



“Synthesis, Processing, and Properties of TaC-TaB₂-C Ceramics”

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NSWCCD**

**Sub-Micron and Nanostructured Ceramics
Colorado Springs, CO
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Background

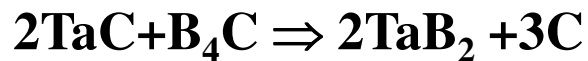
- TaC and TaB₂ with melting temperatures of 3980°C and 3037°C, respectively, are candidates for ultra-high temperature applications, such as propulsion systems and hypersonic vehicles. There are very limited data on the preparation and properties of ceramics containing both TaC and TaB₂.
- TaB₂-TaC system has a eutectic at 2730°C at 34 wt. % TaC and no component solubility below 2100°C.
- Intermediate composition ceramics in the TaC-TaB₂ system had higher hardness and lower wear at 800 - 900 °C than the end members.
- Densification of TaC requires temperatures up to 2400°C and TaB₂ – 2100-2200 °C.
- Densification temperature of TaC was decreased to 2100-2200°C by the addition of 10 wt. % fine TaB₂ and B₄C/C mixture (0.43/0.13 wt. %).
- The reactions of transition metals, carbides, and oxides with B₄C are well known and used for synthesis of diboride-based ceramics.
- Pressureless sintering of fine B₄C to relative density above 95% at 2100-2250°C was accomplished by the addition of Group IV-VI transition metal carbides.
- Diborides and active carbon formed during processing accelerated diffusion in the bulk and along grain boundaries. MeB₂ had a grain-growth-inhibiting effect.



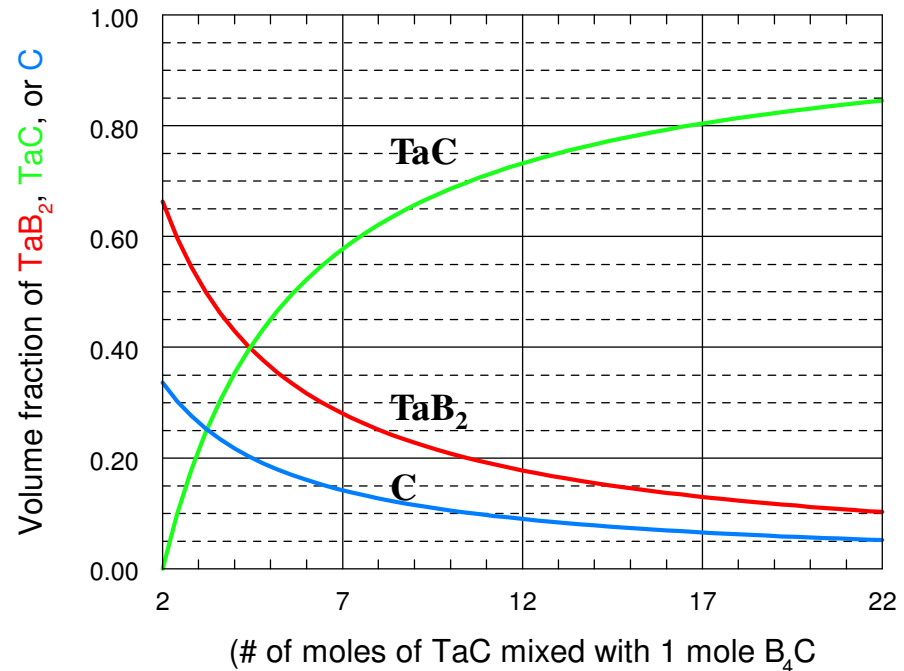
Objective:

- Synthesize ceramic materials in the system $\text{TaC} - \text{TaB}_2 - \text{C}$ using displacement reactions between sub-micron TaC and B_4C
- Develop processing procedure for materials densification
- Characterize the microstructure and properties of ceramics

Reactions in TaC+B₄C Mixtures and Composition of the Reaction Products (in volume fractions)



Volume Fraction of Reaction Products from Heating
x moles TaC + B₄C Mixtures



Composition of Starting and Reaction Product Components

TaC/B ₄ C Ratio	Wt% B ₄ C in raw materials	Calculated Volume% of Reaction Products			Calculated Wt% of Reaction Products		
		TaC	TaB ₂	C	TaC	TaB ₂	C
2	12.5	0	67	33	0	91.8	8.2
4	6.65	35	42.5	22.5	46.6	49.0	4.4
8	3.45	62	25	13	72.4	25.3	2.2
12	2.3	73.8	17.6	8.6	81.4	17.1	1.5
16	1.75	79.9	13.4	6.7	85.9	12.9	1.15

Actual carbon content in ceramics was lower. It was consumed by oxygen (3.02 wt.%) present in starting TaC during firing.



Starting Materials

TaC - 99.9% pure, 100 nm, **made in 1976** by Atomergic Chemetals Corp., which **does not make it any more**.

Stoichiometry - $\text{TaC}_{0.96}$ (Chemical and XRD analysis). Oxygen content – 3.02 wt. % (Laboratory Testing Inc., Hatfield, PA).

Surface area - 11.74 m^2/g (NSWCCD by BET).

W was not detected by EDS or XPS. The presence of Cl and H-C bonds was determined by XPS.

It can be assumed that the powder was prepared by gas phase deposition using Ta chloride/hydrocarbon mixtures.

TaC - 99.5% pure; -325 mesh, CERAC Inc. Surface area - 1.02 m^2/g

B₄C - 99.4% pure (metals basis), 1-7 Micron powder, Alfa Aesar
Surface area - 4.84 m^2/g .

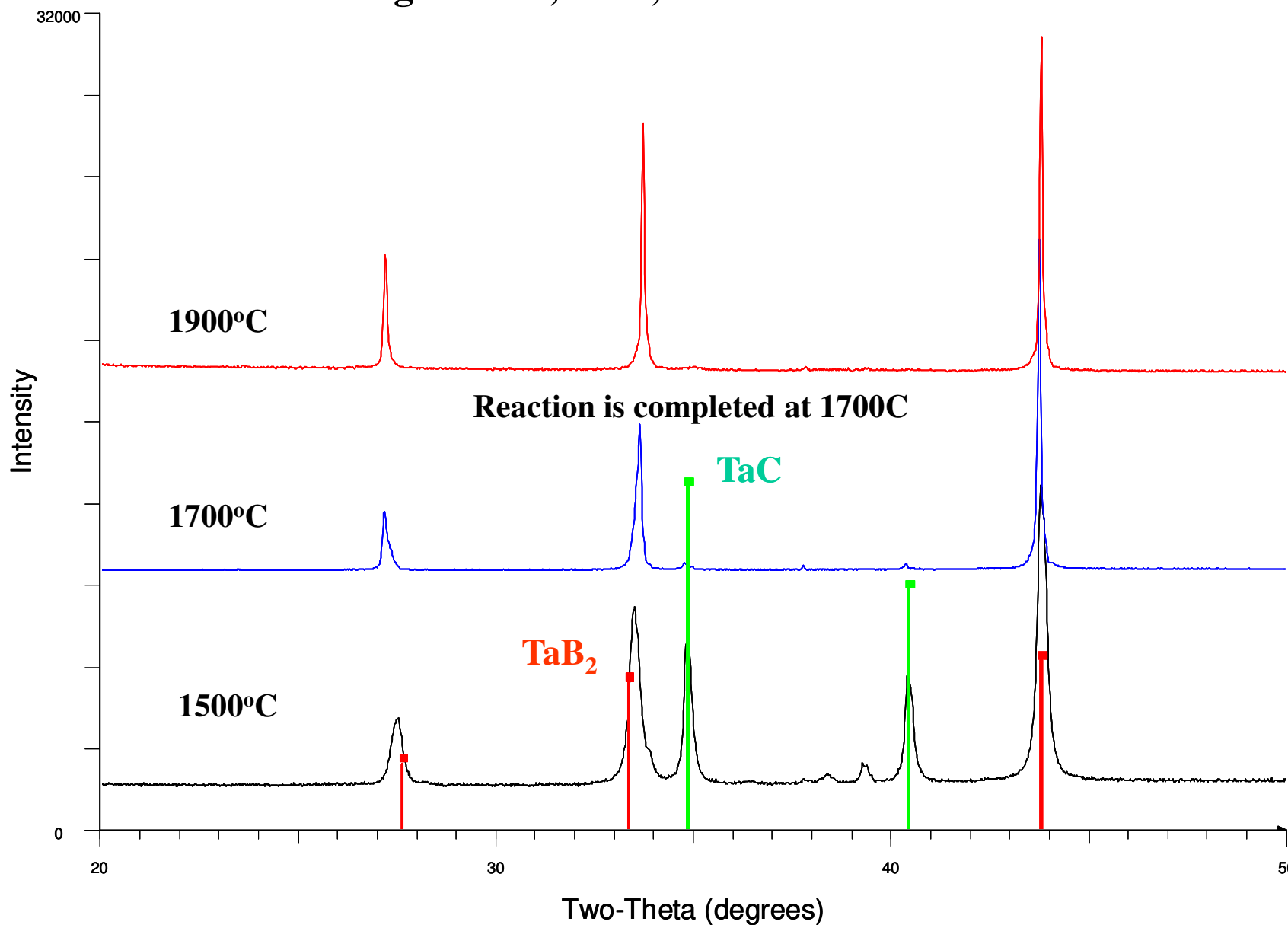
C black – surface area about 25 m^2/g



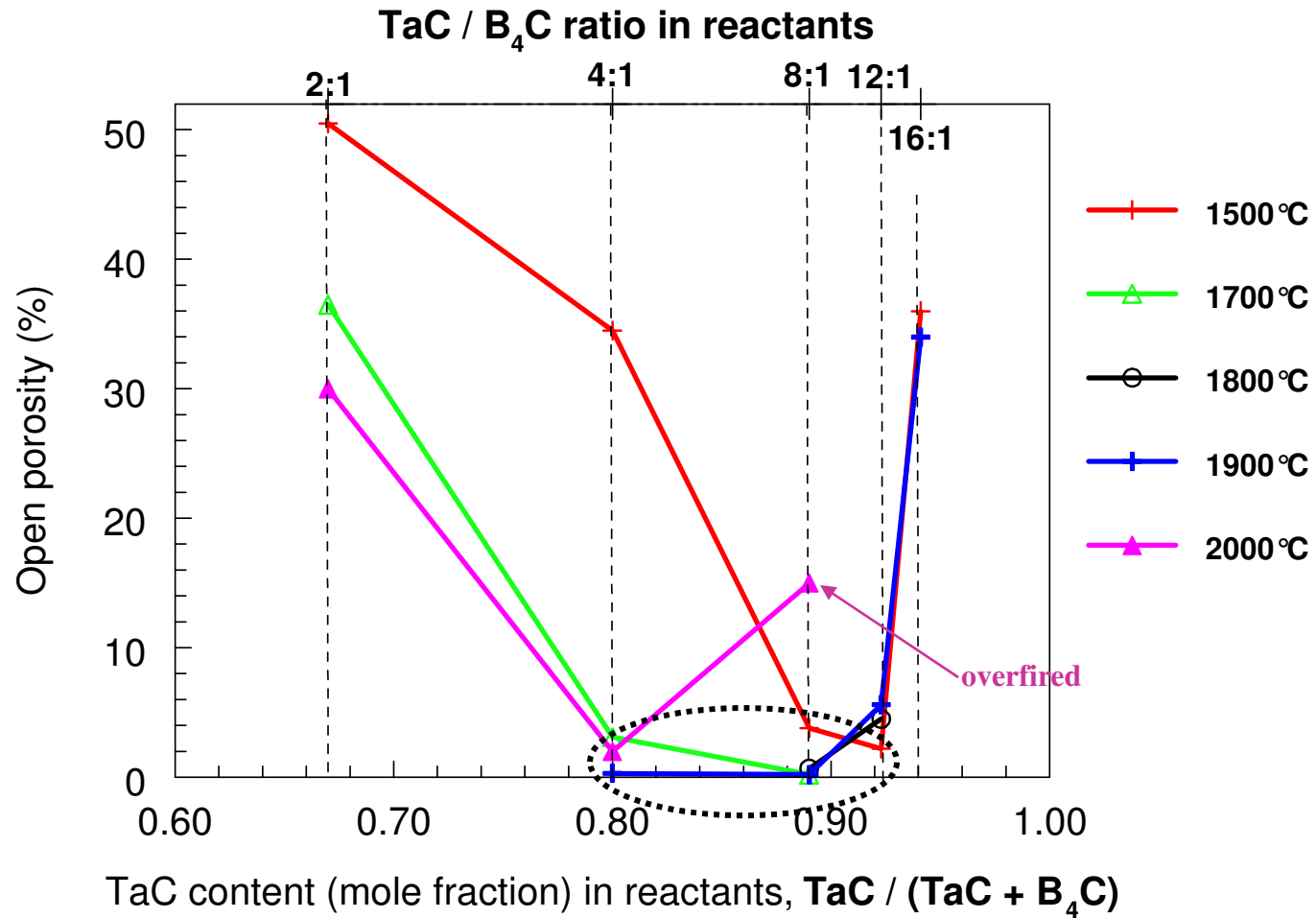
Experimental Procedure

- Mixing the components in selected molar ratios.
- Sample preparation by cold pressing and following CIPing.
- Heating in the furnace with graphite heaters at 1500 –2100°C for 2 hours in Ar.
- Hot Pressing at 1700 and 1900°C and 20 MPa for 1hr in He.
- Characterization:
 - Phase composition by XRD
 - Microstructure by SEM
 - Vickers hardness (Load - 1kg and 10kg for 15 seconds)
 - Flexural strength (3-point)

