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TiN modified SiC with enhanced strength and electrical properties

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ABSTRACT

SiC based composites were manufactured with varying TiN content (0–50 V%) using Al_2O_3 and Y_2O_3 sintering aids. Basic dilatometry measurements were performed to determine when densification begins within the composite system. Samples were consolidated via uni-axial hot pressing at 1900 °C to produce ceramic composites with >98% theoretical density. Electrical measurements show increasing TiN additions reduce resistivity and begin to plateau at 40–50V%. Resistivity decreased from $2.0 \times 10^5\ \Omega - cm$ (0% TiN) to $2.0 \times 10^{-4}\ \Omega - cm$ (50V% TiN). Flexural strengths were characterized and compared against a baseline (0% TiN) SiC. Strengths increased gradually with TiN content. A maximum strength 921 MPa was observed at 40V% TiN content vs. 616 MPa for the baseline SiC. This was a gain of 50% over baseline. Additions beyond that range did not produce further gains in strength.

1. Introduction

SiC based ceramics find broad, far reaching use in technology and manufacturing applications. This is due to many of its key properties. Structural applications (e.g. ballistic strike plates [4], mirror) take advantage of its high hardness, high stiffness, low density, and low coefficient of thermal expansion. High temperature and thermal applications take advantage of the phase stability (no inversions) and high thermal conductivity. Performance automotive brake rotors have been made from SiC-SiC composites. Since SiC is a semi-conductor, its electronic properties can be adjusted by suitable doping to exhibit *n*-type or *p*-type behavior. It also has found use in diodes and LEDs. Polycrystalline SiC based ceramics could find broader use if they could be machined easier by rendering them more electrically conductive. Higher conductively enables efficient electro-discharge machining (EDM) of complex shapes. Strength enhancement would allow for competition with structural Si_3N_4 based applications.

The primary polymorphs of SiC are the hexagonal α-SiC (with over 200 polytypes) and the cubic β-SiC phases. At elevated temperatures, the β phase converts to α [1]. Sintering of SiC ceramics with little to no processing aids is typically done between 2100 and 2200 °C [2,3]. Boron and carbon additives have been used extensively as high temperature sintering aids [2,3]. However, other sintering aids have been of wider interest to lower processing temperatures and to engineer the microstructure enhancing other properties such as toughness. Omori showed the benefit to hydroxide additives [2] based on aluminum and yttrium and the literature is replete with oxides (Al_2O_3, Y_2O_3) and nitrides (AlN) being used to sinter SiC to high density in the 1800–1900 °C range [3–7]. The oxide additions are associated with mass loss during sintering [3,4,6]. Can [3] showed the oxide ratios are important since high Al_2O_3 to Y_2O_3 ratios produced high fired density but higher weight loss and that low ratios (<1) produced lower densities. High toughness SiC ceramics were produced [4] via ABC or YAG additions. Creep resistance was improved with AlN and Y_2O_3 additions [6]. Pressureless sintering using oxide sintering aids has also shown promise when a suitable powder bed is used [7] or without a powder bed [8].

Another route to improve the properties of SiC and Si_3N_4 based ceramics has been through the addition of electrically conductive particulates such as TiN. The addition of electrically conductive particulates to poor conductors allows the electrical properties to be tailored. Improvements in mechanical properties are also observed. This effect has been illustrated via the addition of TiN to Si_3N_4 ceramics [9–12]. TiN particulates at <35 V% improved the strength of Si_3N_4 [9] but at higher levels produced inhomogeneous regions that reduced strength. TiN additions also reduce the variability in measured strengths [11] while leading to enhanced electrical conductivity [12]. TiN additions into SiC ceramics have also produced improvements mechanical properties. Guo utilized nano TiN and achieved strengths of 686 MPa and observed TiN additions inhibited densification and reduced grain growth when pressureless sintered. Strength was optimized at 5 wt% additions [13]. Zhang use nano TiN combined with SiC whiskers to produce composites

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with fracture toughness values of 8.69 MPa-$m^{0.5}$ and strengths of 1123 MPa when pressureless sintered [14].

In the present work, we have processed SiC with micron sized TiN additions. To enhance densification, an oxide (Al_2O_3 and Y_2O_3) sintering aid system was used in combination with hot press sintering. Both the mechanical properties and the electrical properties were characterized as a function of TiN content.

