal Furnace



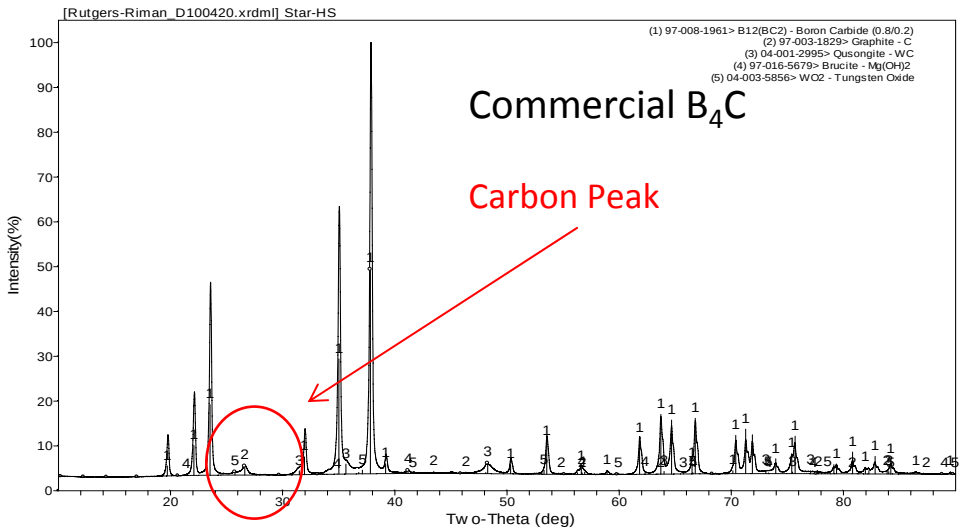

Experimental Procedure

- Graphite crucible placed in furnace and heated to >1750°C
- Intimate $C/B_2O_3$ mixture (precursor) loaded into screw feeder or drop-thru hopper
- Samples are based on a certain mass dropped/fed at a given rate and temp
- Precursor falls through water cooled copper lance placed above hot-zone
- Precursor falls into hot zone and is heated at a rapid rate. Powder accumulates in the crucible
- Precursor feed rate at ~1 g/min
- Product washed in hot, dilute HCl solution (pH = 3) to remove excess boron oxide

# Eliminating Free Carbon




- XRD shows free carbon and other impurities eliminated from $B_4C$ produced by rapid carbothermal reduction




- Commercial $B_4C$ shows free carbon and other impurities, likely from milling/post synthesis processing

# Lattice Parameters and Stoichiometry

| Sample ID | Approximate Composition |
|---|---|
| ESK Tetrabor 3000F | $B_{5.90}C$ |
| UK Abrasive 0.5µm | $B_{5.25}C$ |
| Superior Graphite Grade M | $B_{5.10}C$ |
| UK Abrasive 1.3 µm | $B_{4.99}C$ |
| SSI Grade B | $B_{4.81}C$ |
| Starck Grade MS | $B_{4.71}C$ |
| Electro Abrasives 2.5 µm | $B_{4.49}C$ |
| Electro Abrasives 1200 | $B_{4.24}C$ |
| Rutgers BC-SF1 | $B_{4.10}C$ |
| Rutgers BC-ST1 | $B_{4.00}C$ |
| Rutgers BC-SF2 | $B_{3.95}C$ |
| Rutgers BC-SF3 | $B_{3.95}C$ |