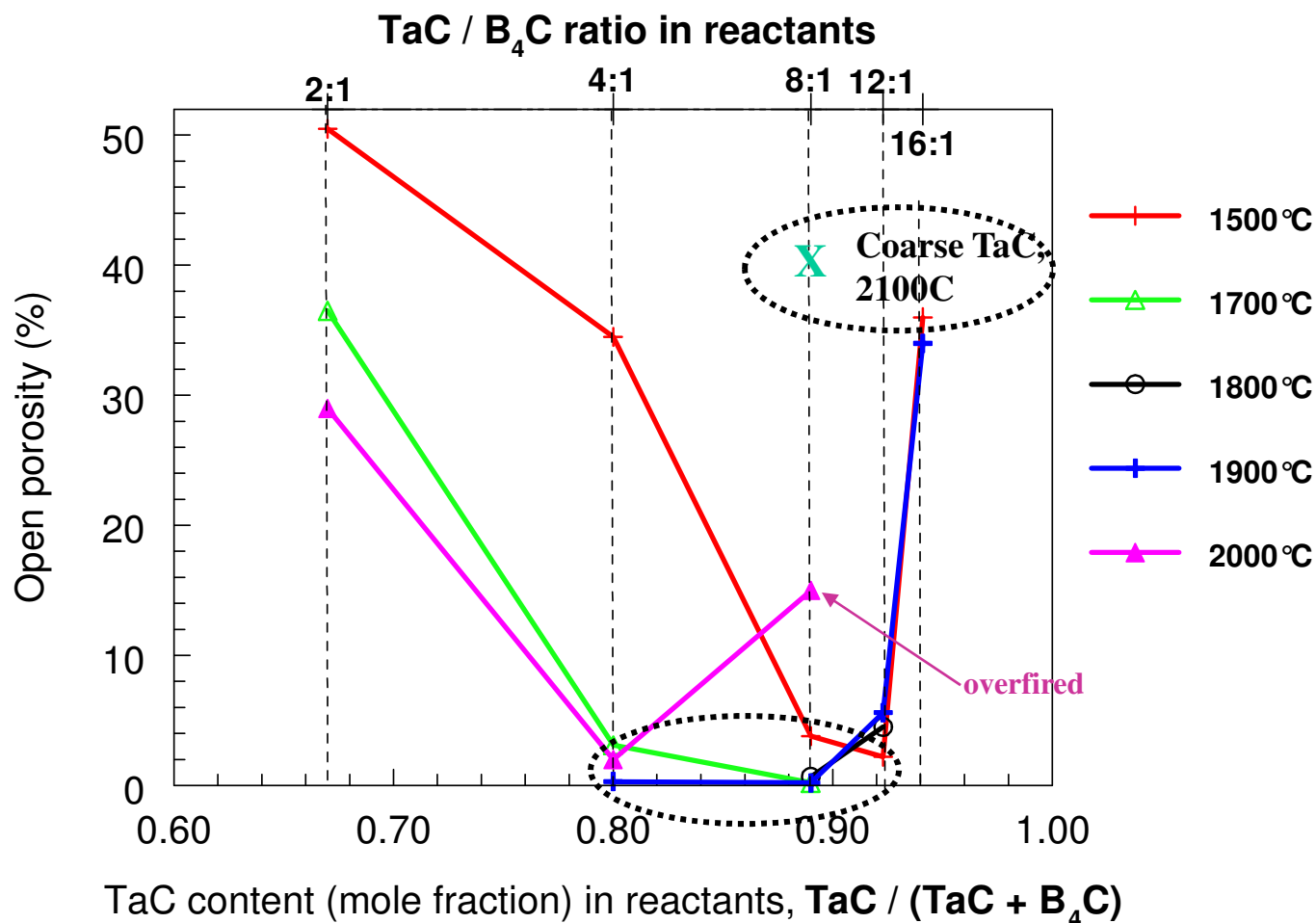
XRD of Ceramics Prepared from $2\text{TaC} + \text{B}_4\text{C}$ Mixture by Pressureless Sintering at 1500, 1700, and 1900°C for 2 hours in He



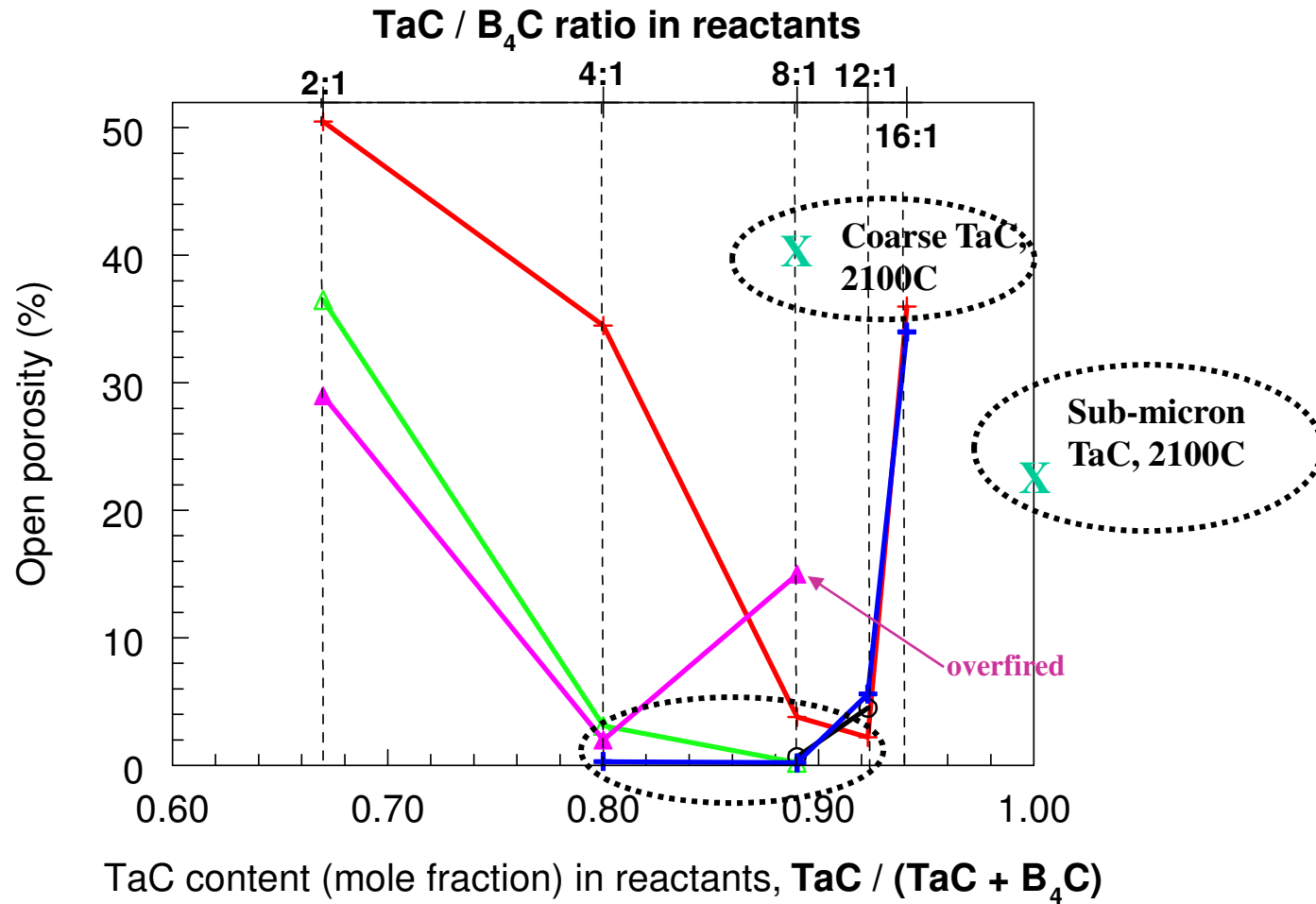
Open Porosity of Ceramics Prepared from TaC/B₄C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



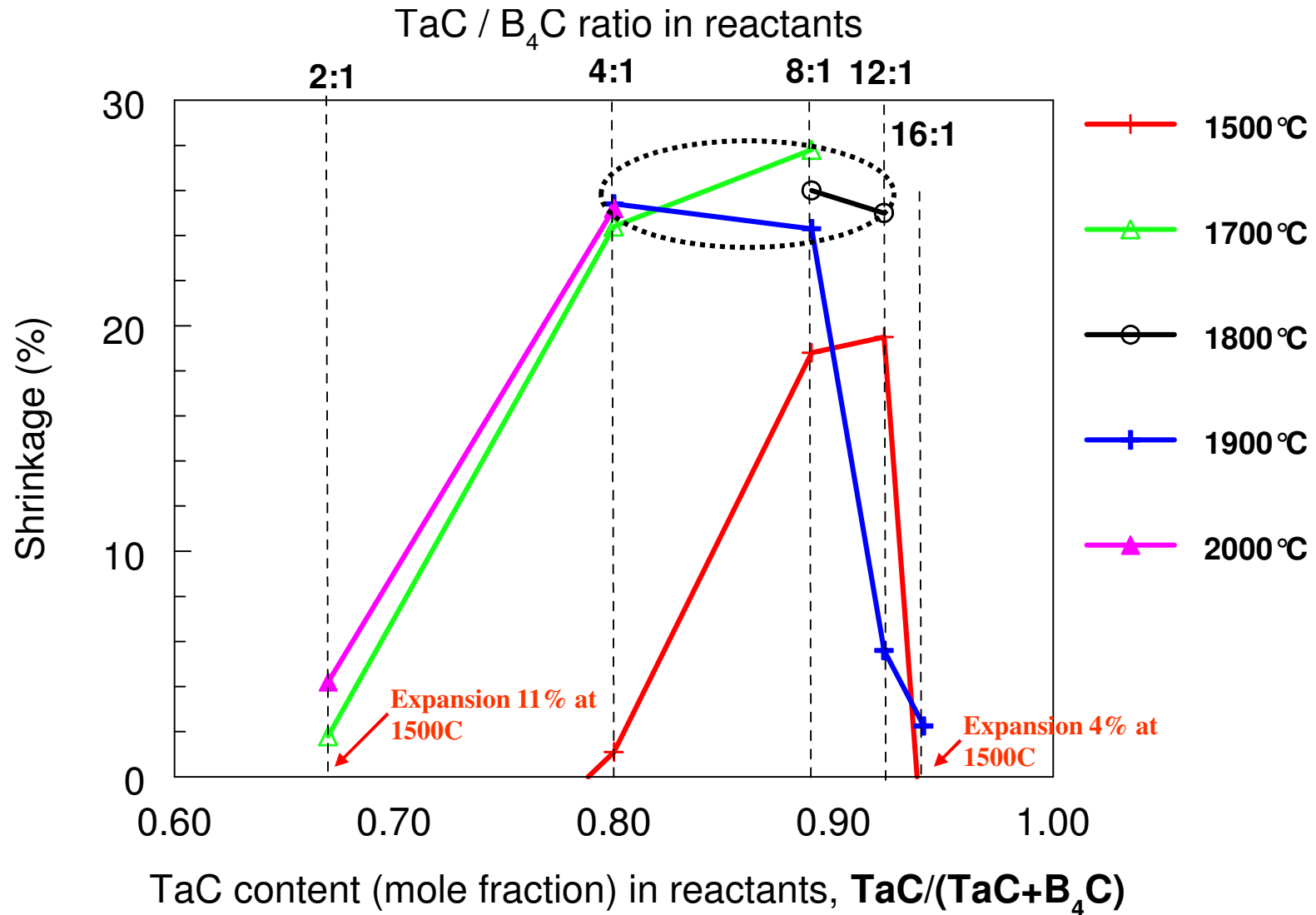
Open Porosity of Ceramics Prepared from TaC/B₄C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



