INTRODUCTION

Titanium diboride (TiB₂) is an extremely hard ceramic which has excellent heat conductivity, oxidation stability, and resistance to mechanical erosion. Applications for TiB₂ include impact resistant armor, cutting tools, crucibles, and wear resistant coatings. TiB₂ is also resistant to oxidation in air at temperatures up to 1100°C. Many TiB₂ applications are inhibited by economic factors, particularly the cost of densifying a material with a high melting point. In this study, reaction bonded TiB₂ (RB-TiB₂) composites are fabricated by the reactive infiltration of molten Si into preforms of TiB₂ plus carbon. Microstructure analysis indicates uniform distribution of TiB₂ particles in the composites. RB-TiB₂ composites with fine particles show higher flex strength and fracture toughness, while composites with larger particles have higher thermal conductivity, measured to be 120 W/(m K) at room. The coefficient of thermal expansion (CTE) of the composites is insensitive to the particle size and can be controlled in the range of 4.0-5.2 ppm/K (room temperature). RB-TiB₂ shows the potential to be used for electronics thermal management applications with a combination of matching CTE, good thermal conductivity, high melting point, and attractive mechanical properties.

KEYWORDS
composites, reaction bonding, silicon, thermal properties, titanium diboride
in the 1950s. Conventionally, the process consists of Si infiltration (liquid or vapor) into preforms of SiC + carbon. During the infiltration step, the Si and carbon react to form SiC. Typically, all carbon is consumed, yielding a product of porous SiC (vapor infiltration) or dense Si/SiC (liquid infiltration).

In this study, a variation to the process has been evaluated. Preforms of TiB$_2$ + carbon were produced and subsequently infiltrated with molten Si. The resultant ceramic bodies contained TiB$_2$, Si, and a small amount of reaction formed SiC (ie, TiB$_2$-Si/SiC) as compared to typical reaction bonded ceramics with a formulation of SiC/Si. One disadvantage of SiC/Si
is a coefficient of thermal expansion (CTE) that is too low for most electronics packaging applications. At room temperature, the CTE of SiC/Si is nominally 3 ppm/K, whereas most applications desire CTEs in the 5-7 ppm/K range for matching to DBC AlN dielectrics, Al₂O₃ dielectrics, and borosilicate glass for glass/metal sealing. The traditional material used for electronics packaging in this CTE range is Kovar, which has a room temperature CTE of 5.9 ppm/K and a thermal conductivity of 17 W/m·K. Kovar's CTE is attractive; however, its thermal conductivity is too low to sufficiently dissipate heat in high power applications. Aluminum-silicon carbide (Al/SiC) metal matrix composites (MMCs) are also interesting thermal management candidates with common varieties having CTEs of nominally 8 ppm/K and thermal conductivities of about 180 W/m·K. The Al/SiC MMCs, however, do not have sufficient melting point to be suited to hermetic glass to metal sealing, and they have CTEs that are higher than desired such that costly design features, such as dome shapes, are required for reliability. The structural properties of TiB₂/SiC have been previously disclosed. The present work focuses on thermal properties, with the goal of achieving CTEs in the range of Kovar with a higher melting point than Al/SiC MMCs (for glass to metal sealing) and a favorable thermal conductivity for dissipating heat from high power electronics.

2 | EXPERIMENTAL PROCEDURES

2.1 | Raw materials, slip, and preform preparation

Two different sizes (42 and 12 μm) of TiB₂ powders (Panadyne Inc) were used for slip preparation. Type I slips (RBTB-1L...
2.2 Preform infiltration

The industrial infiltration process was used, which allows the manufacture of large, complex shapes with minimal or no machining. Components measuring up to 60” × 60” with infiltration depth as thick as 6” can be manufactured by this process. As shown schematically in Figure 1B, reaction bonded TiB₂ is produced in a vacuum furnace (The Furnace Source) by the reactive infiltration of molten high purity (>99%) silicon into preforms (90 mm × 50 mm × 15 mm) containing TiB₂ particles and carbon. The infiltration temperature was set to about 1500°C with a heating rate of 2°C/min and a holding time of 3 hours. During the infiltration process, reaction occurs between the Si and carbon phases, yielding SiC that effectively bonds the TiB₂ particles into an interconnected ceramic structure, while remaining liquid Si infiltrates the open space in the preforms. The result is a composite of TiB₂ particles, residual Si, and reaction formed SiC. RBTB-13-HSC was infiltrated with a silicon alloy (30% Al) with higher CTE and thermal conductivity to modify the thermal properties of the composites.