2. Materials/experimental

2.1. Ceramic processing

Starting powders were obtained from commercial sources. Powder grades included: alpha SiC (0.7 μm, Grade UF-10, HC Starck), TiN (0.8–1.2 μm, Grade C, HC Starck), Y_2O_3 (0.9 μm, Grade C, HC Starck), and Al_2O_3 (0.7 μm Grade RC-HPT (Baikowski-Malakoff)). Powders were ball-milled inside a high density polyethylene bottle using zirconia media and isopropyl alcohol for 24 h. Powder mixing was performed on a laboratory jar mill spinning at ~40 rpm. (Labmill 8000, Advanced Ceramics Manufacturing). After milling, powders were dried in a convection oven. The powder cakes were broken up and sieved prior to hot pressing. Composition details are shown in Table 1. The baseline SiC formulation (ST00) had 0% TiN and contained 6.0 wt% Al_2O_3 and 4.0 wt% Y_2O_3 as sintering aids. Variants with TiN additions were formulated based on adding TiN directly to the baseline formulation (the sintering aids were constant relative to the SiC).

Hot pressing of SiC-TiN composites was performed under a vacuum/argon atmosphere inside a resistively heated 65 ton hot press (Thermal Technologies). The mixed powders were heated to 1000 °C at 10 °C/min in vacuum and then heated to 1900 °C at 5 °C/min (60 min soak) under a flowing argon atmosphere. A pressure of 30 MPa was applied. After the high temperature soak, the temperature was reduced to 1000 °C at a rate of 12 °C/min and then allow to cool at furnace rate. Typical billet dimensions were 25 × 75 × 5 mm after hot pressing.

2.2. XRD

X-ray diffraction was performed on hot pressed samples using a Cu-Kα radiation. The diffraction pattern was taken on a surface normal to the pressing direction. The scan was performed from $20° < 2\theta < 75°$ using 0.02°increments. Diffraction patterns were compared to those expected from the constituent materials (TiN and α-Sic) as well as potential reaction products such as TiC and T_2CN.

2.3. Mechanical/physical characterization

Flexural test specimens were prepared for 4-point bending per ASTM C-1161 using the type "B" geometry. Test specimens were diamond diced and ground from hot pressed billets into rectangular bars with dimension of 3 × 4 × 50 mm. The test fixture utilized a 20 and 40 mm inner and outer span, respectively. Four samples were tested per composition.

Densities were determined use the Archimedes (water immersion) method by weighing samples in air and in deionized water. The theoretical density was determined by a simple rule of mixtures using the mass fraction of constituent materials. Relative density was determined by the ratio of measured density to theoretical density.

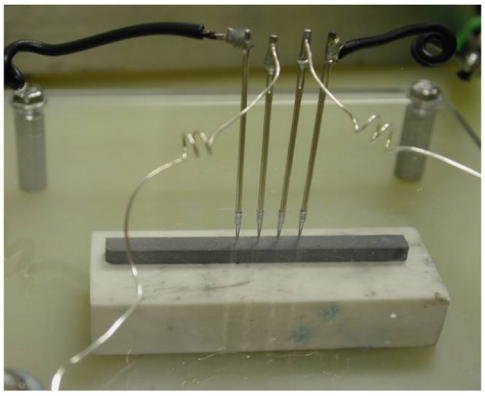

Fig. 1. Set-up to measure bulk resistivity (left) and test fixture (right).

2.4. Electrical characterization

A four-point probe technique was used to determine the material's bulk resistivity on 3 × 4 × 50 mm test bars. A custom set-up was built (Fig. 1). Probe spacing was 4 mm.

The measured voltage (V) vs. current (I) data have been used to calculate bulk resistivity using Eq. (1)

$$\rho = \frac{2\pi s}{F}\frac{V}{I} \quad (1)$$

where, ρ, is the electrical resistivity of the bulk material, s, is the probe spacing, V, is the voltage, I, is the current, and F is an additional correction factor related to the dimensions of the sample and the spacing of the contact probes [15]. For the selected geometry, the correction factor was $F = 8.25$.

Constant current was applied using a computer controlled PAR 173 potentiostat and the voltage was measured. At least four test bars were measured for each sample. The applied current was varied (0.05A–0.2A) for each measurement and the average value was reported.

2.5. Sintering/firing behavior

A gel cast slurry was made from blend ST40 using a proprietary system [16]. Each slurry was cast into aluminum molds to form green pellets 16.0 mm in diameter and 10.2 mm in height. The solid loading of the SiC-TiN slurry was 57 Vol.%. The binder was removed using a 39 h burnout cycle. The samples were heated using at a rate of 5 °C/min, held at a given soak temperature for 10 min, and cooled to room temperature. Sample shrinkage was determined by the change in pellet diameter.

2.6. Microstructure analysis

Scanning Electron Microscopy (SEM) was used to image the surface of polished samples. Polishing was accomplished with diamond paste and finished with a 0.5–1 μm slurry. Surfaces were plasma etched to reveal grain boundaries. Images of the surfaces were taken from planes normal to the uni-axial compression axis.

3. Results

3.1. Densification

Understanding the densification-temperature behavior of ceramics is important for designing and optimizing heating/cooling profiles. The relative density of SiC-TiN samples as a function of temperature is shown in Fig. 2. Densification initiated at 1400 °C and accelerated between 1600 °C and 1900 °C. The onset temper-

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