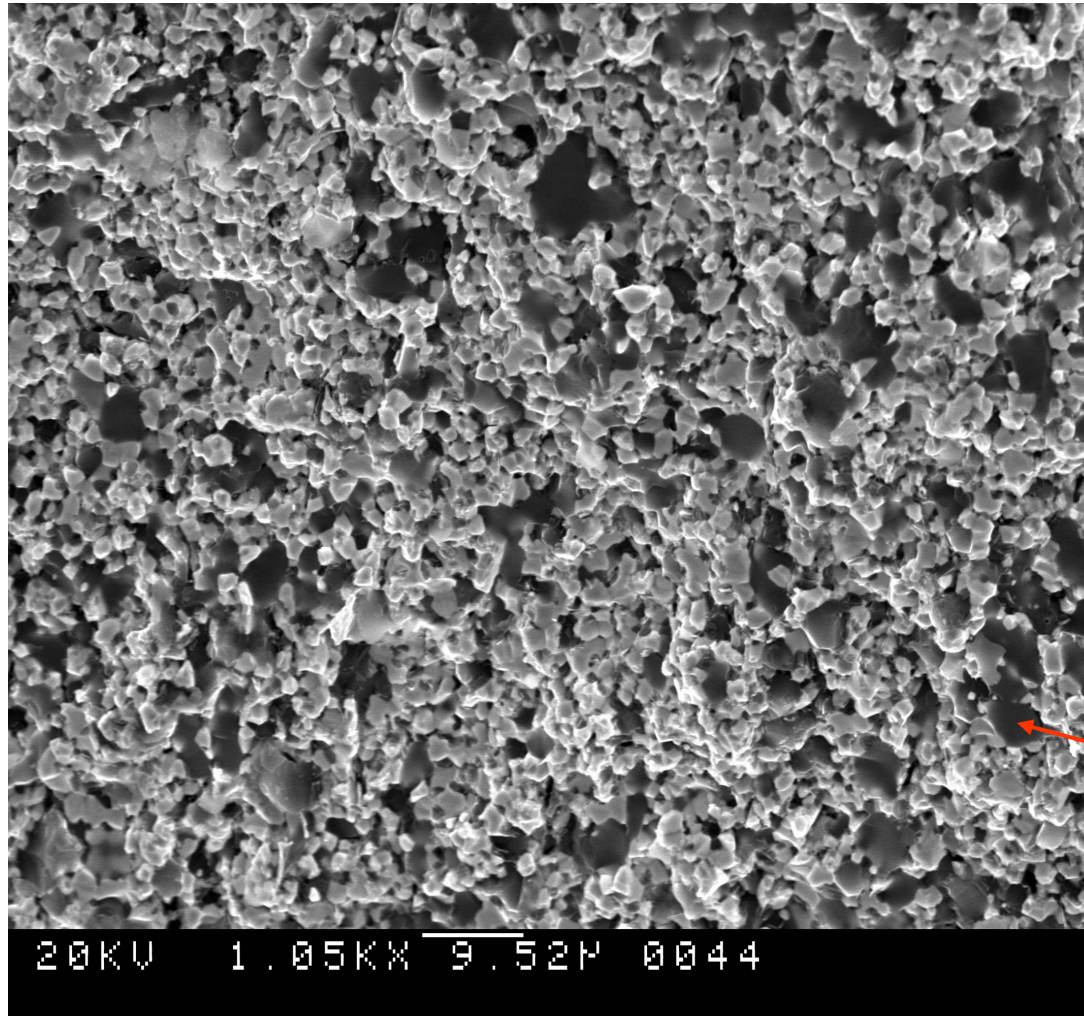
Open Porosity of Ceramics Prepared from TaC/B₄C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



Shrinkage of Ceramics Prepared from TaC/B₄C Mixtures by Pressureless Sintering as a Function of Composition and Temperature

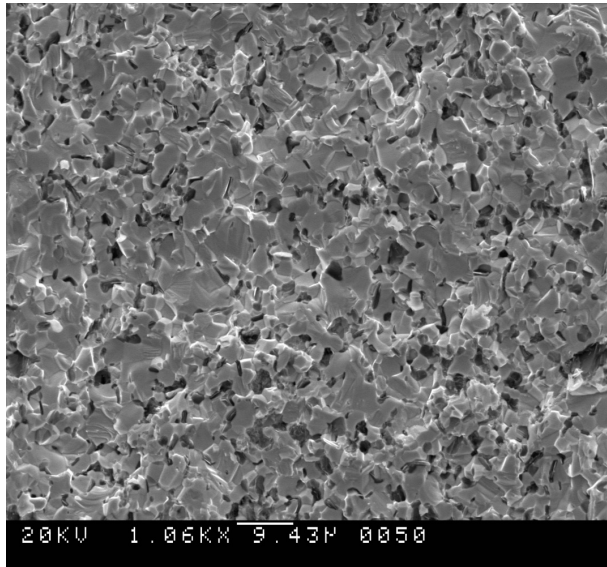


SEM of TaB_2 - C Ceramics Prepared from TaC+B₄C Mixtures by Pressureless Reaction Sintering at 1900°C for 2 hours

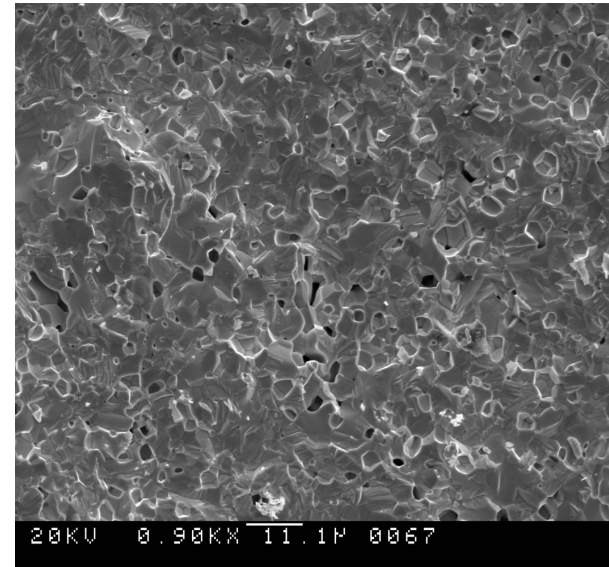


Carbon

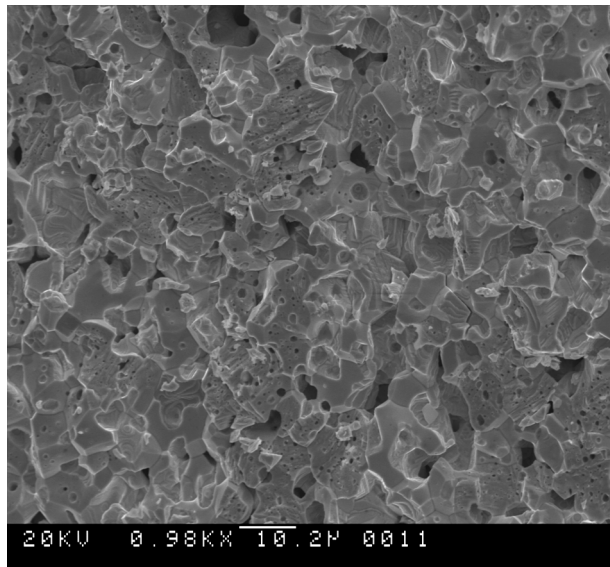
SEM of TaC-TaB₂ - C Ceramics Prepared from TaC+B₄C Mixtures by Pressureless Sintering at 1900°C for 2 hours



4TaC



8TaC



12 TaC

Calculated Composition in vol. %

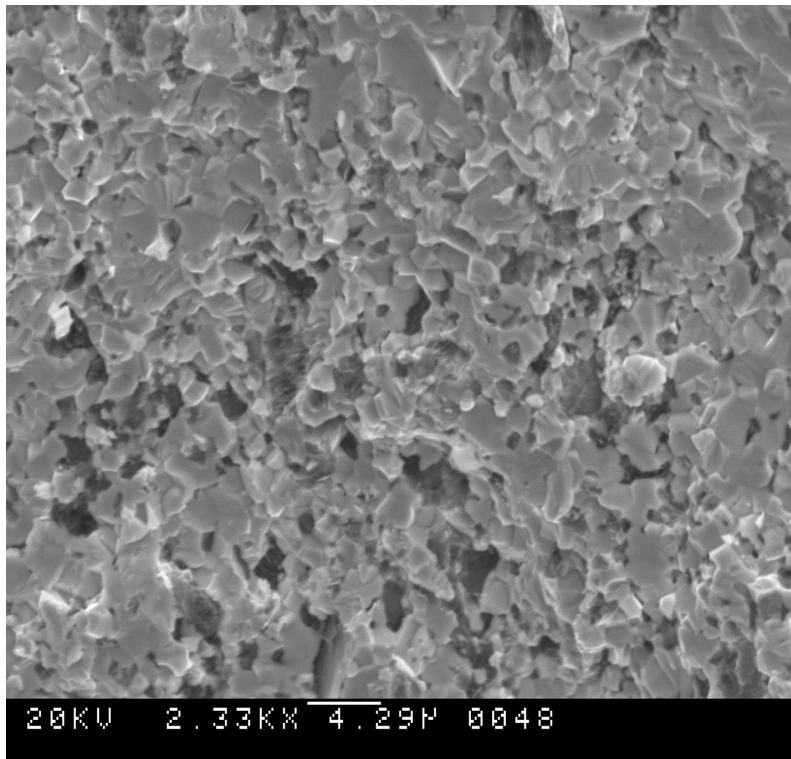
4:1, TaC – 35, TaB₂ – 42.5, C – 22.5

8:1, TaC – 62, TaB₂ – 25, C – 13

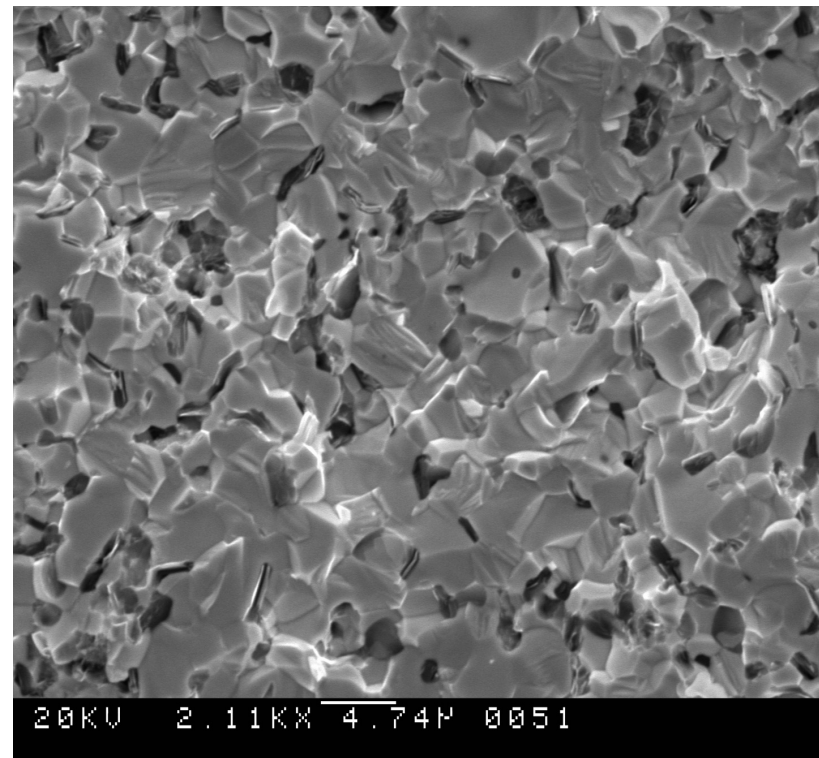
12:1, TaC – 73.8, TaB₂ – 17.6, C – 8.6

SEM of TaC-TaB₂ - C Ceramics Prepared from 4TaC+B₄C Mixture by Pressureless Sintering at 1700 and 1900°C for 2 hours