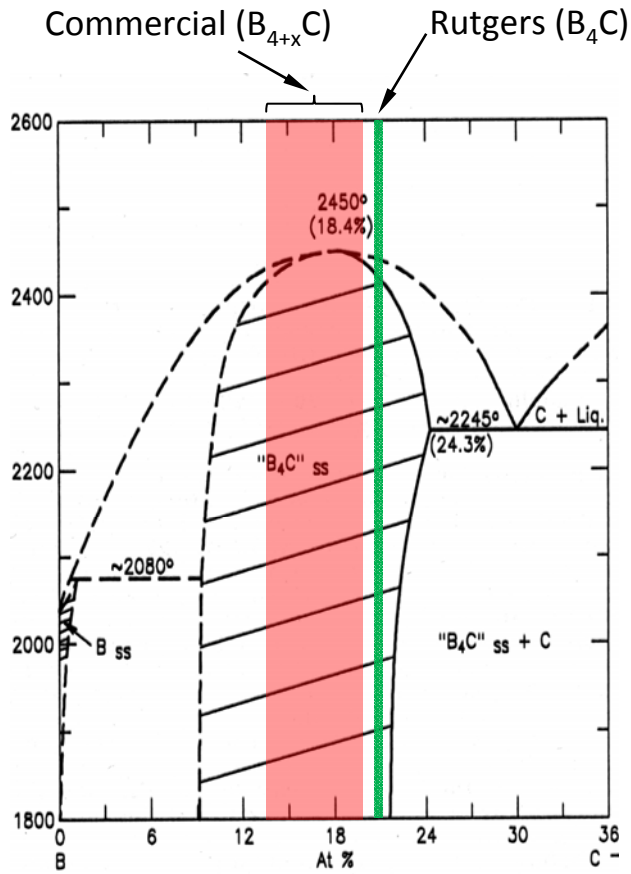
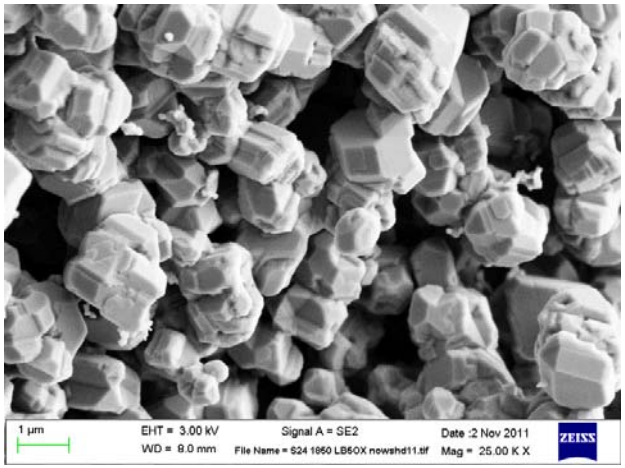


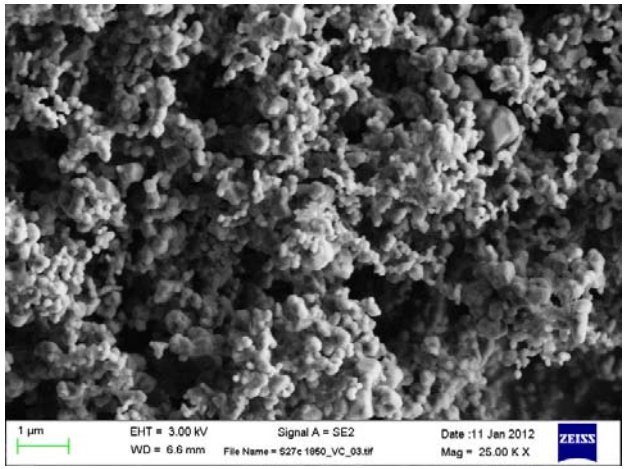

Fig. 8856—System B-C. Solid state phase equilibria
M. Beauvy, *J. Less-Common Met.*, **90** [2] 169-17
(1983).

