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Short communication

Ultra-high elevated temperature strength of TiB_2-based ceramics consolidated by spark plasma sintering

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ABSTRACT

Spark plasma sintering of TiB_2–boron ceramics using commercially available raw powders is reported. The B_4C phase developed during reaction-driven consolidation at 1900 °C. The newly formed grains were located at the grain junctions and the triple point of TiB_2 grains, forming a covalent and stiff skeleton of B_4C. The flexural strength of the TiB_2–10 wt.% boron ceramic composites reached 910 MPa at room temperature and 1105 MPa at 1600 °C. Which is the highest strength reported for non-oxide ceramics at 1600 °C. This was followed by a rapid decrease at 1800 °C to 480–620 MPa, which was confirmed by increased number of cavitated titanium diboride grains observed after flexural strength tests.

1. Introduction

Titanium diboride (TiB_2) is an important ceramic material which is extensively used as a cutting tool material, wear components and lightweight armour for ballistic protection. High elastic modulus and good strength at room temperature is often reported for monolithic TiB_2 and TiB_2-based ceramic composites [1–6]. In view of its refractory nature, high temperature applications are also within reach. In the latter case the significant decrease of strength after 1400 °C is expected due to activation of the high-temperature plastic deformation mechanisms such as grain-boundary sliding and creep [6].

An obvious solution to this problem is the consolidation of composites [6–14]. TiB_2–TaC composites have demonstrated a flexural strength of 480 MPa at 1600 °C, which is twice of that for monolithic TiB_2 ceramics [6]. It was summarized that even in TiB_2–TaC case a decrease in strength is expected at higher temperatures owing to electro-covalent nature of bonding in titanium diboride. Therefore in order to reach higher strength values TiB_2-based ceramics armored with covalent compounds is proposed.

This class of TiB_2-based composites is naturally restricted to TiB_2–AlN [8,9], TiB_2–SiC [10,11] and B_4C–TiB_2 [12–17] ceramic composites, which show high room-temperature strength and toughness. High-temperature performance of these TiB_2-based composite is scarcely reported and is limited to the B_4C–TiB_2 eutectic composites [14–17].

The B_4C–TiB_2 eutectic composites are known to have a complex preparation route, and have a certain size limitation. Therefore, it was an objective of this study to propose a simple route for manufacturing TiB_2–B_4C composites, that is by the reaction spark plasma sintering [18–20] using commercially available powders of TiB_2 and amorphous boron. A reactive consolidation approach was used in order to ensure homogeneous distribution of secondary phase, which is formed in situ during spark plasma sintering. In the framework of this study, characterization of high-temperature mechanical properties was performed using the three-point flexural strength tests at temperatures between 25 °C and 1800 °C.

It is important to note that, in the present study, we seek to consolidate a high-temperature ceramics using a titanium diboride as a matrix material, which is different from previous reports on the B_4C–TiB_2 system where titanium diboride served as a reinforcement phase [12–17]. Hence, it is our understanding that the results of the present study may show a certain limit for the flexural strength at elevated temperature for ceramic composites where TiB_2 serves as a matrix phase.

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2. Materials and methods

Commercially available TiB_2 (d_{av} = 1.0–2.4 μm) and amorphous boron (d_{av} = 0.1–1.0 μm) (Wako Pure Chemicals, Osaka, Japan) powders were used as starting materials. A powder mix of TiB_2 + 10 wt % aB was prepared by wet-chemical mixing in alcohol with low temperature drying (~100 °C) to remove moisture. The resultant powder was screened through a 60 and 400 mesh screens.

The SPS experiments were performed using the 'Dr. Sinter' machine produced by Sumitomo, Japan. Initially, a pressure of 20 MPa was applied to ensure the proper electric contact between the powder tablet and the graphite die and then pressure was increased to 40 MPa at 800 °C. A dwell time of 1 min at 800 °C was adopted for setting up the pyrometer. The heating rate was 140 °C min^{-1} from room temperature up to 800 °C followed by a heating rate of 50 °C min^{-1} up to sintering temperatures of 1900 °C, with a dwell time of 15 min. SPS was performed in argon gas medium with a flow rate of 2 L min^{-1}.

Sintered specimens were first surface-ground flat with #600-800-1000-grit SiC paper, followed by diamond disks of up to 0.5 μm. The three-point flexural strength was determined using rectangular blocks ($2 \times 2.5 \times 20\ mm^3$) cut from specimens with diameters of 30 mm using electric discharge machining. Their lateral surfaces were grounded and polished using diamond pastes. Three-point flexural strength tests were conducted at room temperature and at high-temperature up to 1800 °C in argon flow using a Shimadzu AG-X plus (Shimadzu, Japan). Testing of specimens was performed in the direction parallel to the pressing directions in SPS. The loading speed was 0.5 mm min^{-1}. Six samples were tested at each temperature, and the measurement accuracy was taken as the standard deviation. For the tests at 1800 °C, only three samples were tested. For the high-temperature flexural tests, the following heating schedule was used: room temperature to 200 °C in 10 min and from 200 °C to testing temperature at a speed of 18 °C min^{-1}. A dwell time of 5 min was employed before the flexural test at a testing temperature. After testing, cooling from the testing temperature to room temperature was performed at a rate of 20 °C min^{-1}.