Calculated composition in vol. %: TaC – 35, TaB₂ – 42.5, C – 22.5



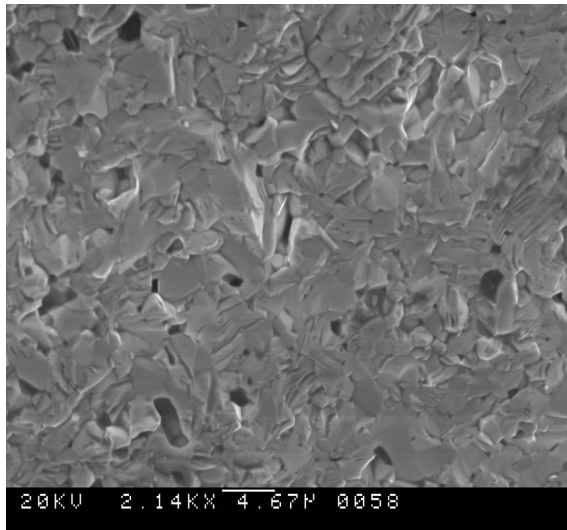
1700°C (Open porosity 3.1%)



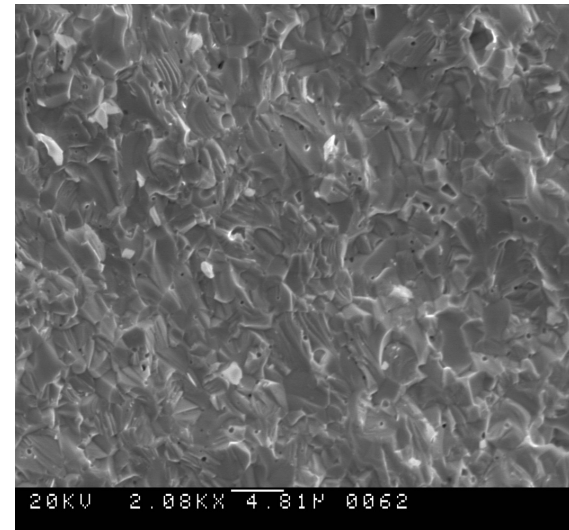
1900°C (Open porosity 0%)

SEM of TaC-TaB₂ - C Ceramics Prepared from 8TaC+B₄C Mixture by Pressureless Reaction Sintering

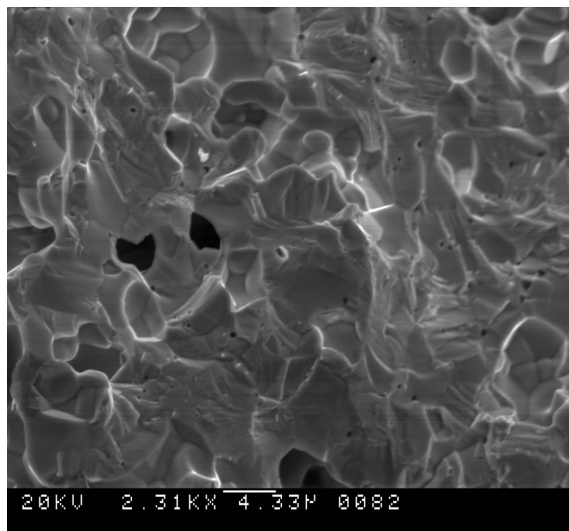
(TaC – 62, TaB₂ – 25, C – 13 vol. %)



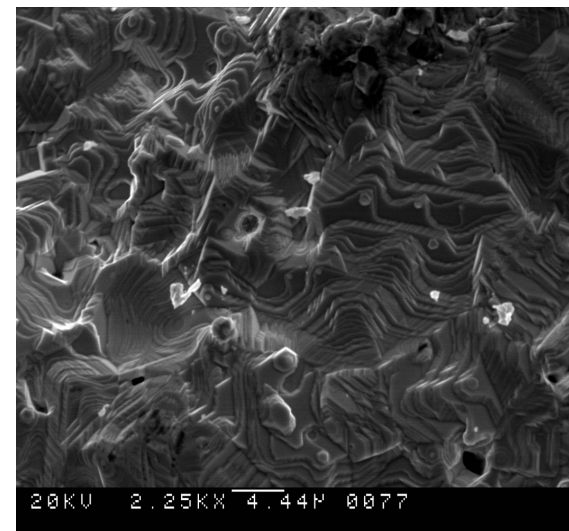
1700°C



1800°C

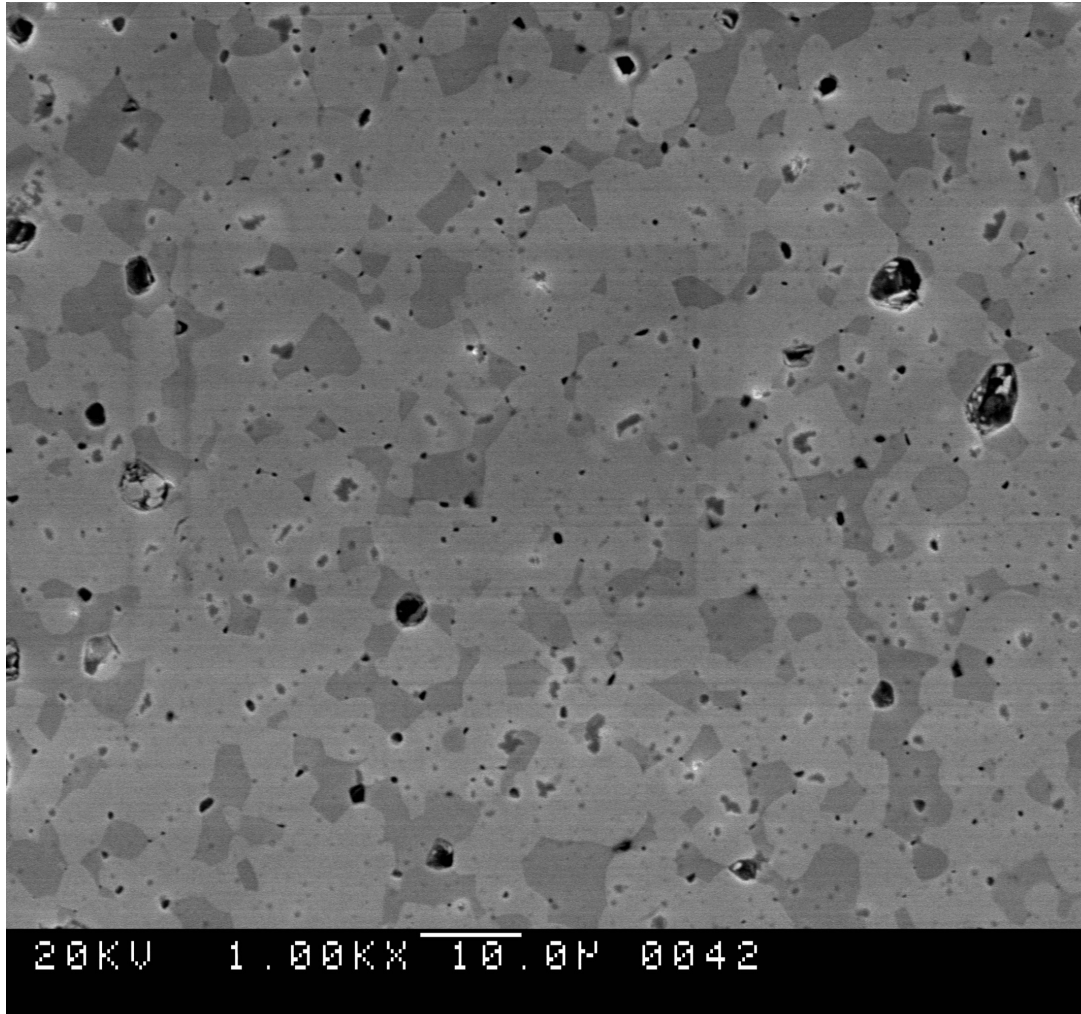


1900°C



2000°C,
overfired

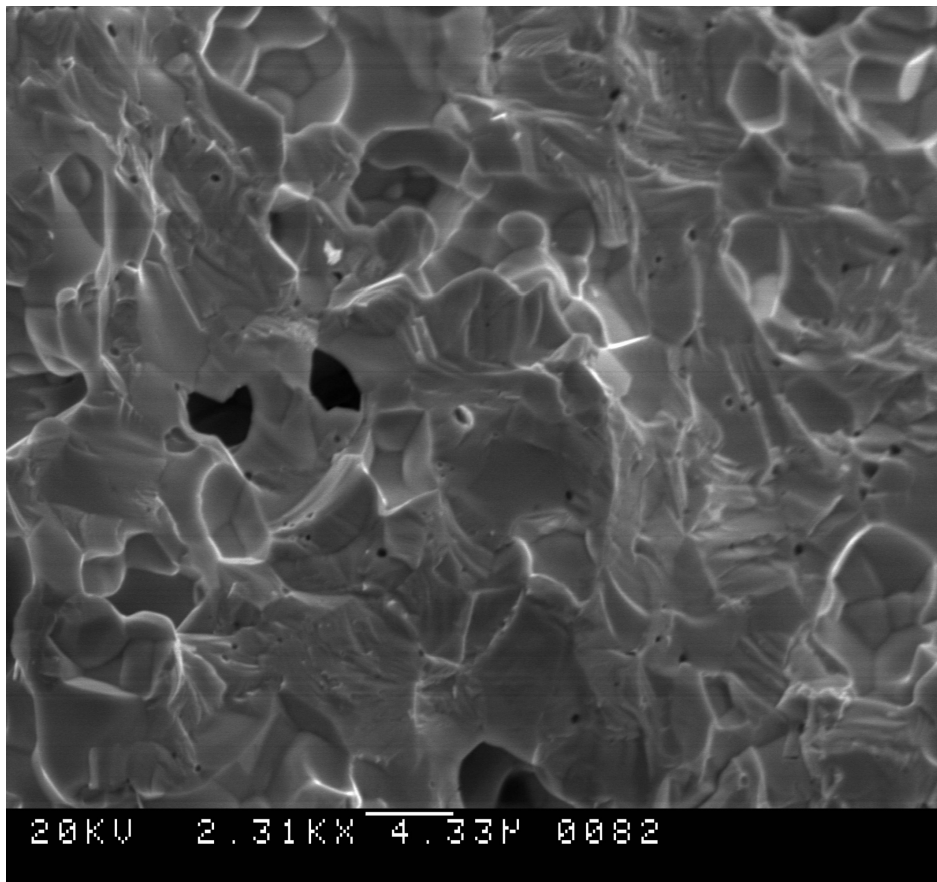
**SEM of TaC-TaB₂ - C Ceramics Prepared from 8TaC+B₄C Mixture
by Pressureless Reaction Sintering at 1900°C for 2 hours in He**