# Particle Size Distribution

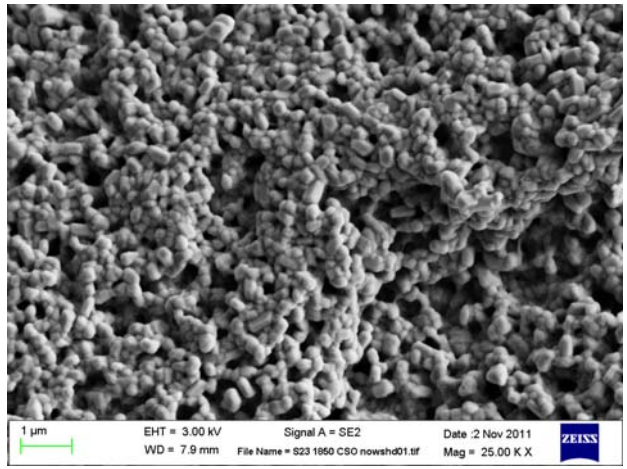
Lamp Black




Vulcan XC-70




Corn Starch



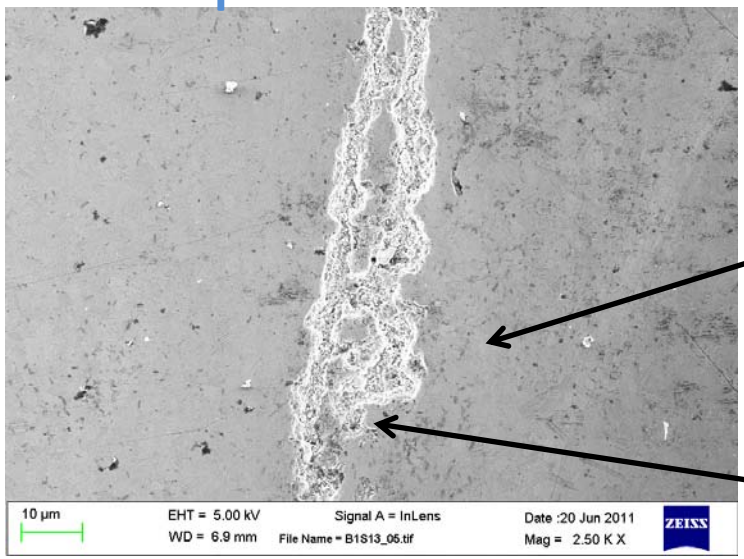

- Clear morphological difference between the boron carbide processed with lamp black, Vulcan XC-70 and cornstarch
- Particle size distributions
  - Lampblack → d(0.9)=0.9µm
  - VC XC-70 → d(0.9)=0.35µm
  - Cornstarch → d(0.9)=0.30µm

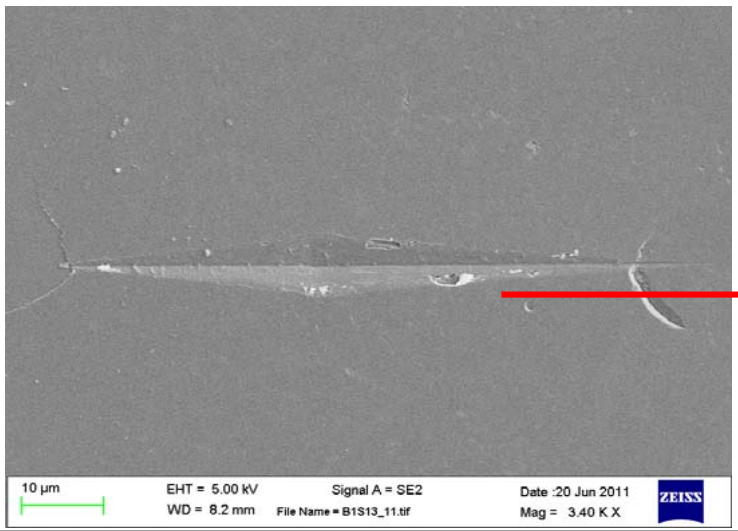
# Spark Plasma Sintering

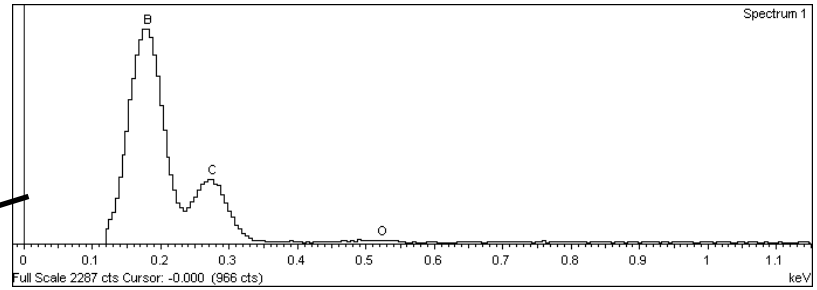
| Sample | Conditions | C % (powder) | Density | HK Low | HK Avarage | HK High |
|---|---|---|---|---|---|---|
| Rutgers B1 LB | 1850 C - 50 MPa | 7.70% | 2.485 g/cm3 | 2179 | 2237 | 2321 |
| Rutgers B2 LB | 1850 C - 50 MPa | 8.50% | 2.398 g/cm3 | 2163 | 2216 | 2268 |
| Rutgers B3 CS | 1850 C - 50 MPa | 4.00% | 2.492g/cm3 | 2026 | 2263 | 2400 |
| Rutgers B4 CS | 1850 C - 50 MPa | 4.50% | 2.514g/cm3 | 2132 | 2295 | 2370 |
| Rutgers B5 LBCS | 1850 C - 50 MPa | -- | 2.494g/cm3 | 2280 | 2315 | 2380 |
| Rutgers B6 VC | 1850 C - 50 MPa | -- | 2.514g/cm3 | 2280 | 2295 | 2309 |
| Rutgers B7 VC | 1850 C - 50 MPa | -- | 2.511g/cm3 | 2300 | 2359 | 2400 |
| Commercial 5 | 1850 C - 50 MPa | 3-4 % | 2.49 g/cm3 | 2100 | 2148 | 2212 |

