# Novel Structure, Properties, and Synthesis of Refractory Carbides

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# ABSTRACT

Our efforts report on new approaches to synthesize and sinter ultra high temperature ceramics (UHTCs) including boron carbides, silicon carbides, and zirconium carbides. We incorporate elemental inclusions, heterogeneous carbide phases, and carbon allotropes into carbides to improve the strength and shock resistance of the resulting composites. We developed a novel route that synthesizes shaped carbides from compressed powder mixtures of metal precursors and a carbon resin (1,2,4,5-tetrakis(phenylethynyl)benzene, or TPEB). This one-step approach yields dense ceramics with application-specific shapes such as disks and spheres and relies on pressureless tube furnace synthesis at temperatures below 1,500 °C. In an alternative to energy-intensive and commercially inefficient hot pressing, we developed a sintering approach that densifies greenbody ceramics with microwave irradiation. This method compacts boron carbides and yields highly dense structures. This technique requires shorter sintering times (< 30 minutes) and temperatures (< 1,300 °C), which improves the commercial viability of B<sub>4</sub>C in a broad range of commercial and military applications. This nanostructuring approach uses commercially viable high-energy ball milling and slurry dispersion methods and yields powders, monoliths, laminates, and coatings of optimized ceramics.

*Keywords*: carbides; armor; ultra high-temperature ceramics; sintering

## **1 INTRODUCTION**

Ultra-high temperature ceramics (UHTCs) and refractory carbides demonstrate significant promise in armor and hypersonic engine applications. These materials offer melting points above 3,000 °C, high hardness, and exceptional oxidation and corrosion resistance. However, to date, they have been too brittle, too heavy, or too costly to widely implement in military applications.. Traditional synthesis methods include hot-pressing ceramic tiles; this process requires high temperatures (> 2,000 °C), high pressures, and long synthesis times. These energy-intensive steps make the resulting materials prohibitively expensive on an industrial scale. Boron carbide (B<sub>4</sub>C), which offers high hardness and low densities, has poor shock resistance.

Subsequently, it cannot offer reliable ballistic protection against sharp ogives and dense armor-piercing ammunition.

The U.S. Naval Research Laboratory (NRL) has developed several methods to synthesize and/or sinter refractory carbides at low temperatures and optimize their structure at the nanoscale. An in situ Reactive Melt Infitration (RMI) nanocrystalline ceramic synthetic method relies on meltable precursor compositions of elemental metals and their one-step pyrolysis conversion into high density shaped solid ceramic components.[1] The carbon source uses 1,2,4,5-tetrakis(phenylethynyl)benzene (TPEB) polymer resin that melts below 200 °C, cures to a shaped thermoset, and chars into carbon above 600 °C. [2] This approach yields carbide disks, cones, and spheres at low temperatures.[3] In addition to this method, recent efforts have substituted carbon with silicon in B<sub>4</sub>C nanostructures and demonstrated improved hardness.[4] In order to economize the sintering process, NRL has also developed microwave sintering technology that pressurelessly, rapidly heats materials with an 85 GHz, 15 kW gyrotron.[5]

We implement these techniques and present top-down and bottom-up approaches to synthesize high-performing, dense boron carbide (B<sub>4</sub>C), zirconium carbide (ZrC), and B<sub>4</sub>C infused with Si (B<sub>4</sub>C-Si/SiC). Our methods apply pressureless, low-temperature (< 1,500 °C) heating and adjust the nanoscale parameters of the materials to optimize resulting composites. The complementary methods yield shaped metal carbides with customized properties that are geared for high-performance ballistic and thermal protection in a broad range of U.S. military applications.

#### **2 EXPERIMENTAL**

## 2.1 Materials and Preparation Techniques

All experimental precurosor materials were commercially available and inexpensive. Precursor materials were cold-pressed (either with uniaxial pressing at 558 MPa or cold isostatic pressing (CIPping) at 1.37 GPa PSI) into 6 -40 mm disks (0.5 -12 mm thicknesses).

For the polymer-derived ceramic/RMI route, the synthesis relied on boron (B), silicon, (Si), zirconium (Zr), or zirconium hydride (ZrH<sub>2</sub>) powders (99% pure,  $1 - 5 \mu m$  diameter). Metal precursors were mixed with TPEB (C<sub>38</sub>H<sub>22</sub>), which acted as the carbon source. Si and B were

mixed with TPEB in 1:1.1 metal-to-carbon atomic ratios; Zrcontaining precursors were mixed with TPEB in varios ratios in the range of 1:1.0 – 1:1.75 Zr:C. Prior to mixing, TPEB was heated at 225 °C and produced a partially crosslinked Bstage prepolymer solid. Ball milling pulverized and homogenized the polymer/metal mixtures.