Polished Surface

Composition in vol. %: TaC – 62, TaB₂ – 25, C – 13

Mechanical Properties of **8TaC/B₄C** (TaC–62, TaB₂–25, C – 13 vol. %) Ceramics Pressureless sintered at 1900°C



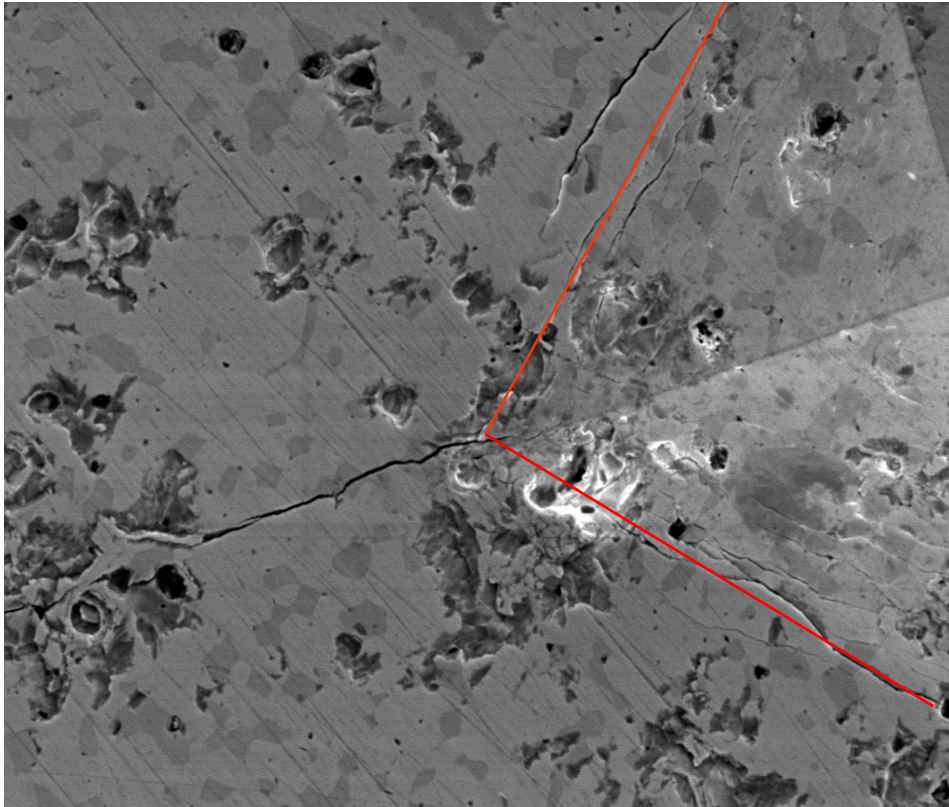
Flexural Strength (3-point)

221 MPa

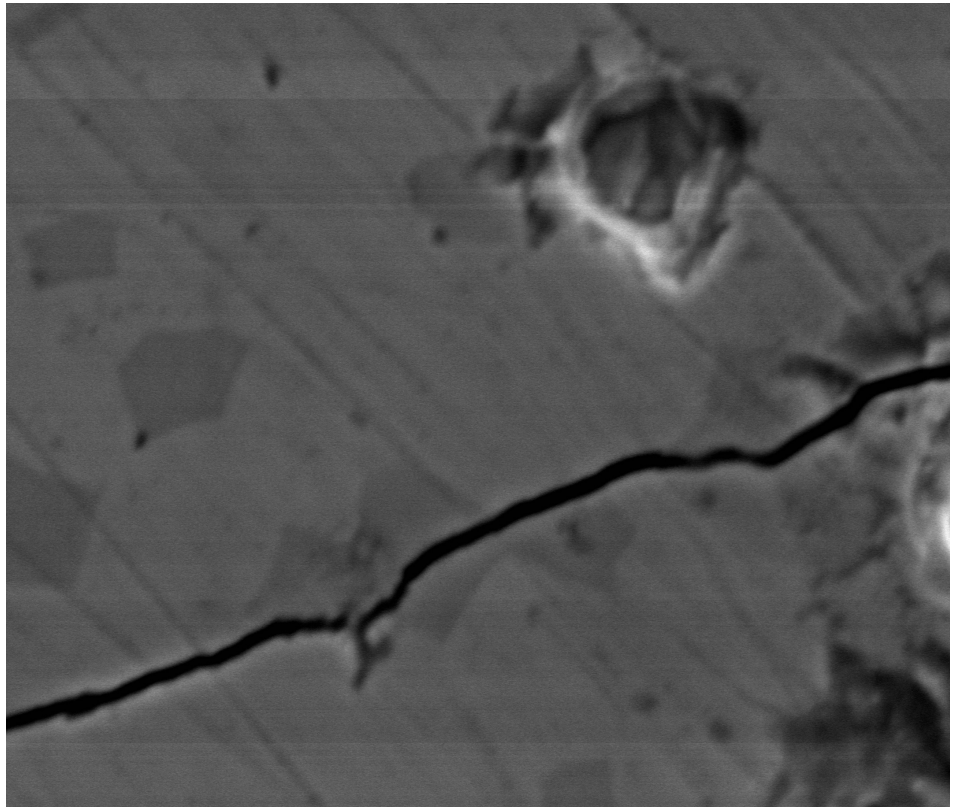
Vickers Hardness

22.2 GPa

SEM of an Indent (10 kg load) in Ceramics from **8TaC+B₄C** Mixture Pressureless Sintered at 1900 C

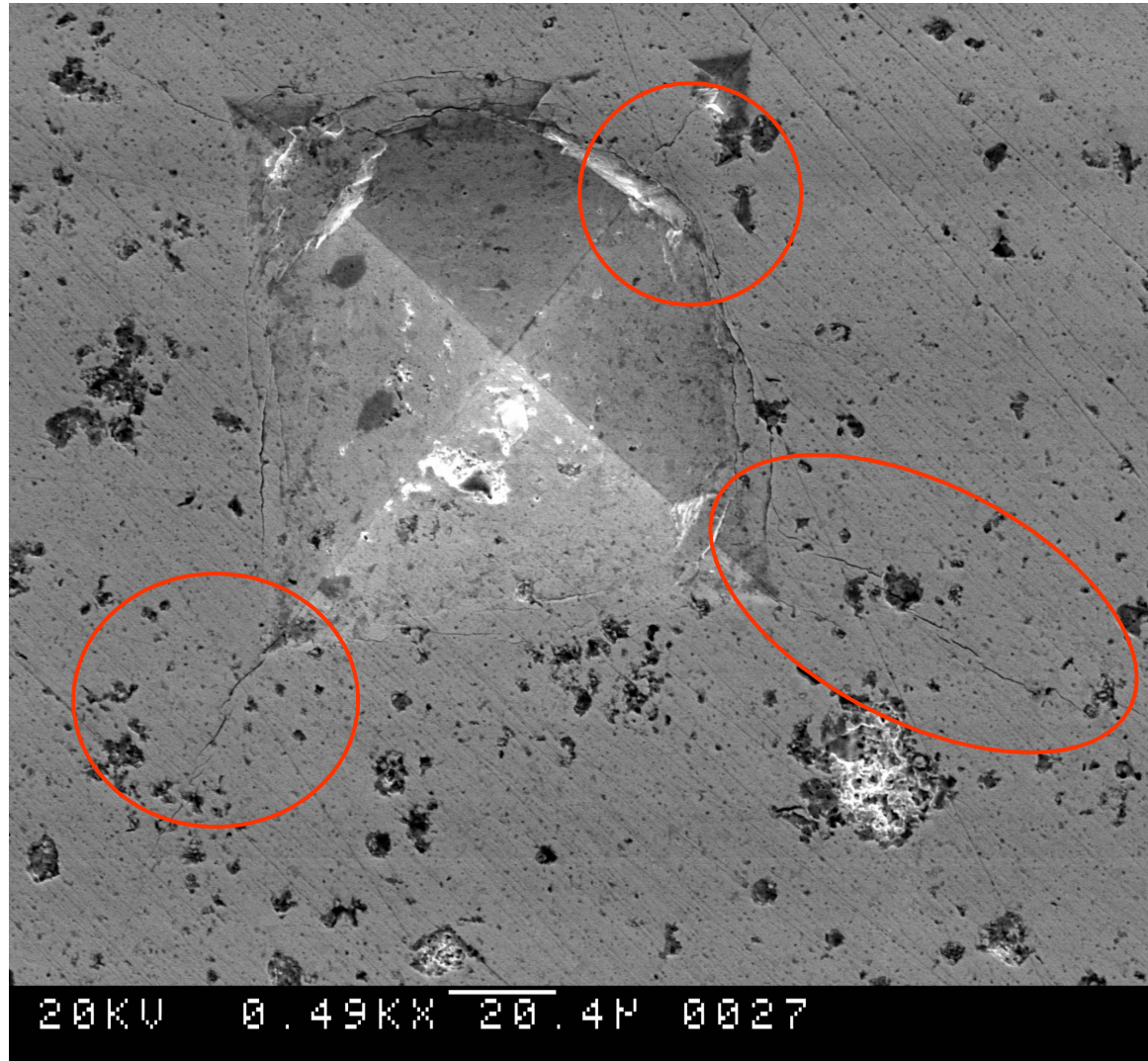


20KV 1.00KX 10.0P 0035



20KV 04.9KX 2.04P 0039

**SEM of an Indent (10 kg load) in Ceramics from $12\text{TaC} + \text{B}_4\text{C}$ Mixture
(TaC – 73.8, TaB₂ – 17.6, C – 8.6 vol. %) Hot Pressed at 1700 C**



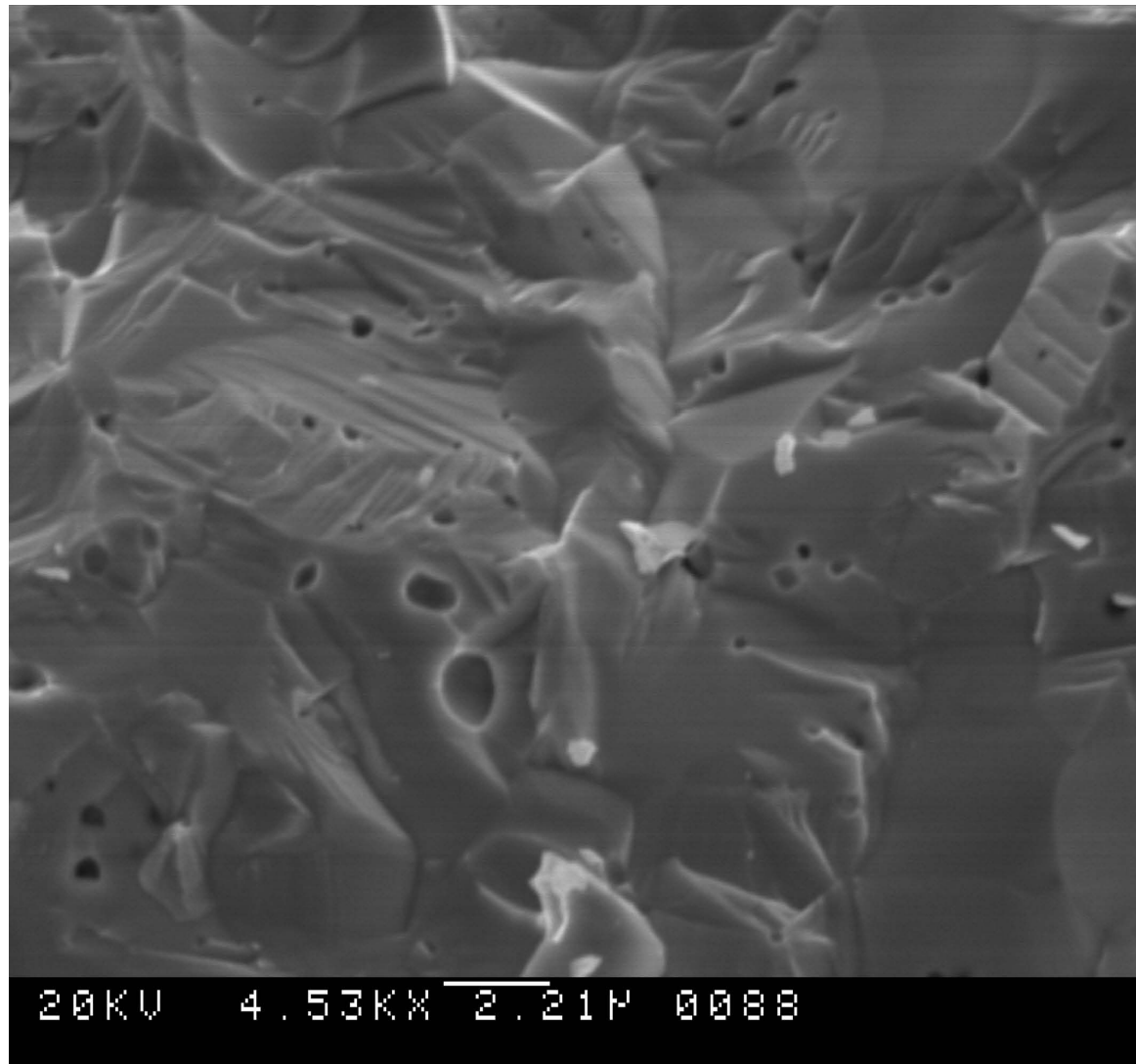
Use of nano-TaC and nano-C black to Densify the End Members of the Reaction:



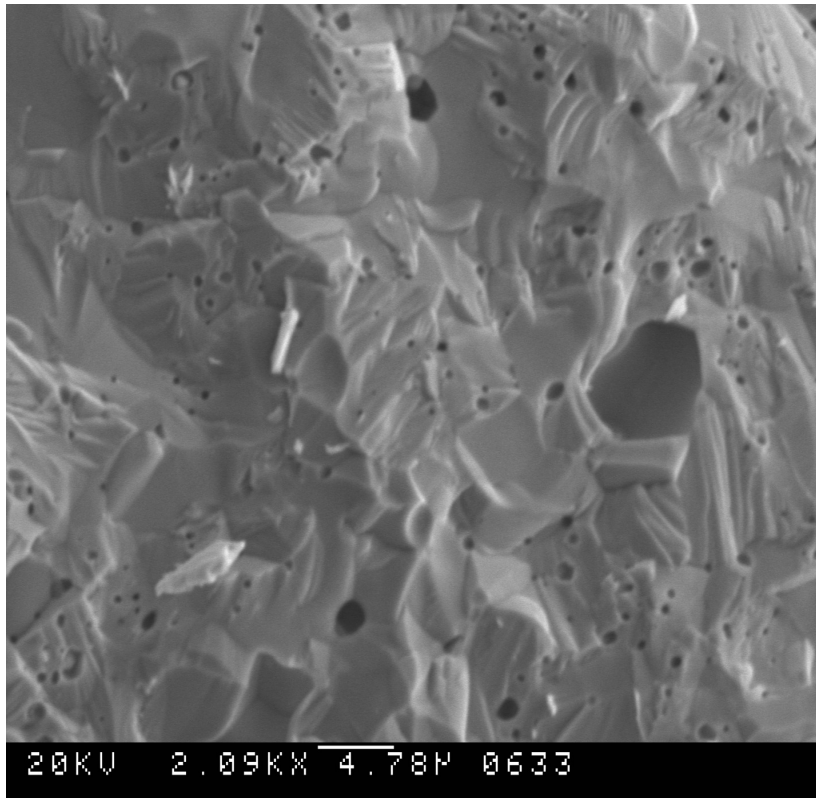
- The end-member mixture was pressureless sintered to full density at 1850°C (2 hours).
- The mixture of **nano TaC and TaB₂ (without carbon black)** had open porosity of 19% after firing at 1800°C for 2 hours.
- The mixture of **6TaC, 2TaB₂ and 3C** containing **coarse TaC (-325 mesh) and C black** had open porosity of 32.5% after pressureless firing at 2100°C

Both sub-micron TaC and carbon black are needed for pressureless densification of TaC/TaB₂/C ceramics. **C black should be in the range of 2 to 8 wt. % of the TaC/Cmixture.**

**SEM of TaC-TaB₂ - C Ceramics Prepared from $6\text{TaC} + 2\text{TaB}_2 + 3\text{C}$
Mixture Pressurless Sintered at 1850°C**

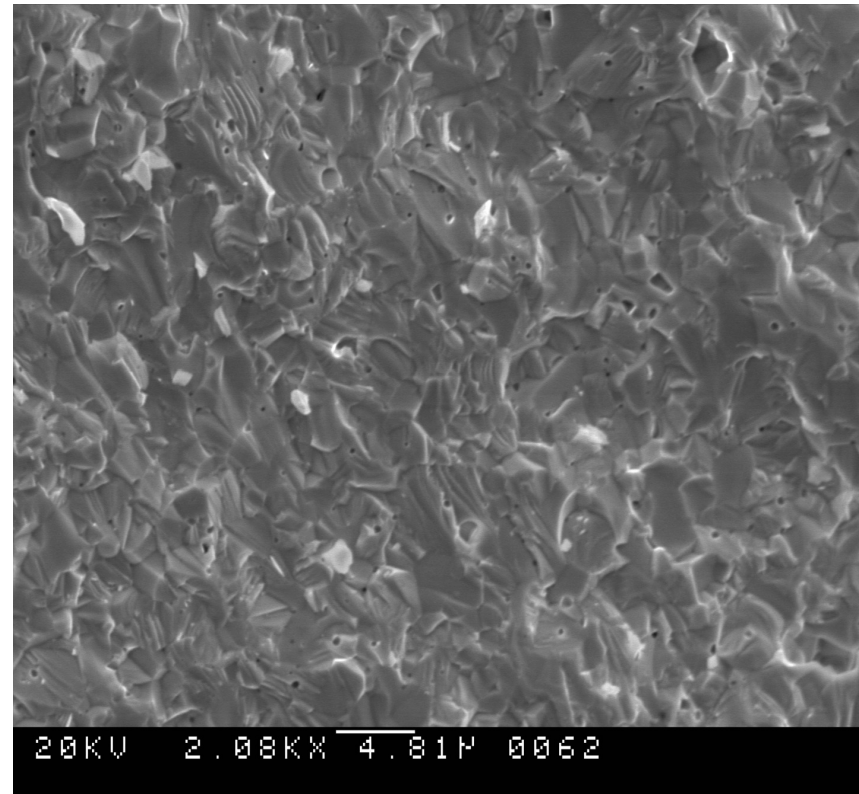


**SEM of TaC-TaB₂ - C Ceramics Prepared from $8\text{TaC} + \text{B}_4\text{C}$ (reaction)
and from $6\text{TaC} + 2\text{TaB}_2 + 3\text{C}$ (end members) Mixtures by Pressurless
Sintering**



$6\text{TaC} + 2\text{TaB}_2 + 3\text{C}$, 1850°C

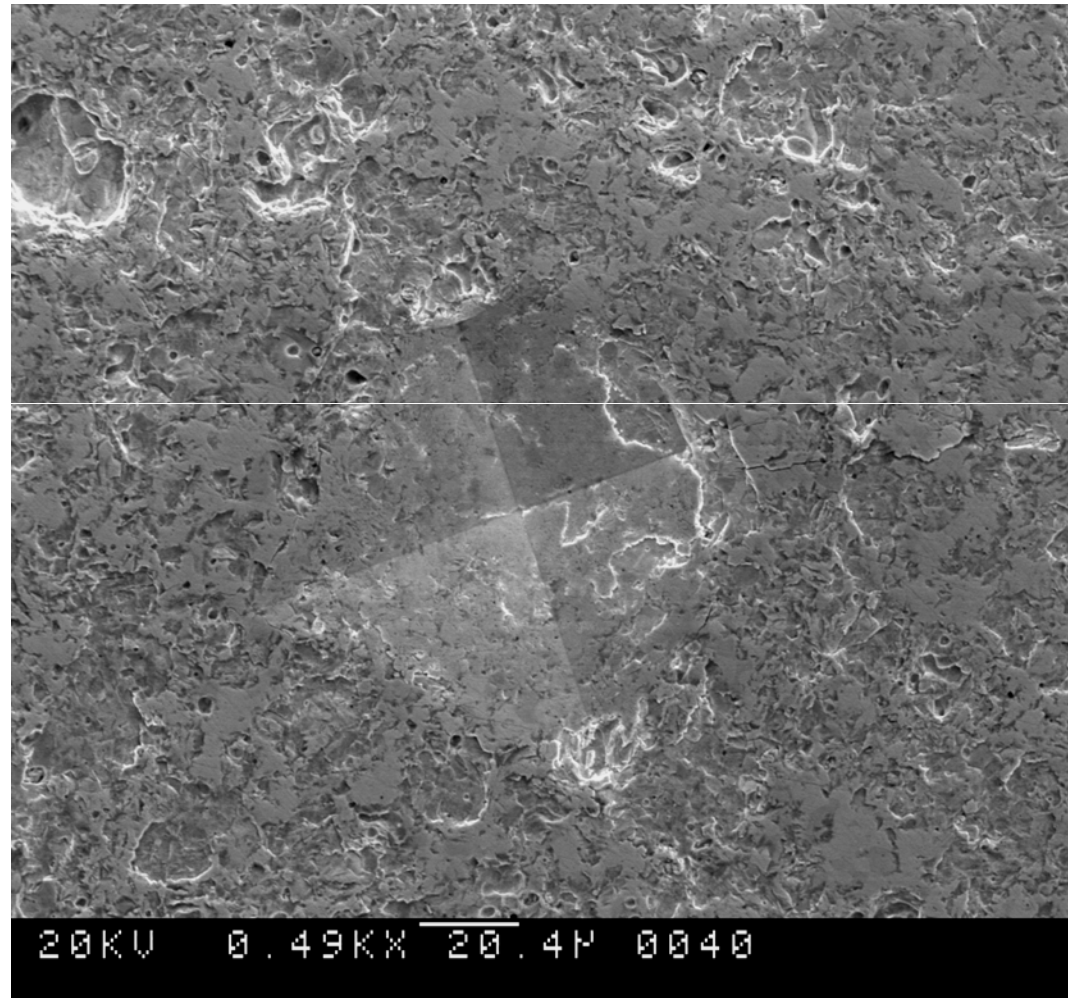
Flexural Strength – 391 MPa



$8\text{TaC} + \text{B}_4\text{C}$, 1800°C

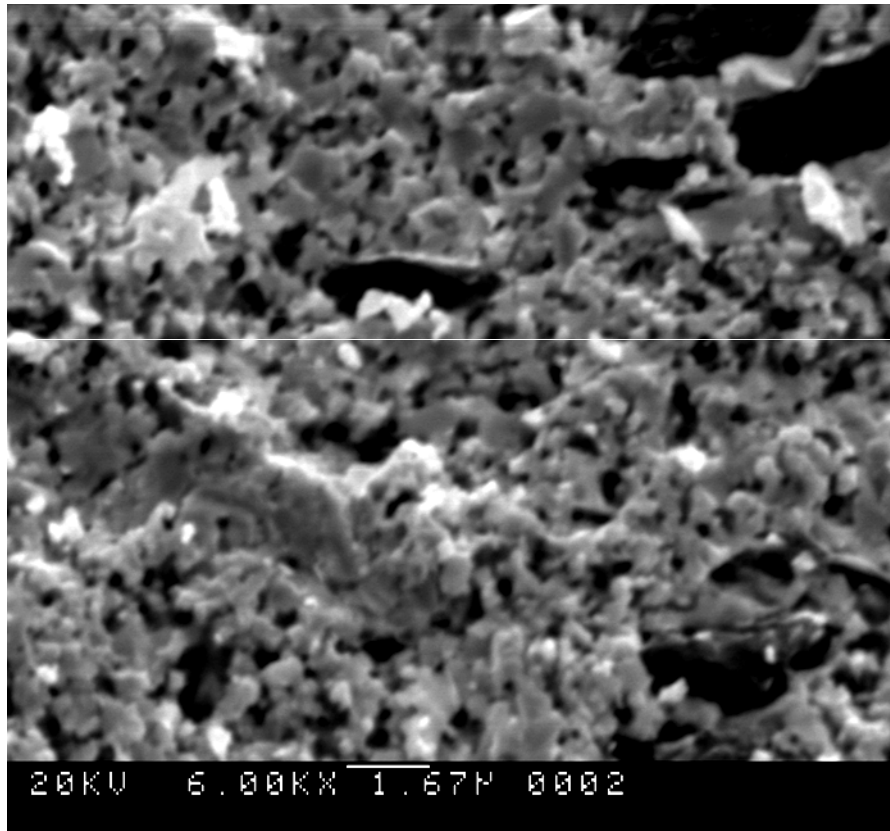
Flexural Strength – 221 MPa

**SEM of an Indent (10 kg load) in Ceramics from $6\text{TaC} + 2\text{TaB}_2 + 3\text{C}$
(end members) Mixture Pressurless Sintered at 1850°C**