2.3 Characterization

The samples infiltrated from different slips were sectioned by electrical discharge machining (EDM), ground, and polished with 3, 1, and 0.1 μm diamond suspensions. Microstructure of polished samples was observed using an OLYMPUS GX41 optical microscope. An X-ray diffractometer using CuKα radiation (λ = 1.54 Å) was used to determine the phase composition of the composites. The volume fraction of components in TiB₂-SiC-Si composites was determined using the quantitative image analysis software (ImageJ, NIH) on at least 5 optical micrographs for each composite. Density of the composites was determined by the water immersion technique in accordance with ASTM Standard B 311. Elastic properties were measured by an ultrasonic pulse-echo technique following ASTM Standard D 2845. Flexural strength in four-point bending was determined following ASTM C1161-18 (SIZE B). Fracture toughness was measured using a four-point-bend-chevron-notch technique following ASTM C1421-01B (CONFIG D). At least 5 specimens from each composite were tested for flexural strength and fracture toughness measurements. Fracture surfaces from flex strength and fracture toughness tests were observed using a FEI Quanta 250 FEG field emission scanning electron microscope. Thermal expansion was measured in accordance with ASTM E288-17, Standard Test Method for Linear Thermal Expansion of Solid Materials with a pushrod dilatometer, using a NETZSCH model DIL 402C pushrod dilatometer. Thermal diffusivity and specific heat capacity were measured by the laser flash method using a NETZSCH LFA 467 HyperFlash™ instrument and the test method conform to ASTM E1461-13, “Standard Test Method for Thermal Diffusivity by the Flash Method.”

3 RESULTS AND DISCUSSION

3.1 Microstructure and elastic properties

All composite samples show the same phase composition in the XRD patterns. Figure 2 shows the XRD pattern of RBTB-1H.
The infiltrated composite consists three phases, TiB₂ (JCPDF 85-2083), infiltrated Si (JCPDF 27-1402), and reaction formed SiC (JCPDF 72-0018). Figure 3A,B is microstructure images of RBTB-1L and RBTB-1H. The microstructure contains: (a) interconnected TiB₂ particles (white); (b) Si matrix (gray); (c) reaction formed SiC (dark gray); and (d) infiltration defects (black). As shown in Table 1, the composites have 65-66 vol% of uniformly distributed TiB₂, ~4 vol% reaction formed SiC and small amount of infiltration defects (1.8 vol% for RBTB-1L and 1.6 vol% for RBTB-1H). RBTB-1H has more particle agglomeration that led to larger particle size after higher temperature exposure. Both RBTB-5S and RBTB-13-HSC used 12 μm small TiB₂ powder and have slightly higher volume fraction of TiB₂ (67-69 vol%) and reaction formed SiC (~5.5 vol%), with porosity of 3.0 and 3.4 vol%. High porosity in RBTB-5S and RBTB-13-HSC is possibly due to the not optimized infiltration parameters. Binary powder mixtures with different particle sizes usually can reach higher packing density those that of single size powder systems. In this case, low wettability of the large TiB₂ powder with DI H₂O caused slightly lower packing density in the slips and the preforms. More surface area of 12 μm TiB₂ preforms absorbed more carbon source that results in higher volume fraction of reaction formed SiC. Both RBTB-5S and RBTB-13-HSC have more infiltration defects (~3 vol%) with lower elastic modulus, due to the smaller particle size and internal channel size that make it difficult for an effective Si infiltration.