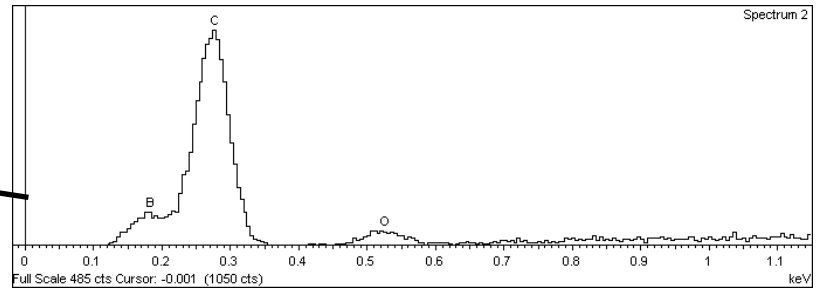
- High densities with existence and absence of free carbon
- Standard deviation is high because of existence of free carbon
- Increased hardness with decreased residual carbon
- XRD results shows no residual carbon in Rutgers B5, B6 and B7

# Spark Plasma Sintering (Rutgers B1)



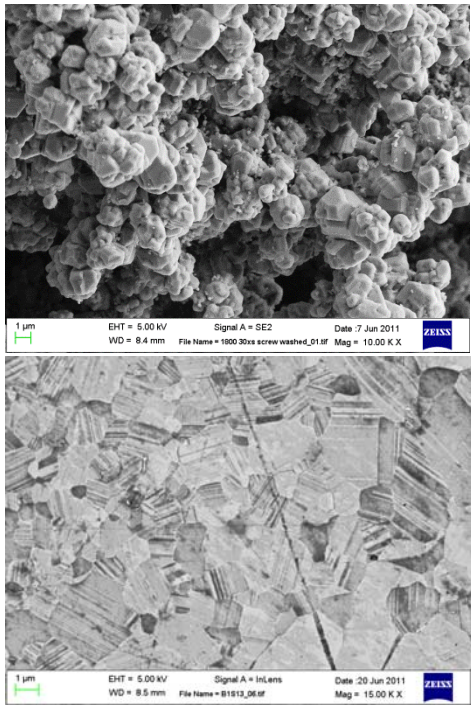



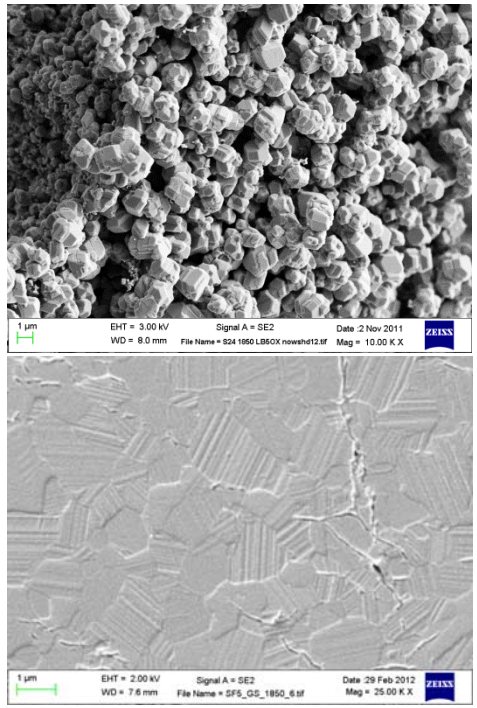




- EDS and micrographs suggest that Carbon is isolated
- Carbon free high hardness indentation (2321 HK)
- Average 2237HK

