Silicon carbide–titanium diboride ceramic composites

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Abstract

The effect of TiB_2 content on mechanical properties of silicon carbide–titanium diboride ceramic composites was studied. The hardness of the ceramics decreased from 27.8 GPa for nominally pure SiC to 24.4 GPa for nominally pure TiB_2. In contrast, fracture toughness of the ceramics increased from 2.1 MPa m$^{1/2}$ for SiC to ∼6 MPa m$^{1/2}$ for SiC with TiB_2 contents of 40 vol.% or higher. Flexure strengths were measured for three composites containing 15, 20, and 40 vol.% TiB_2 and analyzed using a two parameter Weibull analysis. The Weibull modulus increased from 12 for 15 vol.% TiB_2 to 17 for 20 and 40 vol.% TiB_2. Microstructural analysis revealed microcracking in the ceramics containing 20 and 40 vol.% TiB_2. The ceramic containing 40 vol.% TiB_2 had the best combination of properties with a fracture toughness of 6.2 MPa m$^{1/2}$, hardness of 25.3 GPa, Weibull modulus of 17, and a strength of 423 MPa.
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1. Introduction

Silicon carbide (SiC) is a strong, hard, and chemically inert ceramic used in several applications that involve extreme environments.[2–6] In armor applications, the high hardness of SiC, which is commonly reported to be in the range of 20–27 GPa, is advantageous for projectile defeat.[7,8] Like most ceramics, SiC is brittle due to its low fracture toughness (2–5 MPa m$^{1/2}$), whereas a high fracture toughness is advantageous for multi hit capability in armor materials.[5,6,9,10] The fracture toughness of SiC based ceramics can be improved to 6–9 MPa m$^{1/2}$ with additives that promote densification and crack propagation along the grain boundaries as well as increasing the grain size.[2,9,11] However, an increase in toughness is typically accompanied by a drop in hardness using this approach.[9,10,12–14] Flinders et al. reported a hardness of 20 GPa and a fracture toughness of 2.6 MPa m$^{1/2}$ for SiC with no sintering additives, but saw the hardness drop to 14 GPa while fracture toughness increased to 6.7 MPa m$^{1/2}$ for SiC containing 3 wt.% aluminum as a sintering aid.[9] Titanium diboride (TiB_2) exhibits a high hardness (25–35 GPa) and may help combat the tradeoff

of decreasing hardness with increasing fracture toughness when added as a reinforcing phase in SiC.[15–18]

Studies on SiC–TiB_2 composites have mainly focused on the increase in toughness, which has been attributed to crack deflection and bridging effects due to the presence of TiB_2 particles.[18–22] Alpha-SiC (6H) has a thermal expansion coefficient (CTE) along the c-direction of $4.16 \times 10^{-6}/°C$ and $3.63 \times 10^{-6}/°C$ along the a-direction. TiB_2, however, has a higher CTE in each direction: $8.6 \times 10^{-6}/°C$ along the c-direction and $6.6 \times 10^{-6}/°C$ along the a-direction.[15,23,24] For SiC–TiB_2 ceramics, the mismatch in CTE values puts the SiC matrix in compression and the TiB_2 particles in tension after cooling from the typical densification temperatures (1900–2200 °C).[18,25,26] The mismatch promotes toughening due to the thermal residual stresses and resulting crack deflection that can occur as cracks are drawn from the SiC matrix, which is in compression, toward the interface with the TiB_2 particles where the highest tensile stresses exist.[27] Blanc et al. showed an increase in toughness from 3.5 MPa m$^{1/2}$ to 3.9 MPa m$^{1/2}$ with a hardness decrease from 30 GPa to 23 GPa as TiB_2 content increased from 5 vol.% to 15 vol.%.[16] Bucevac et al., measuring toughness using the indentation method, observed a toughness boost from 4.3 MPa m$^{1/2}$ to 5.3 MPa m$^{1/2}$ as TiB_2 content increased from 12 vol.% to 24 vol.%, although hardness data were not presented.[28] Along with thermal residual stresses that develop due to thermal expansion mismatch, when

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the residual stresses are large enough, stress-induced micro-cracking can also occur, enhancing crack deflection and the measured fracture toughness.[29–33] In areas with large enough particles, thermal stresses may become significant and induce spontaneous microcracking, which can render toughening mechanisms such as thermal residual toughening ineffective near such particles.[29,34–37]

The purpose of this paper is to examine the properties of SiC–TiB$_2$ ceramic composites with TiB$_2$ contents ranging from 0 vol.% to 100 vol.%. Fracture toughness and hardness were measured for each composition. Based on their measured hardness and fracture toughness values, Young's modulus and flexure strength were measured for SiC–TiB$_2$ ceramics containing 15, 20, and 40 vol.% TiB$_2$. The results show how both hardness and fracture toughness change over the range of SiC–TiB$_2$ ceramics. The Weibull analysis also shows the importance of microstructural changes on the performance of SiC–TiB$_2$ ceramics.