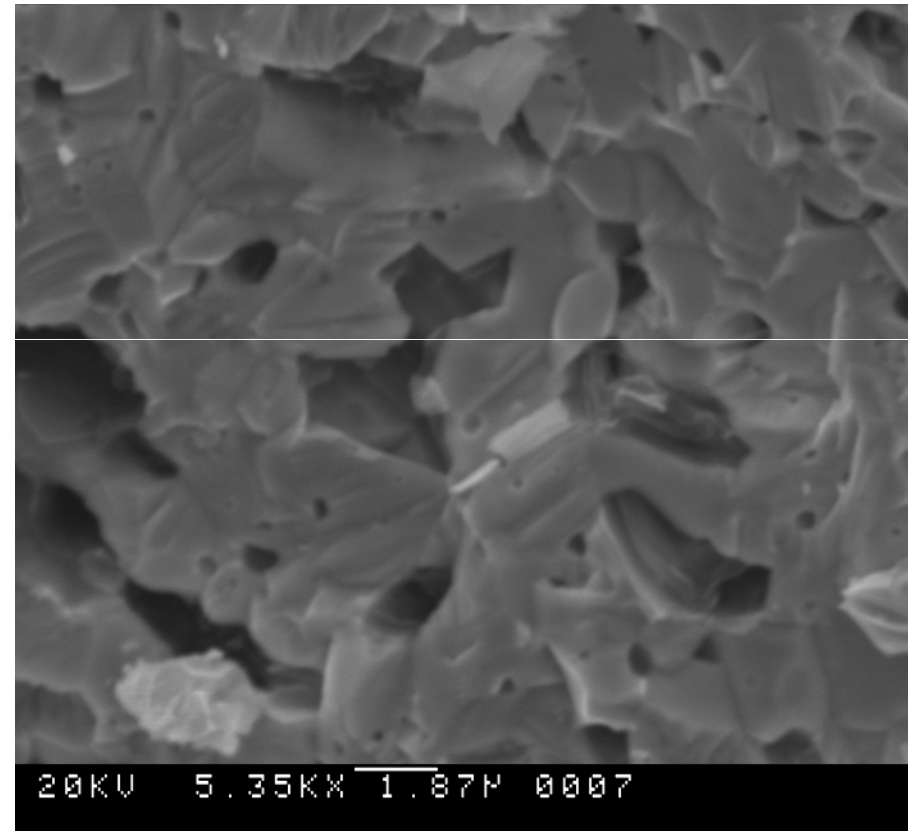


Hot Pressing Experiments

SEM of TaC-TaB₂ - C Ceramics Prepared from 8TaC+B₄C Mixture by Reaction Hot Pressing at 1700 and 1900°C for 1 hours in Ar



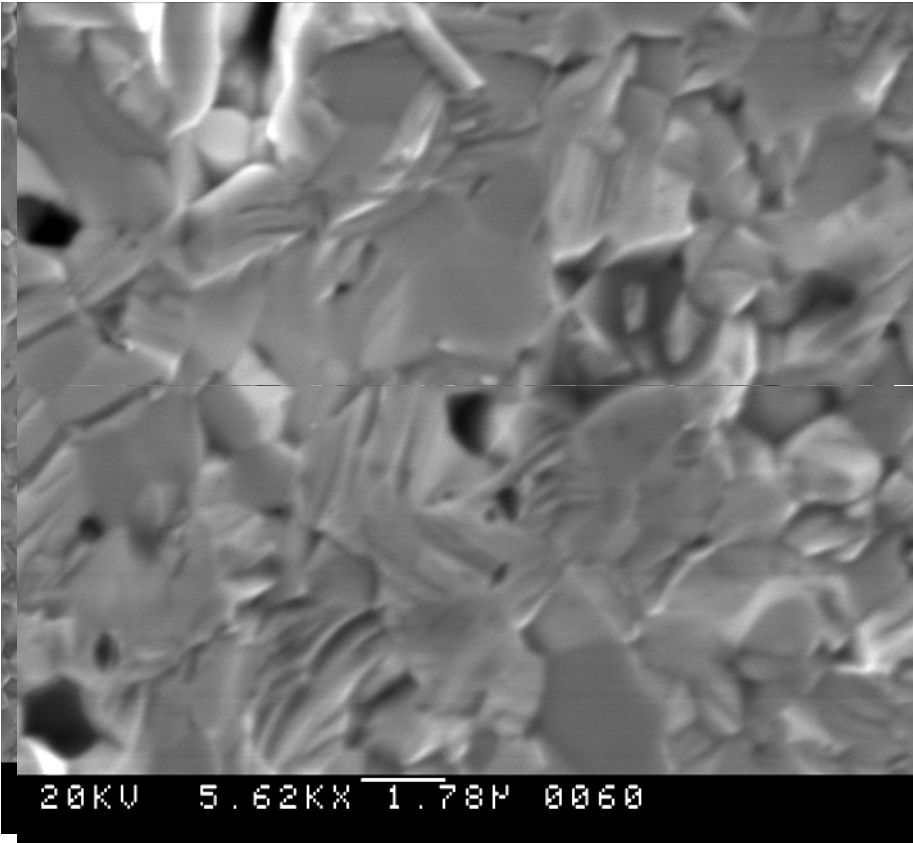
1700°C



1900°C

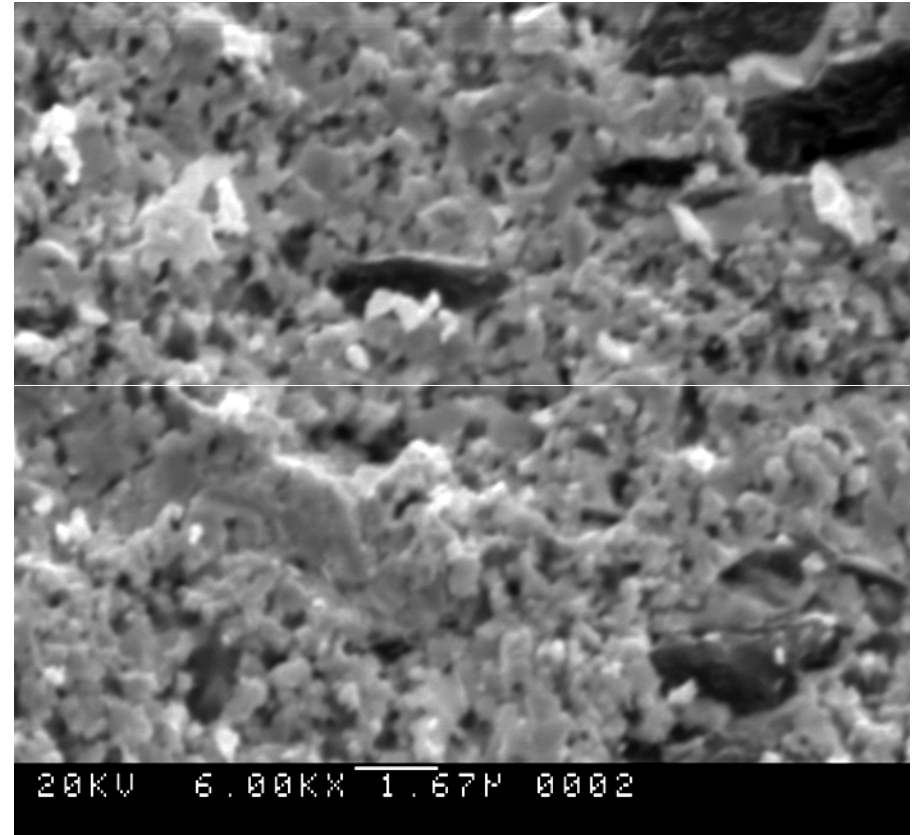
Open porosity about 12%

**SEM of TaC-TaB₂ - C Ceramics Prepared from 8TaC+B₄C Mixture
by Reaction Pressureless Sintering and Hot Pressing at 1700 C**