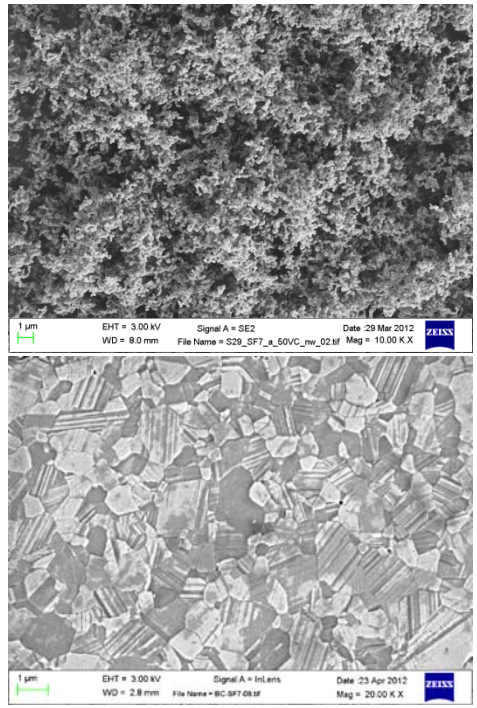
# Spark Plasma Sintering (Rutgers B1-B5-B7)



Sample SF1 (LB)
Avg.=0.95µm
Density: 2.49 g/cm3
Hardness (1kg): 2237
Grain Size: 1.8µm

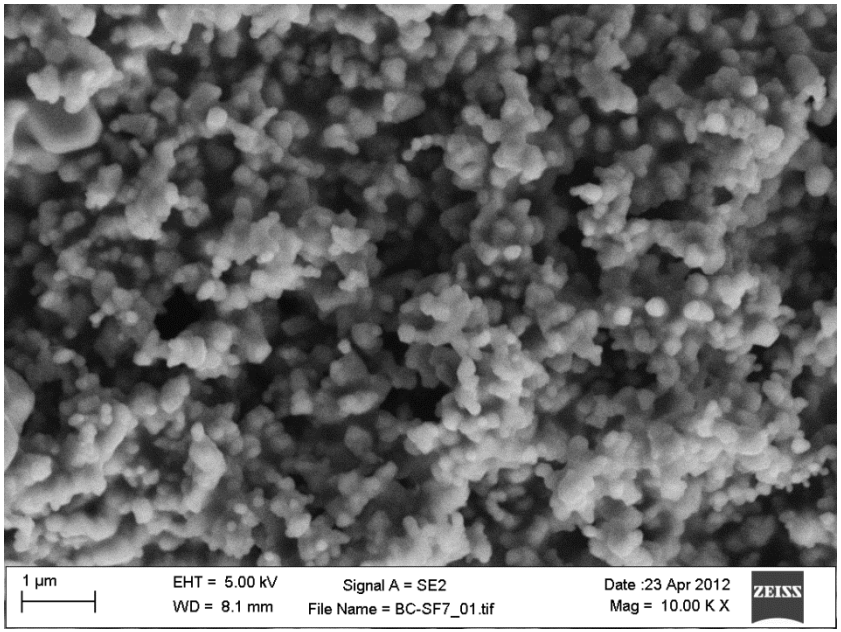


Sample SF5(LB)
Avg.=0.80µm
Density: 2.49 g/cm3
Hardness (1kg): 2315
Grain Size: 1.75µm

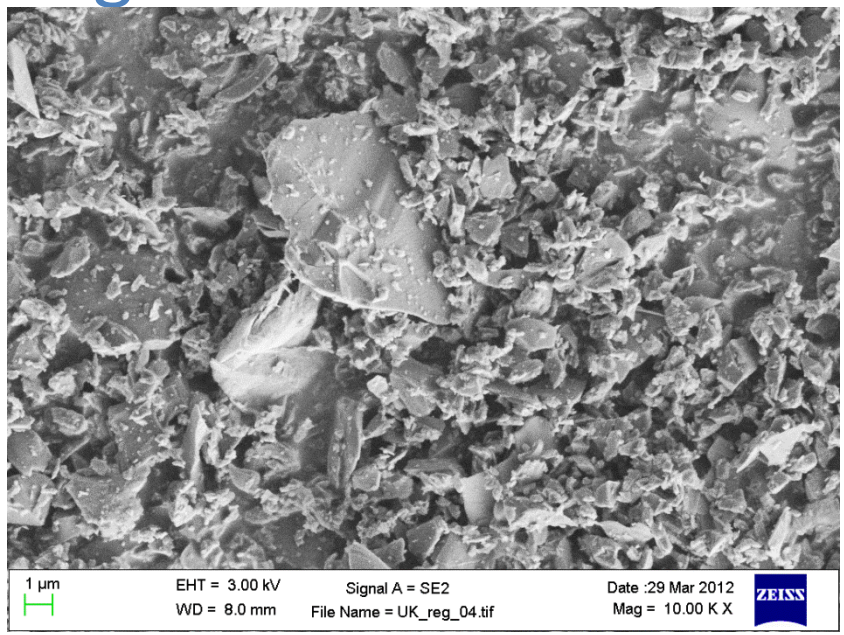


Sample SF7(VC)
Avg.=0.35µm
Density: 2.51 g/cm3
Hardness (1kg): 2359
Grain Size: 0.9µm

