

Reinforced Ceramic Composites Fabricated From High Char Yield Polymers

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ABSTRACT

Ultra-high temperature ceramics (UHTCs) such as transition metal borides, nitrides, and carbides melt at temperatures greater than 3000 °C, thereby exceeding the temperature threshold required for hypersonic applications. However, these materials are quite brittle which leads to low fracture toughness, and poor thermal shock resistance. In addition, the extensive synthesis and processing that is required to produce UHTC materials with shapes machined for specific applications substantially increases their production costs. To this end, a variety of reinforced UHTC materials were synthesized using polymeric method to fabricate ceramic phases *in situ* enabling the production of near-net-shape composites. This method exploits the chemical reaction between elemental metals or metal hydrides and a high char-yield polymeric resins—which acts as a carbon source, as well as a binding phase—to produce low-cost composite materials. This method can be adapted to produce composites reinforced with chopped and continuous reinforcement phases. The composite matrix can also be varied by altering the precursor composition to produce carbon-carbon (C/C), carbon-ceramic, and ceramic matrix composites (CMCs).

1 INTRODUCTION

Improvements in high speed propulsion systems has increased the demand for high-temperature materials which can be fabricated through cost-effective processes, and withstand harsh thermal and mechanical conditions.¹ Given these stringent requirements, suitable materials are relatively scarce, nevertheless, ultra-high temperature ceramics (UHTCs) such as transition metal borides, nitrides, and carbides melt at extremely high temperatures (>3000 °C)—thereby exceeding the required temperatures for most applications.^{2,3}

Due to their brittle nature, UHTC materials typically exhibit low fracture toughness and poor thermal shock resistance, ultimately limiting their application. In order to dampen these effects,

composite materials have been made with a variety of reinforcement phases (carbon nanotubes, carbon fiber, silicon carbide fibers). While this strategy has been effectively used to boost the mechanical performance of UHTC materials, the production of materials with acceptable hardness and density can be cost prohibitive. For instance, multiple processing methods are often coupled together in order produce fully dense materials.⁴ The added processing complexity increases the cost and also limits the scalability of these technologies.

Like their UHTC counterparts, carbon-carbon (C/C) composites are high-temperature materials with prohibitive manufacturing costs. Though these materials offer intriguing thermal and mechanical properties, their synthetic pathway often includes multiple polymer or vapor reinfiltration steps to produce robust materials—preventing large scale usage in high-temperature applications.⁵

To improve the manufacturing of both UHTC and C/C composites, a novel method was developed which utilizes a high char yield resin to act as a carbon source as well as bind composites together.⁶ This is a very versatile process which can accommodate milled, chopped and continuous reinforcement phases. For UHTC composites, the carbonized resins react with metal inclusions to form ceramic phases *in situ* which allows for fabrication of near net shape ceramics and reduces the number of steps needed to produce materials.⁷ Producing C/C composites with this method also reduces manufacturing costs since the higher char yield compared to traditional resins is much higher and fewer reinfiltration steps are required.

In addition to reducing manufacturing costs, these two processes can be combined in order to produce carbon-matrix composites with additional carbide phases. By making multiphase composites using high char yield resins, different material properties can be optimized using this straightforward approach.

2 EXPERIMENTAL

2.1 Preparation of TiB₂ Composite precursors with Chopped Reinforcements

Ceramic precursors for TiB₂ composites with chopped carbon fiber reinforcements were prepared by ball milling elemental titanium and boron powders in a 1:2 molar ratio with 5 wt. % of high char yield resin 1,2,4,5-tetrakis(phenylethynyl) benzene (TPEB). In some formulations, B₄C was added as a sintering additive. Chopped carbon fiber (Zoltek, 6 mm dry chop flake) reinforcements were dispersed via sonication in an ethanol solution prior to mixing with a precursor slurry in ethanol. After evaporation of the ethanol, TiB₂/carbon fiber precursor was consolidated into 25 mm disks by applying 1000 psi using a hydraulic press heated to 225 °C