Microstructural observations and analyses were carried out on the fracture surfaces by scanning electron microscopy (SEM) SU 8000 (Hitachi, Japan) in secondary electrons, using low-angle back scattered electrons filter for specimens tested at room temperature and at 600 °C.

3. Results and discussion

TiB_2–boron ceramics show good flexural strength at room temperature ($\sigma_{25\,°C}$) ranging from 740 to 910 MPa, with a mean value among six tested specimens of 820 MPa, (Fig. 1) [3–6,12–14,21,22]. Fig. 1 shows data for three-point (open figures) and four-point (closed figures) configurations obtained for TiB_2, B_4C and TiB_2-based composites at room and elevated temperatures. It is known that the difference in configuration for three- and four-point methods does not allow comparing them directly. In this respect data for four-point method presented in Fig. 1 show general trends observed in original studies. Furthermore, in order to verify high values obtained by the three-point method, we also conducted some reference tests using the four-point method (using a 20/10 mm span of the supports and specimens with size $2 \times 2.5 \times 26$ mm) using four specimens. The mean value obtained was 829 ± 17 MPa. These data points are not presented in Fig. 1. When comparing two testing methods, we should note that, since only six samples were tested using the three-point set-up, it is clear that the difference in strength can be treated as minor, since it is well within the measurement error. Further large-scale testing is suggested to confirm these findings.

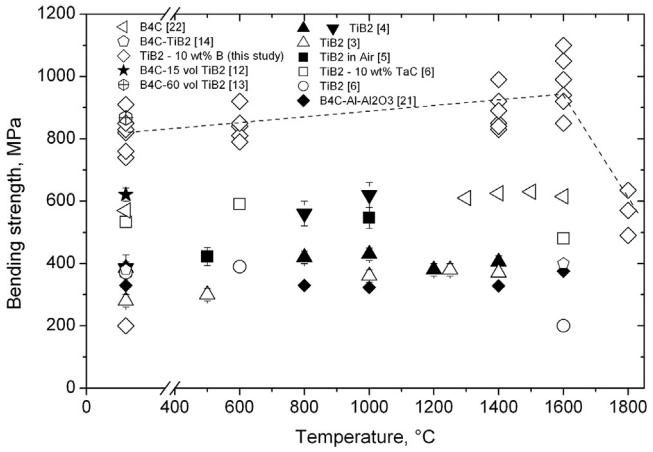

Fig. 1. Temperature dependence of strength for TiB_2–boron ceramic composites consolidated by SPS and data on high-temperature flexural behavior of TiB_2 [3–6], B_4C [21,22] and TiB_2–B_4C [12–14] ceramics. Closed figures indicate that four point flexural strength test was performed, while open figures are for three-point strength tests.

Nevertheless, among TiB_2–based ceramics the results of the present study show one of the best values reported so far. Only Huang et al. [13] for TiB_2–B_4C (60/40 vol %) showed higher mean value of 867 MPa at room temperature using three-point configuration.

There are two possible reasons for such high values: (i) a complex composite structure with uniform distribution of newly formed secondary boron carbide phase (Fig. 2); and (ii) interfacial microcracking [23] as result of large difference in the linear thermal expansion between TiB_2 matrix and B_4C inclusion. Finally, (iii) small value of the grain size, which corresponds to the initial particle size of raw TiB_2 powder (i.e. 2–5 μm). Recent analysis in [6] showed that strength of monolithic titanium diboride ceramic have a peak in strength for a grain size between 3 and 5 μm. This shows a good correlation with data obtained in the present study.

In case of composites, there is no obvious interdependence between the TiB_2 grain size in TiB_2–B_4C ceramic composites, since in the majority of these ceramic composites titanium diboride was added as the reinforcement phase, while in the present study it serves as a matrix. One noticeable observation is that microcracking [23] was observed after room temperature and in part at 600 °C flexural strength test.

This situation may be attributed to the residual stresses formed during the cooling process. In case of TiB_2-B_4C system consolidated at temperature of 1900 °C, the mismatch in the coefficients of thermal expansion (CTE) between TiB_2 and B_4C will result in formation of the residual stresses in the bulk ceramic composite [23,24]. Using the Taya's [24] model and data of [12] and temperature difference of 1600 °K one may evaluate that residual stresses on the diboride matrix σ_m and boron carbide σ_i are 348 MPa and −1165 MPa, respectively. Here negative value of the residual stress indicates compression, while positive value suggests tension.

Finite elements calculations of residual stresses formed upon cooling in B_4C–TiB_2 were presented in [25]. An average compressive stress of 424 MPa on B_4C matrix was found has a good agreement with the results of B_4C–TaB_2 eutectics prepared by SPS (336 MPa with ΔT of 2000 °C or 391 MPa with ΔT of 2325 °C) [26].

One may see that the main difference between eutectic composite of B_4C–MeB_2 and that in the present case for TiB_2-boron ceramics after reactive SPS consolidation, constrains TiB_2 matrix in tension, while stiffer boron carbide inclusions are in compression. This may cause the different toughness behavior of these composites: since the crack will be deflected around boron car-

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