# Commercial vs. Rutgers Powder

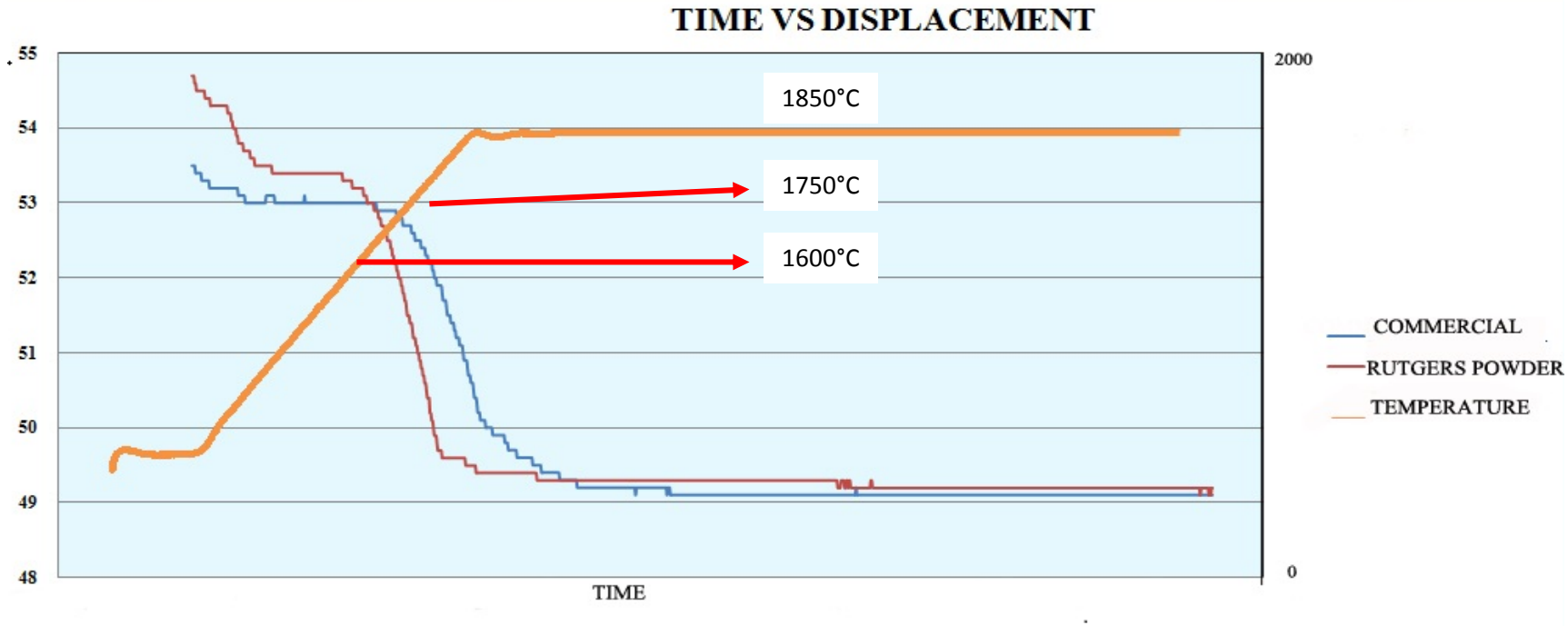



- d(0.9)=0.350 µm
- Homogeneous particle size distribution
- No sign of residual carbon proves XRD results
- Stoichometric composition