2.2 Fabrication of Woven Carbon Fiber Prepreg

Prepregs were made from a resorcinol based phthalonitrile resin (RES). All composites were prepared by infiltrating resins into unsized woven carbon fiber fabric. To fabricate the prepreg, RES resin (46.23 g) was dissolved in 120 mL of acetone and the resulting solution was then painted onto the woven carbon fiber preform. For samples with TiC, ceramic phases were induced by coating each ply with a RES/Ti precursor powder mixed in the proper ratio (i.e. 1:9 and 1:1, RES:Ti). The impregnated fabrics were dried in air for 30 min before cutting them into 6" x 6" pieces. A total of 8 plies were cut from the larger impregnated fabric sheet and then dried overnight in an oven heated to 100 °C.

2.3 Consolidation of Woven Samples.

The prepreg was consolidated using a heated hydraulic press. All samples were heated at 150 °C under vacuum while using the press to apply a gentle pressure. Following removal of the vacuum, the temperature and pressure were increased to 175 °C and 50 psi, respectively. After 60 minutes, the temperature was further increased to 225 °C and heated for an additional 60 min before cooling to room temperature and removing the pressure.

2.4 Conversion to Ceramic Phase

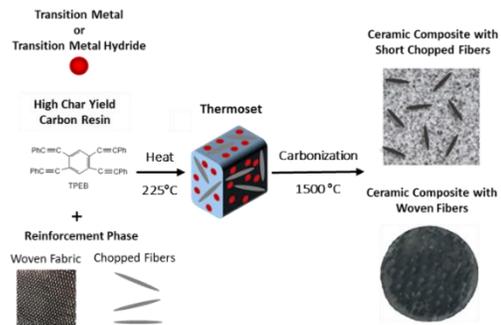
Composites were placed on alumina stubs inside of a mullite tube furnace. Samples were heated under flowing Ar (100 ml min⁻¹) to 1450 °C at a rate of 2.0 °C min⁻¹ up, and isothermally heat treated for 2 hours.

2.5 Materials Characterization

Thermal characterization of precursor powders were performed using a TA Instruments Q600 Simultaneous TGA-DTA. Powder x-ray diffraction (XRD) patterns for structural characterization were obtained using a Rigaku SmartLab diffractometer. Scanning electron microscopy (SEM) images were gathered using a JEOL SEM in order to examine fiber-matrix bonding and fiber dispersion within the sample.

3 RESULTS

Thermosetting resins with high char-yield resins were used to fabricate composite materials (Scheme 1). When carbonized as thermosets, these resins exhibit char-yields in excess of 80 %, which is higher than most commercially available resins.⁶ In addition to exhibiting slight mass loss when, these resins are also highly reactive after pyrolysis—making them an ideal carbon source for the formation of ceramic phases at lower temperatures (1500 °C) than typical synthetic pathways. Given the facile processing of thermosetting materials, the construction of ceramic materials in this manner enables the production of near net-shape designs, which further reduces manufacturing costs. While this strategy represents a significant enhancement in their fabrication, it also presents the opportunity to make ceramic composites by incorporating chopped fiber reinforcements within the precursor mixture, or infiltrating the precursor into continuous reinforcement phases.