Sintering experiments used commercially available B<sub>4</sub>C  $(0.5 - 5.0 \,\mu\text{m}$  diameter powder) and 1 mm-sized undoped Si chips. We used varying ratios of Si to C atoms in the B<sub>4</sub>C structure: 1 Si: 0.33 C (5.5 wt.% Si in B<sub>4</sub>C), 1 Si: 0.66 C (11.0 wt.% Si), 1 Si: 1.0 C (16.5 wt.% Si), and 1 Si: 1.5 C (24.8 wt.% Si). The materials were ball-milled together using high-energy ball-milling (HEBM).

### 2.2 In Situ RMI Synthesis

Disks were placed on alumina stubs inside of a mullite tube furnace. Under flowing Ar (300 ml min<sup>-1</sup>), samples were heated at a rate of 2.0 °C min<sup>-1</sup> up to 1400 - 1500 °C and isothermally heat treated for 2 hours.

### 2.3 Microwave-Assisted Sintering

Disks were held under a vacuum in a steel enclosure. An 85 GHz gyrotron irradiated the samples with a microwave beam ( $\lambda = 1.0$  mm). The instrument applied maximum power (27 kV cathode voltage and 17 A filament current). The samples were sintered for 20 minutes.

#### 2.4 Materials Characterization

A thermogravimetric analyzer with a calorimetry component (TGA-DSC) provided thermal analysis of the precursor mixtures heated with the same conditions. X-ray diffraction (XRD) provided information about the phase composition and crystalline domain sizes. Densities of materials were derived using Archimedes' principle mass measurements and calculations. Specific surface area (SSA) and porosimetry measurements were collected using an N<sub>2</sub> gas sorption analyzer at 77 K.

## **3 RESULTS**

#### 3.1 Polymer-Derived Synthesis of ZrC

Disks of Zr:TPEB and ZrH<sub>2</sub>:TPEB fully convert to ZrC after thermal treatment at 1400 °C under Ar. The images of the resulting materials are shown in Figure 1a. X-ray diffractograms are shown in Figure 1b.

Crystallographic analysis shows that both Zr and ZrH<sub>2</sub> precursors completely convert to ZrC, with negligible ZrO<sub>2</sub> impurities (< 1% for materials with 1:1.1 – 1:1.21 metal-to-carbon ratios). ZrH<sub>2</sub> yields slightly more pure ZrC with no leftover Zr. Low metal-to-carbon ratios decrease domain sizes; the lattice dimension decreases from 75 nm (1 Zr: 1.75 C) to 35 nm (1 Zr: 1.11 C).



Figure 1: (a) ZrC disks with 6-25 mm diameters. (b) XRD of ZrC produced from  $ZrH_2/TPEB$  and Zr/TPEB precursors.





Figure 2: (a) TGA and (b) DSC thermal analysis data for conversion of ZrH<sub>2</sub> and TPEB into ZrC.

Different metal-to-carbon ratios exhibit individual thermal conversion profiles. Specific reaction steps, such as hydrogen desorption from  $ZrH_2$  and TPEB, occur at the same temperatures for each molar ratio. However, mass loss directly correlates with the amount of carbon in the prepreg mixture. Therefore, some of the excess carbon decomposes (likely as hydrocarbons), rather than char into a solid graphite phase.

The metal-to-carbon ratio also influences the density of resulting shaped zirconium carbide. The 1.0 mol Z: 1.11 mol C ratio with the  $ZrH_2$  precursor demonstrates the highest density (5.77 g cm<sup>3</sup>; 86% of its 6.73 g cm<sup>3</sup> theoretical maximum density).



Figure 3: (a) Relationship between prepreg carbon-to-metal ratio and SSA. (b) Pore size distribution of ZrC/C foam.