Pressureless Sintering

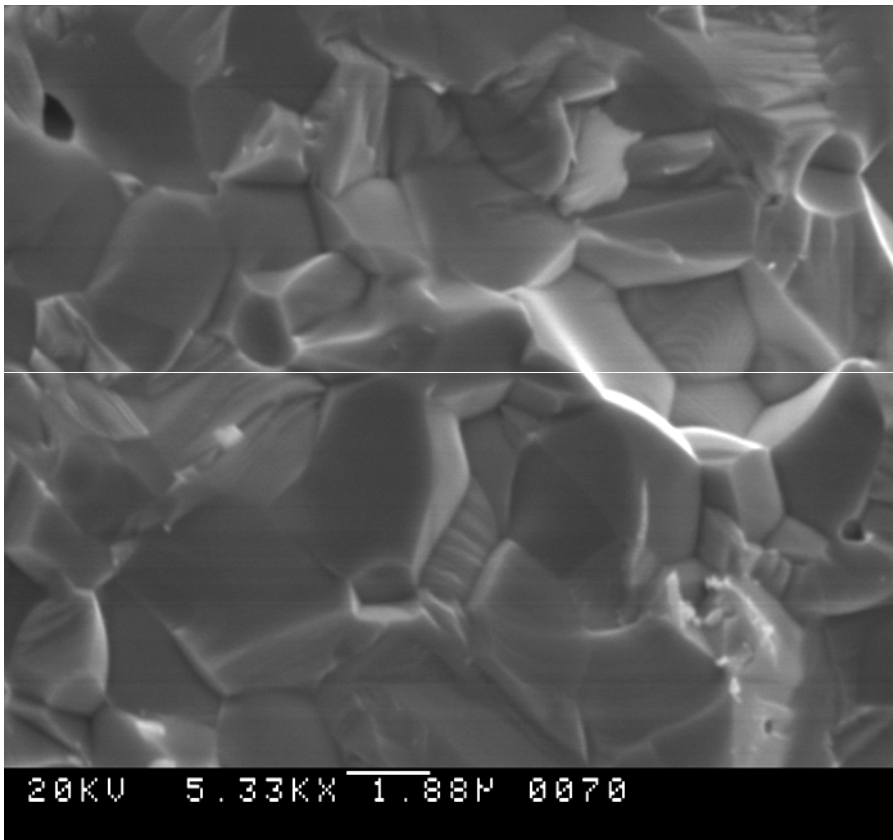
Open porosity 0.2%



Hot Pressing

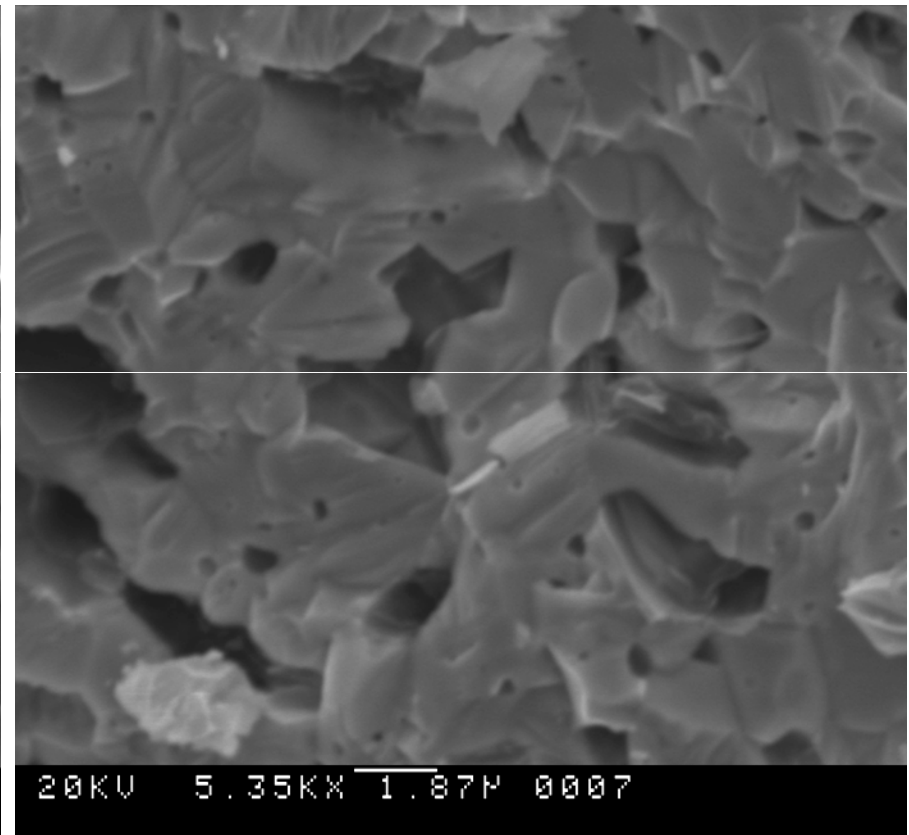
Open porosity 12%

SEM of TaC-TaB₂ - C Ceramics Prepared from **8TaC+B₄C** Mixture by Reaction Pressureless Sintering and Hot Pressing at 1900° C



Pressureless Sintering

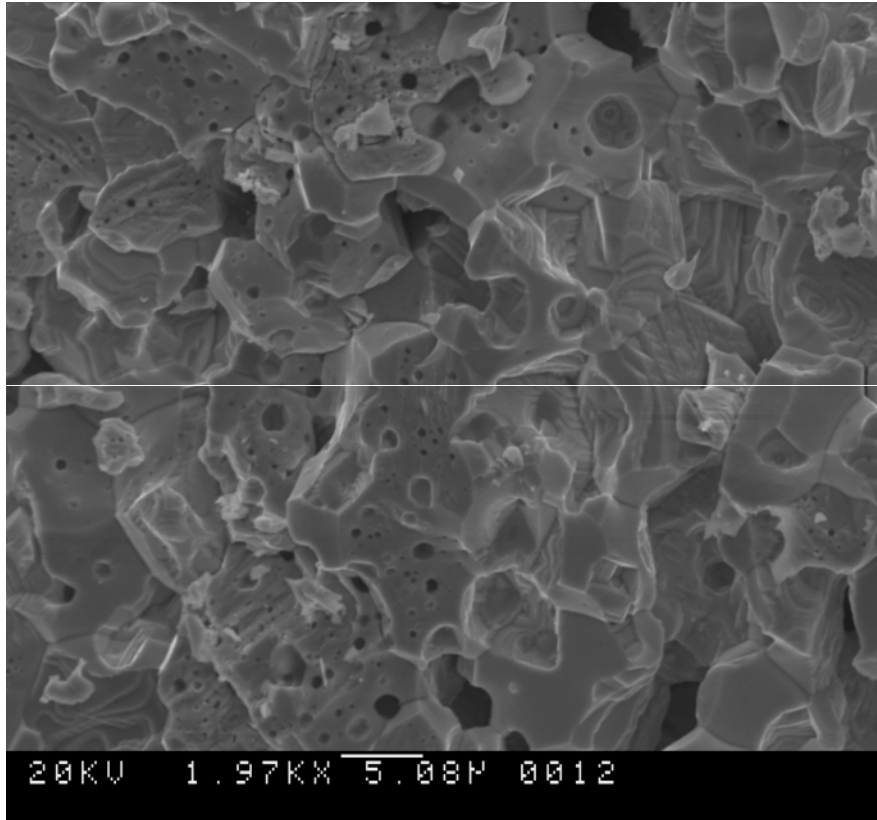
Fully dense sample



Hot Pressing

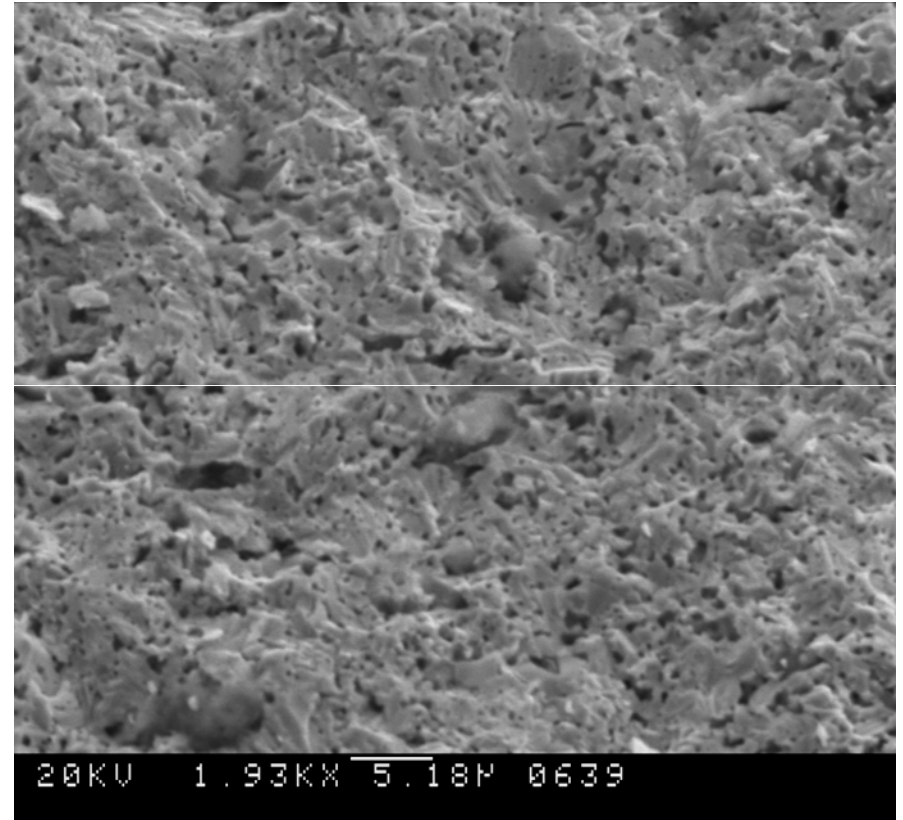
Open porosity 12.5%

SEM of TaC-TaB₂ - C Ceramics Prepared from 12TaC+B₄C Mixture by Reaction Sintering and Hot Pressing



Pressureless at 1800°C for 2 hours

Open porosity 4.5%

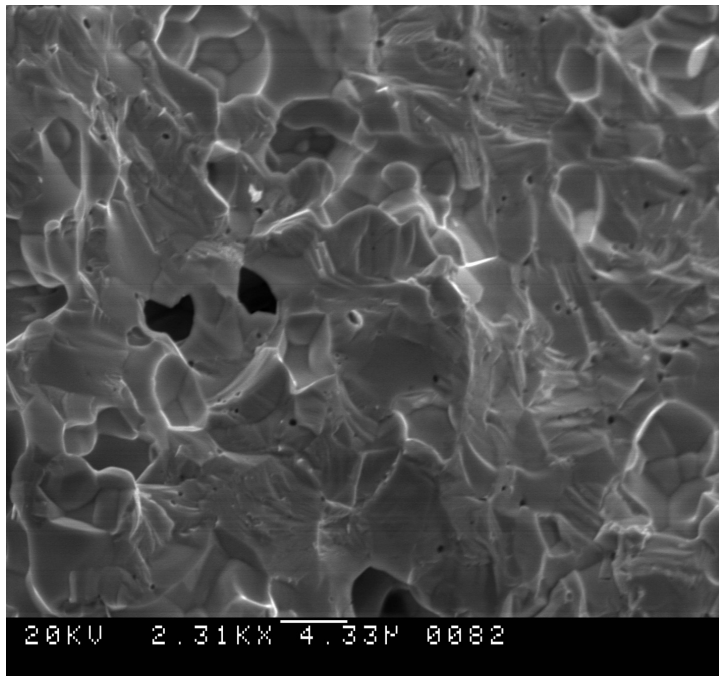


HP at 1700°C for 1 hour

Open porosity 12.5%

SEM, Flexural Strength (3-point), and Vickers Hardness of Ceramics: **8TaC/B₄C** (TaC – 62, TaB₂ – 25, C – 13 vol. %)

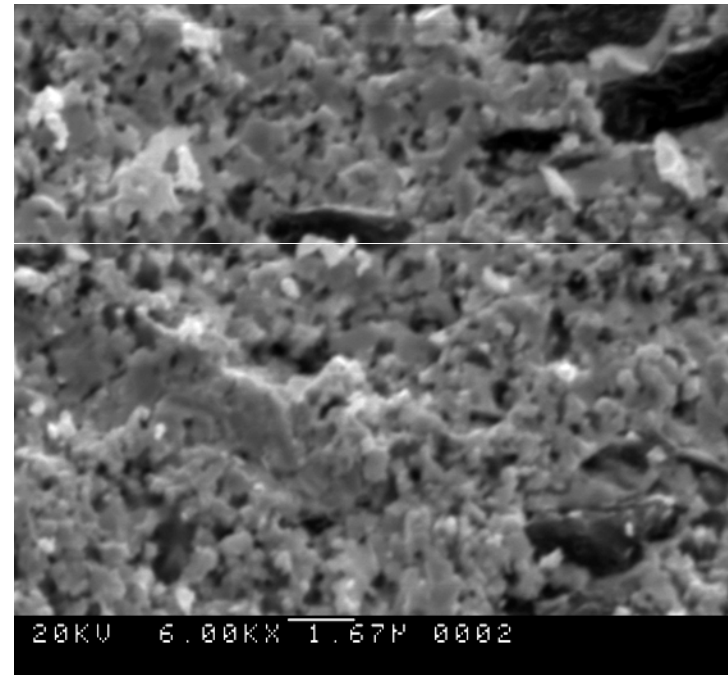
Pressureless sintered 1900°C



Strength-221 MPa

Hardness-22.2 GPa

Hot pressed 1700°C and 20MPa



Strength-293MPa

Hardness-8.2 GPa

Summary

- Dense ceramics containing (in v.%) 35-73.8 TaC, 25-62 TaB₂, and 8.6-22.5 C were prepared by reactive pressureless sintering of sub-micron TaC with B₄C at 1700-1900°C.
- Reaction between TaC and B₄C was completed at about 1700°C.
- The densification of multi-phase ceramics was promoted by the formation of TaB₂ and active carbon. Carbon eliminated oxygen from the grain boundaries additionally enhancing sintering.
- Use of sub-micron TaC and carbon black together led to pressureless densification of non-reactive mixture of 6TaC, 2TaB₂, 3C at 1850°C.
- The materials of all the tested compositions were not densified if a coarse TaC powder was used even in the presence of carbon black.
- Additional work is necessary to optimize processing parameters to remove oxygen at low temperatures, decrease shrinkage and stresses to increase the strength of ceramics.
- Low-temperature hot pressing is very promising for the development of high-strength multi-phase ceramics with a sub-micron grain size.
- Based on the results of this work and considering high potential of TaC for UHT applications, it is important to develop feasible low-cost method to produce sub-micron TaC and other carbides.