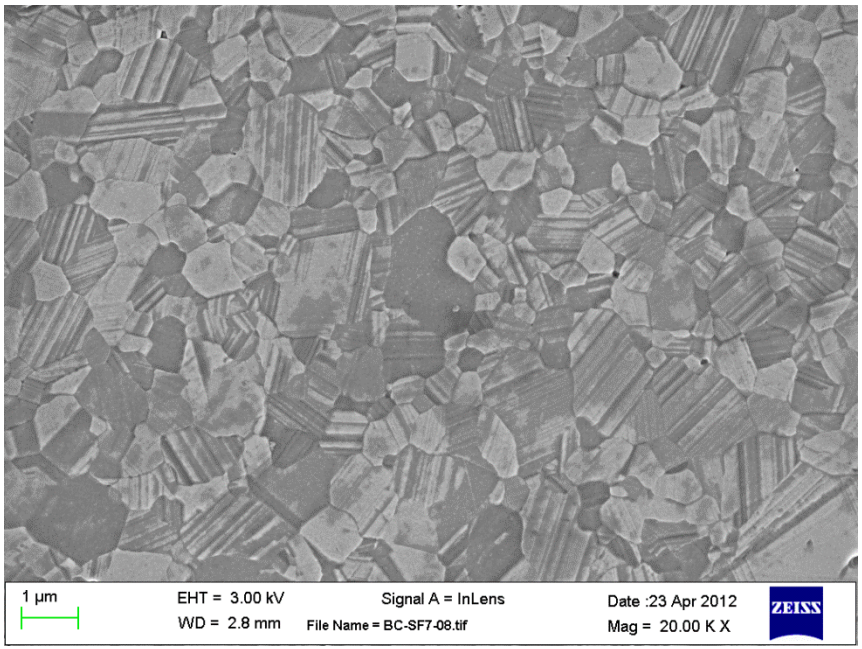

- d(0.9)=1.9 µm
- Non-homogeneous particle size distribution
- Carbon particles attached to boron carbide particles
- Non-stoichometric composition

# Densification

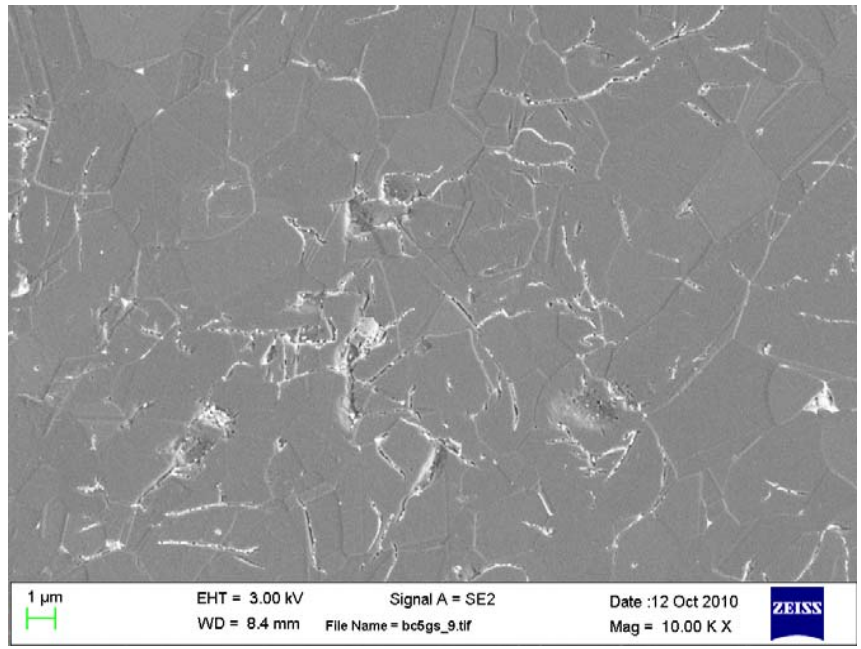



- Powders densified at 1850$^{o}$C, 50MPa, 300$^{o}$C and 20mins dwell time
- Commercial powder  shrinkage starts later than RCR powders
- RCR powders' shrinkage finishes faster
- Further tests are going to be done to examine shrinkage-densification relationship

# Microstructure




- Very limited grain growth
- Average grain size is 0.9 µm
- $HK_{1000gr}$ is 2359




- Limited grain growth
- Average grain size is 2.8 µm
- $HK_{1000gr}$ is 2150

# Future Work

**Second Quarter 2012**

•Continue to optimize $B_4C$ synthesis parameters to produce bulk boron carbide powders with continuous feeding.

•Densification of synthesized powders with changing dwell time at target temperature.

•Characterization of densified samples and determination of optimum conditions for minimum grain size.

**Third Quarter 2012**

•Densification and processing more commercial powders

•Increase B/C ratio

•Produce dense bodies with varied microstructures using different powders