Excess carbon controls the specific surface area (SSA) and porosity. As shown in Figure 3a below, higher amounts of TPEB increase SSA from 1.0 to 33.1 m<sup>2</sup> g<sup>-1</sup>. The polymer charring process involves a significant amount of hydrogen evolution and leaves behind low-dense carbon, which yields microscale pores in the Zr/C composite matrix. Rapid microwave irradiation of a sample with 1.5 C:Zr ratio significantly accelerates this process and yields a highly porous foam with an SSA of 104 m<sup>2</sup> g<sup>-1</sup> (porosity shown in Figure 3b). Combustion analysis suggests that the resulting structure is composed of 5 wt. % carbon and 95 wt. % ZrC. Therefore, this approach also effectively produces lightweight, porous ZrC composites with high accessible surface areas and structured porosities. These materials demonstrate promise for applications in infiltrated polymer composite systems and catalyst supports.

### 3.2 Polymer-Derived Synthesis of B<sub>4</sub>C/SiC

Pure B-TPEB prepreg compositions and blends of B-Si-TPEB use a similar *in situ* RMI process to yield, respectively, dense  $B_4C$  and  $B_4C/SiC/B_xSi_yC_z$  systems. Various resulting shapes are shown in Figure 4 below.



Figure 4:  $B_4C/SiC$  composites with 6 - 40 nm diameters.

Although the resulting composite structure include several distinct phases with unique crystal structures, the materials demonstrate high densities. Most compositions fall into the range of 2.32 - 2.37 g cm<sup>-3</sup> range, which constitutes 91 - 94 % of B<sub>4</sub>C's theoretical maximum density.

Crystallography analysis (Figure 5a) shows that the SiC phase, as expected, becomes more prominent for prepregs with higher Si wt. %. No leftover Si or B are present, which suggests that this multiphase reaction is an equilibrium process.



Figure 5: (a) X-ray diffraction analysis of B/Si/TPEB RMI products after thermal treatment at 1500 °C. (b) Grain size analysis of SiC and B<sub>4</sub>C phases in the resulting shaped carbide composites.

As Si wt. % increases, a  $B_{12.97}Si_{0.3}C_2$  phase becomes more prominent. This rhombohedral material makes up 25% of the material with 24.8 wt. % Si and suggests a substitution of Si into the polar sites of the ( $B_{11}C_p$ )-CBC boron carbide polytype. Lattice parameter analysis (Figure 5b) shows that, while SiC domains are unaffected by Si ratio,  $B_4C$  domains shrink with greater Si prevalence.

### 3.3 Microwave Sintering of B<sub>4</sub>C-Si

Microwave irradiation of cold-pressed B<sub>4</sub>C and Siinfused B<sub>4</sub>C disks yields highly compacted ceramics after short sintering times. The maximum sintering temperature of the material never exceeds 1,400 °C, which falls significantly lower than the 2,200+ °C conditions used for hot-press sintering of B<sub>4</sub>C. Cold-pressed greenbody ceramics (shown in Figure 6a) exhibit a density in the range of 55 – 64 % of B<sub>4</sub>C's theoretical maximum. However, after 20 minutes of microwave sintering (shown in Figure 6b), the materials reach densities as high as 2.42 g cm<sup>-3</sup> (95.9 % of B<sub>4</sub>C's TMD).



Figure 6. (a) 10 mm B<sub>4</sub>C disks before sintering and (b) after sintering. (c) X-ray diffraction analysis of B<sub>4</sub>C infused with different weight percentages of Si after sintering.

In addition to compacting the disks, the energetic microwave treatment also introduces Si into the  $B_4C$  lattice. Silicon bonds with the carbon (most likely from the 3-atom carbon chains) to form SiC phases. Larger amounts of Si also potentially introduce a new  $B_xSi_yC_z$  rhomobohedral structure. These substitutions are expected to reduce shock-induced failure of  $B_4C$  and improve its ballistic protection performance.

## **4** CONCLUSIONS

We developed several pathways to synthesize ZrC,  $B_4C$ , and SiC refractory ultra high-temperature ceramics. The approaches yield dense, shaped carbides with tunable form factors and compositions. The low-temperature synthesis and/or sintering processes are more energy-efficient than conventional hot-pressing methods. The RMI and microwave sintering methods are applicable to a large family of UHTC materials, including carbides, metal oxides, borides, and nitrides. Our approach allows adjustments of the structure at the nanoscale and integration of multiple phases into composites that can be optimized for specific applications. Carbon nanostructures incorporate into these materials and yield novel carbon-reinforced structures and ceramic matrix composites (CMCs). Beyond novel armor composites, these materials demonstrate promise in thermal protection of hypersonic engines, ablation protection in heat shields, anode materials in energy storage, high-temperature electronics, and catalyst supports.

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