Scheme 1. Fabrication of Reinforced Ceramic Composites

3.1 Evaluation of Precursor Compositions

Ceramic sintering agents, such as B_4C , are often used to react with oxide phases that are formed during pressureless sintering of UHTC materials.⁸ To investigate if B_4C can react with oxide phases during the *in situ* synthesis of TiB_2 , and improve the density of the resulting ceramic composites, precursor formulations with varying concentrations of B_4C were heated to 1450 °C (10 °C min⁻¹) under an Ar atmosphere. During synthesis the sample mass and heat flow were measured using TGA-DTA (Figure 1). The TGA thermograms show two peaks, centered near 450 °C and 1000 °C, for all samples. This may indicate that some oxidation is occurring while heating due to oxygen impurities in the Ar gas. Given that all samples exhibit similar peak intensities at 450 °C, and have the same concentration of TPEB, it is possible that the low temperature peak represents oxidation of TPEB. The high temperature peak may result from oxidation of boron or Ti contained in the precursor. Examination of heat flow in the various precursor indicates that all samples exhibit a transition near 375 °C, which may be attributable to the conversion of TPEB to a thermoset phase, or oxidation of the sample. A second transition is also observed near 900 °C. While this may also be the result of oxidation, further study is needed in order to confirm this assertion.

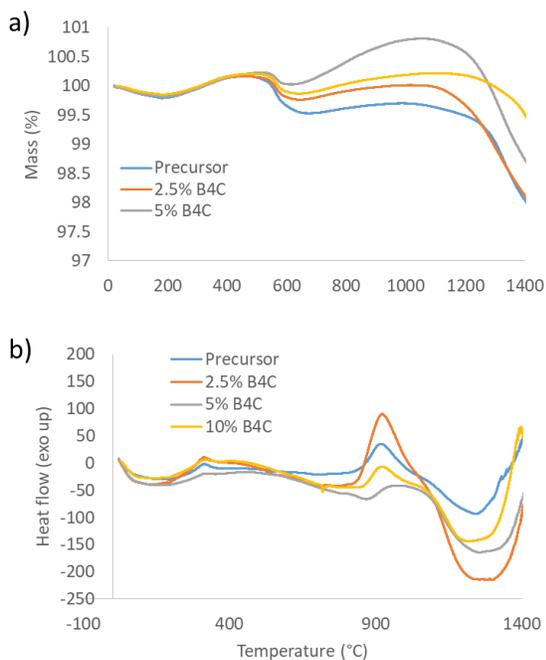


Figure 1. Thermogravimetric (a) and differential thermal analysis (b) thermograms of TiB_2 precursor powders with B_4C sintering aids.

3.2 Chopped Carbon Fiber Reinforced Ceramics

Composites, containing a TiB_2 matrix, were reinforced with 5 wt. % of chopped carbon fiber. Powder XRD and SEM were used to identify the phases present in the sample and investigate morphology and fiber bonding at the sample surface (Figure 2). According to the powder XRD pattern, the sample predominantly consists of TiB_2 , however TiB phases are also observed. Given the *in situ* formation of the ceramic, it is not surprising to observe multiple phases. Despite inclusion of carbon fiber reinforcement, peaks corresponding to carbon phases are not clearly observable in the XRD pattern. However, examination of the SEM images clearly indicates that some fibers are observable, which likely indicates that regions with exposed carbon fiber at the sample surface are relatively scarce. When further magnified, bonding between the TiB_2 matrix and carbon fiber reinforcements is observed in SEM images. These bonding interactions suggest that formation of the ceramic phases *in situ* may improve adhesion between the composite matrix and reinforcement phase.

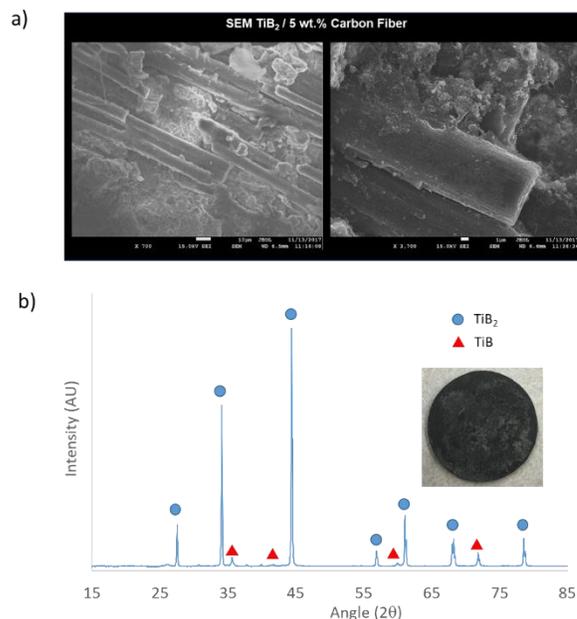


Figure 2. Representative SEM images (a) and powder XRD patterns (b) of TiB_2 composites with chopped carbon fiber reinforcements (inset: image of sample under ambient light).