3.2 | Flex strength and fracture toughness (effects of particle size)

Flex strength and fracture toughness data of RBTB-1 and RBTB-5S are shown in Table 2. All three composites used pure silicon as infiltration material. RBTB-5S has higher flex strength (205 MPa vs 164 and 158 MPa) and fracture toughness (4.95 vs 4.7 and 4.52 MPa m^1/2) than those of RBTB-1L and RBTB-1H, due to the finer microstructure using only small size 12 μm TiB₂ powder. RBTB-1H has slightly lower flex strength and fracture toughness than those of RBTB-1L, due to the larger particle size. All flex strength and fracture toughness samples show complex fracture surfaces with a mixture of intergranular and transgranular fracture (Figures 4 and 5). The flex strength and fracture toughness surfaces of RBTB-5S are rougher, due to the finer TiB₂ particles. Larger surface feature size of RBTB-1H than that of RBTB-1L is also noticed, which is coincident with the lower flex strength and fracture toughness.

3.3 | Thermal conductivity and CTE

Thermal conductivity of the composites was measured by the laser flash method (Figure 6A). RBTB-1L and 1H samples have higher thermal conductivity (120 and 114 W/(m K) at 25°C) than those of RBTB-5S and RBTB-13-HSC (95 W/(m K) at 25°C).
An interface between materials with different elastic properties (~500 GPa for TiB₂ and ~160 GPa for Si) will introduce phonon scattering, the smaller the particle size, the more interface areas per unit volume and the more phonon scattering is expected. Therefore, thermal conductivity decreases for the fine grain size RB-TiB₂ and RB-TiB-13-HSC that were made with only 12 μm TiB₂ powder. Also, more infiltration defects exist in RBTB-5S and RBTB-13-HSC and those pores add additional travel paths for phonons to bypass the porosities that further reduce the thermal conductivities of the composites. Nevertheless, the thermal conductivity of all RB-TiB₂ composites is significantly higher than those of Kovar (17 W/(m·K) at 25°C) and Al₂O₃ (37.2 W/m·K at 25°C) and can be further improved by optimizing particle size, infiltration parameters that can reduce the porosity.

TiB₂ has higher CTE than that of Si (7.4 vs 2.6 ppm/K at 25°C). RBTB-1 and RBTB-5S have similar CTE profiles over the temperature range of 20-500°C, which is between 4 and 6 ppm/K (Figure 6B). By using a higher CTE (8-9 ppm/K) 70/30 Si-Al alloy, the CTE of RBTB-13-HSC ranges from 5 to 7 ppm/K over the temperature range of 20-500°C, which is similar to the CTE of Kovar and Al₂O₃ in the same temperature range and the average CTE of the composites is identical to that of the Al₂O₃ (7.1 ppm/K) over the range of 20-500°C. The higher thermal conductivity and similar CTE to those of currently used electronics packaging materials, such as Kovar and Al₂O₃, indicate that RB-TiB₂ composites can be applied for electronics packaging and thermal management applications. Moreover, owing to its high melting point of 1410°C, RB-TiB₂ is suited to glass to metal sealing. The electrical resistivity of the RB-TiB₂ composites can be controlled by the purity of the Si matrix. Table 3 summarizes the thermal properties of RB-TiB₂ developed in this study, in comparison with some typically used electronics packaging and sealing materials. RB-TiB₂ composites combine the advantages of high melting point and good thermal conductivity with similar CTE values.

| Materials          | CTE (ppm/K) (20°C) | Thermal conductivity W/ (m K) | Melting Point (°C) |
|--------------------|--------------------|-------------------------------|--------------------|
| RB-TiB₂            | 4.5-2              | 95-120                        | 1410               |
| Kovar              | 5.9                | 17                            | 1450               |
| Al₂O₃              | 4.6                | 37                            | 2072               |
| Al/SiC MMC MMC     | 8                  | 180                           | 500-600            |

TiB₂ (12 μm) powder exhibit higher flex strength and fracture toughness. RB-TiB₂ composites that contain large TiB₂ (42 μm) powder show higher thermal conductivity, while CTE is not sensitive to the powder size. CTE of RB-TiB₂ can be further increased by using high CTE Si-Al alloy. The RB-TiB₂ composites have CTE similar to those materials used in electronics packaging, sealing, and thermal management applications, while combining good thermal conductivity, attractive mechanical properties, and high melting point for potential applications in those areas.