2. Experimental procedure

SiC–TiB$_2$ ceramic composites with TiB$_2$ contents ranging from 0 vol.% to 100 vol.%, were batched using commercially available SiC (H.C. Starck; Grade UF-25; α-SiC; Newton, MA, with an average particle size of 0.14 μm) and TiB$_2$ (Momentive; Grade HCT-F; Columbus, OH, with an average particle size of 1.45 μm) powders. To promote densification, 1 wt.% B$_4$C (H.C. Starck; Grade HS) and 2 wt.% C, in the form of phenolic resin (GP 2074, Georgia Pacific Chemicals, Atlanta, GA), were ball milled with the SiC and TiB$_2$ powders in a polyethylene jar using TiB$_2$ milling media and acetone. For the nominally pure SiC specimen, the same procedure was used except that SiC media were used instead of TiB$_2$ media. Compositions were designated as SiC–"X"TiB$_2$ where "X" is the nominal volume percentage of TiB$_2$. Resulting slurries were dried by rotary evaporation to minimize segregation of the constituents. The SiC–TiB$_2$ powders were then ground and sieved to −60 mesh before hot-pressing.

Initial billets of each composition, nominally 2.5 cm in diameter, were densified by hot pressing in a graphite element furnace (Thermal Technologies, HP20-3060, Santa Rosa, CA) using a graphite die. To minimize reaction between dies and billets, dies were lined with graphite paper (0.254 mm thick GTA, Leader Global Technologies, Deer Park, TX) that was coated with boron nitride spray (SP-108, Materion, Milwaukee, WI) before the powder was loaded. Die assemblies were heated under vacuum at a rate of 50 °C/min. Isothermal holds were employed at 1450 °C and 1650 °C to facilitate removal of oxide contamination from the surfaces of the powder particles. At 1450 °C the isothermal hold time was 2 h. The furnace was then held at 1650 °C until the chamber pressure returned to the nominal vacuum pressure of ∼27 Pa (200 mtorr). Above 1650 °C, and up to the final densification temperature, the atmosphere was changed to flowing argon at a pressure of ∼10^5 Pa (1 atm) and a uniaxial pressure of 32 MPa was applied. The final densification temperature was 2100 °C for nominally pure SiC and TiB$_2$ billets, but 1980 °C for the intermediate compositions. Pressing ceased after ram

travel had stopped for a period of 10 min, and the furnace was allowed to cool to room temperature naturally. For compositions that were selected for flexure testing, billets that were nominally 55 mm by 55 mm by 5 mm were hot pressed in a graphite element furnace (Thermal Technologies Inc., Model HP50-7010G). Because of the larger die size, and increased powder volume, 50 °C was added to the isothermal hold temperatures, including the final densification temperature.

The bulk densities were measured for all billets using the Archimedes' method. The theoretical density for each composite was calculated based on the nominal volumetric ratios of SiC and TiB$_2$. The 55 mm by 55 mm by 5 mm billets were machined into mechanical test bars using an automated surface grinder (Chevalier Machinery Inc., Model FSG-3A818, Santa Fe Springs, CA) following the guidelines of ASTM C1161-02c for B-bars (3 mm by 4 mm by 45 mm). Specimens were tested in four point bending with a fully articulated fixture (20 mm upper span × 40 mm lower span), using a screw-driven load frame (Instron, Model 5881, Norwood, MA) that was computer controlled (Instron, Bluehill 2, Norwood, MA). For SiC–15TiB$_2$, 39 bars were tested to failure while 36 bars were tested for SiC–20TiB$_2$, and 38 for SiC–40TiB$_2$. For each of these three compositions, failure strengths of all of the specimens were analyzed using a two parameter Weibull distribution. Elastic constants were determined using the impulse excitation method (Grindosonic Mk5 Industrial, J.W. Lemmens Inc., Heverlee, Belgium) following ASTM C1259-08e1.

Vickers' hardness was measured (Struers Inc., Duramin 5, Cleveland, OH) using a load of 9.8 N (1 kg) with a 15 s dwell time. Reported values were an average of 10 hardness indents. Hardness specimens were prepared by mounting sections of broken flexure bars and cross-sectioned billets in an epoxy resin and polishing to a mirror finish using successively finer diamond abrasives to a 0.25 μm surface finish. Fracture toughness was determined using direct crack measurements. Specimens were indented (Leco Corporation, Model V-100-A2, St. Joseph, MI) with a load of 49 N (5 kg) on a polished surface with a Vickers diamond tip followed by measurements of the radial median cracks formed during indentation.[38] Fracture toughness values were obtained from an average of ten indents using Eq. (1) where E is the Young's modulus determined through impulse excitation, H is the Vickers' hardness measured at a load of 9.8 N, P is the load used for indention (49 N), and $2c$ is the length of the radial median cracks.[38]

$$K_{IC} = 0.016 \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \tag{1}$$

Polished specimens were examined using scanning electron microscopy (S-570, Hitachi, Tokyo, Japan or Helios Nanolab 600, FEI, Hillsboro, OR). Area fractions of the constituent phases and porosity were determined using computer image analysis (ImageJ, National Institutes of Health, Bethesda, MD). Particle sizes were determined by equating average particle areas to the areas of spheres with equivalent diameters.