3.3 Composites from Woven Carbon Fiber Preforms

Unlike samples with chopped fibers, RES was used to fabricate composites with continuous reinforcement phases (Figure 3). It was selected because it has a high char yield (73.6 % after heating to 1000 °C) and has been previously used to make polymer composites. By impregnating woven fiber preforms with RES and consolidating them, the resultant material can be carbonized at 1000 °C to produce a C/C composite. Because of the high char-yield of RES compared to traditional resins, a composite with 84 % theoretical mass density was obtained after a single impregnation step. Given the higher mass retention observed for these samples, fewer reimpregnation steps will be needed to produce C/C with requisite densities—representing a significant reduction of manufacturing costs.

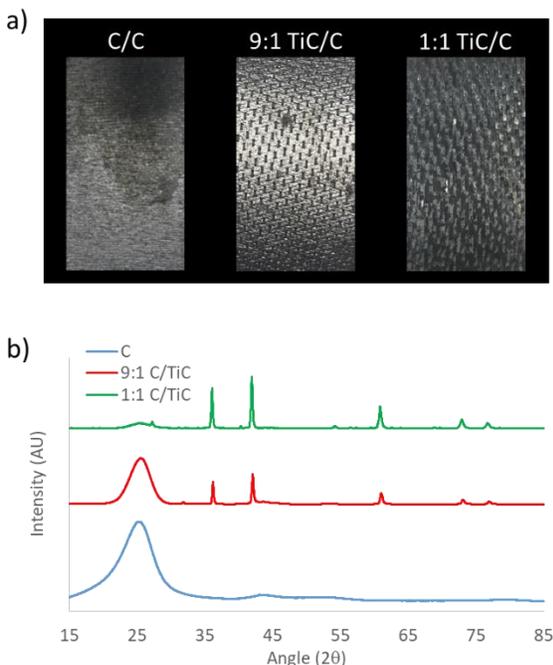


Figure 3. Image of woven composites under ambient light (a) and their corresponding powder XRD patterns (b).

Fabrication of C/C composites using this method also presents a facile strategy for incorporating ceramic phases to augment material properties, or forming ceramic matrix composites (CMCs). To demonstrate this method, carbon fiber preforms were coated with precursors containing RES and Ti powders before consolidation. When the resulting composites were heated to 1450 °C, TiC ceramic phases were formed and identified using powder

XRD. Inspection of the XRD patterns indicates that variation of the RES/Ti ratio determined the amount of ceramic phase formed in the composites. When coating the prepreg with a precursor containing 9:1 RES/Ti, only a small amount of TiC is detected. However, the matrix of composites made with 1:1 RES/Ti precursor is almost entirely TiC. Therefore, the matrix composition can be altered simply by changing the concentration of metal source present in the precursor composition.

4 CONCLUSIONS

High-char yield resins can be used to fabricate a variety of composite materials for high-temperature applications. Not only can these systems be used to produce carbide and boride UHTCs, but their *in situ* synthesis simplifies the incorporation of different types of reinforcement phases. This was demonstrated by making TiB₂ and TiC composites with chopped carbon fibers and woven carbon fiber fabrics. Additionally, the composition of woven samples can be easily modified to produce C/C, C-ceramic, and CMCs by changing the concentration of the metal source in the precursor mixture. The versatility of this method combined with its enhanced processing capabilities aids in the production of a variety of low cost composite materials.

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