**REFERENCES**

1. Basu B, Raju GB, Suri AK. Processing and properties of monolithic TiB₂ based materials. Int Mater Rev. 2006;51:352–74.
2. Haggerty JS. Ceramic-ceramic composites with reaction bonded matrices. Mater Sci Eng A. 1989;107:117–25.
3. Taylor KM. Cold molded dense silicon carbide articles and methods of making the same. U.S. Patent 3 205 043. 1965 Sept. 7.
4. Popper PP. Production of dense bodies of silicon carbide. U.S. Patent 3 257 722. 1966 Sept. 27.
5. Forrest CW. Manufacture of dense bodies of silicon carbide. U.S. Patent 3 495 939. 1970 Feb 17.
6. Marshall AL, Aghajanian MK, Karandikar P. Reaction bonded silicon carbide materials with favorable properties for thermal management applications. Proceedings-2008 International Symposium on Microelectronics. IMAPS 2008; 822–6.
7. Wilson J. Thermal conductivity of common alloys in electronics packaging. Electronics Cooling. 2007;13(6):6–7.
8. Chen Z, Yao Y, Zhang W, Boroyevich D, Ngo K, Mattavelli P, et al. Development of a 1200 V, 120 A SiC Mosfet module for high-temperature and high-frequency applications. Wide Bandgap Power Devices and Applications (WiPDA), IEEE, 2013; 52–9.
9. Schutze T, Berg H, Hierholzer M. Further improvements in the reliability of IGBT modules. Conference Record of 1998 IEEE Industry Applications Conference. Thirty-Third IAS Annual Meeting (Cat. No.98CH36242), St. Louis, MO. 1998;2: 1022–25.
10. Zhang C, You T, Zhao L, Xia Q, Qin Z, Liu Y, et al. Effect of particle size distribution on microstructure and mechanical properties of TiB₂-SiC-Si composites. IOP Conf Ser Mater Sci Eng. 2019;678:012066.
11. Aghajanian MK, Morgan BN, Singh JR, Mears J, Wolffe RA. A new family of reaction bonded ceramics for armor applications. Ceram Trans. 2002:134:527–39.
12. Karandikar PG, Aghajanian MK, Morgan BN. Complex, net-shape ceramic composite components for structural, lithography, mirror and armor applications. Ceram Eng Sci Proc. 2003;24(4): 561–6.
13. Zheng J, Carlson WB, Reed JS. The packing density of binary powder mixtures. J Eur Ceram Soc. 1995;15(5):479–83.
14. Munro RG. Material properties of titanium diboride. J Res Natl Inst Stand Technol. 2000;105:709–20.
15. Molina JM, Narciso J, Weber L, Mortensen A, Louis E. Thermal conductivity of Al-SiC composites with monomodal and
bimodal particle size distribution. Mater Sci Eng A. 2008;480: 483–8.

16. Hasselman DPH, Donaldson KY, Geiger AL. Effect of reinforcement particle size on the thermal conductivity of a particulate-silicon carbide-reinforced aluminum matrix composite. J Am Ceram Soc. 1992;75(11):3137–40.

17. NIST Property Data Summaries for Advanced Materials. https://srdata.nist.gov/CeramicDataPortal/Pds/Scdaos. Accessed August 20, 2020.

How to cite this article: Wang J, McDannald A, Karandikar P, Aghajanian M. Fabrication of reaction bonded TiB₂/Si/SiC composites for thermal applications. Int J Ceramic Eng Sci. 2020;2:264–270. https://doi.org/10.1002/ces2.10067