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Short Communication

The processing and properties of (Zr, Hf)B_2–SiC nanostructured composites

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Abstract

(Zr, Hf)B_2–SiC nanostructured composites were fabricated by high energy ball milling and reactive spark plasma sintering (RSPS) of HfB_2, $ZrSi_2$, B_4C and C. Highly dense composites with homogeneously intermixed ultra-fine (Zr, Hf)B_2 and SiC grains (100–300 nm) were obtained after RSPS at 1600 °C for 10 min. The densification was promoted by high energy ball milling and $ZrSi_2$ additive. The additives were almost completely transformed into ZrB_2 and SiC during densification. The improvement of flexural strength and fracture toughness (641 MPa and 5.36 MPa $m^{1/2}$, respectively) was achieved. The relationships between the ultra-fine microstructure and mechanical properties were discussed.

Keywords: Spark plasma sintering; Mechanical properties; Borides; Nanocomposite

1. Introduction

Hafnium diboride (HfB_2) and Zirconium diboride (ZrB_2) ceramics have been intensively studied in recent years because of their great potential for ultra-high temperature applications such as high melting temperature, excellent chemical stability, and thermal and mechanical properties at application temperatures.[1] However, their industrial application has been limited so far, partly owing to their poor sinterability and oxidation resistance at high temperature. Previous works indicated that the addition of SiC to monolithic HfB_2 and ZrB_2 ceramics can improve the sinterability, oxidation resistance and mechanical properties of the borides.[2,3] However, the improvement of mechanical properties has been limited by the grain size of SiC. Zhu et al.[4] investigated the effects of SiC particle size on the mechanical properties of ZrB_2–SiC composites, and reported that fine SiC particles improved the densification and strength as well as decreased the grain size of the composites. Similar results about the improvement of strength and fracture toughness have been reported.[5–7] Nevertheless, major problems which may encounter during the fabrication of nano ZrB_2–SiC or HfB_2–SiC composites involve the homogeneous distribution of nano SiC particles and the restriction of grain growth during sintering.

The uniform mixing and ultra-fine comminution of starting powders down to 10 nm have been achieved by using high energy ball milling.[8] Spark plasma sintering (SPS) is currently one of the most widely used techniques to develop bulk nanostructured composites by virtue of the combination of unique properties such as fast heating/cooling rates and high applicable pressure.[9] $ZrSi_2$ has been used as an efficient sintering additive of borides, but its low melting temperature (1620 °C) strongly decreased the high temperature properties of the borides.[10] The present work focused on the fabrication of dense (Zr, Hf)B_2–SiC nanostructured composites by high energy ball milling and reactive SPS (R-SPS) using a source material which has molecular-level homogeneity between Zr and Si ($ZrSi_2$) together with B_4C and C. The relationships between the obtained nano-materials and their mechanical properties were discussed.

2. Experimental procedure

Synthesized HfB_2 powder (average particle size: 200 nm) and commercially available $ZrSi_2$ (particle size: 1–2 μm, purity: >99%; Alfa Aesar, Ward Hill, USA), B_4C (particle size:

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<10 μm, purity: 99%; Alfa Aesar, Ward Hill, USA) and carbon black powers (S.A.: 60–80 m^2/g, purity: 99.5%; Alfa Aesar, Ward Hill, USA) were used as starting materials. The synthesis of the nano HfB_2 powder was described elsewhere.[11] 70 wt% HfB_2 + 30 wt% ($ZrSi_2 + B_4C$ + carbon) was selected for the present study. The stoichiometric amount of $ZrSi_2$, B_4C and carbon were used according to the following reaction; $2ZrSi_2 + B_4C + 3C = 2ZrB_2 + 4SiC$ ($\Delta G = 49.078T–547686$).

Raw powders were ball-milled for 2 h in dry conditions using a shaker mill (Spex D8000, SpexCertPrep, Metuchen, NJ). The WC/Co ball-to-powder weight ratio was 10. After mixing, the obtained powders were dispersed using the shake mill with ethanol for 5 min. Then, the resulting slurry was homogenized again through high powder sonication for 30 min, and was dried using a rotate evaporator. Subsequently, the power mixture was densified using SPS (Dr. Sinter 2020, Sumitomo Coal Mining Co., Tokyo, Japan) in a vacuum (~6 Pa) at 1600 °C for 10 min under a uniaxial pressure of 40 MPa (heating rate: 100 °C/min).

The bulk densities of sintered samples were measured using Archimedes' method. The theoretical density of the composites obtained by the rule of mixture was 7.69 g/cm^3. Flexural strength was determined by means of a four-point bending test (test bars 2 mm × 1.5 mm × 25 mm) with inner and outer span of 10 and 20 mm, respectively, and a crosshead speed of 0.5 mm/min. Young's modulus was measured using an ultrasonic tester at 20–22 °C (ICP-MS. DRC 3000, Perkin/Elmer, USA). The hardness and fracture toughness of the specimens were calculated using the equation proposed by Anstis et al. after Vickers indentation (AVK-A, Akashi, Tokyo, Japan; loading condition: 1 kg, 15 s).[12] The diagonal length of 60 indents was determined for each sample in order to have a representative mean value.

The microstructure and phase fraction of sintered specimens were analyzed by scanning electron microscopy (SEM, JEOL JSM-6700F, Tokyo, Japan) and X-ray diffraction analysis (XRD, D/MAX 2200, Rigaku, Tokyo, Japan) using Cu Kα radiation. The TEM specimens were thinned by the focused ion beam technique (FIB, Helios Nanolab, FEI, Eindhoven, The Netherlands), and were examined using transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan) equipped with an energy dispersive X-ray spectroscope (spot diameter: 1.0 nm).

3. Results and discussion

Fig. 1(a) shows the densification curve during the sintering of the raw powder mixture at 1600 °C. The shrinkage initiated ($T_{initial}$) at 1456 °C. The shrinkage rate increased with increasing sintering temperature (Fig. 1(b)). The maximum shrinkage rate (10.8 μm/s) occurred at 1590 °C, at which temperature the sintering mechanism changed from surface diffusion to grain-boundary diffusion.[13] The particle size decreased and the reactions between the raw powders were promoted by high energy milling, which facilitated densification through the promotion of mass transport by diffusion.[14–16] Removing oxygen contaminants from the surface of HfB_2 particles during high energy milling also facilitated the densification. In addition, $ZrSi_2$ is a highly efficient sintering additive of diborides.[17] The

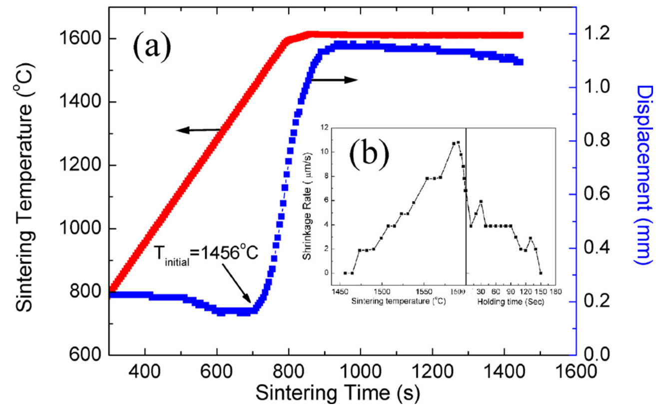

Fig. 1. The displacement (a) and shrinkage rate (b) of the (Zr, Hf)B_2–SiC composites during reactive spark plasma sintering.

exothermic reaction between the reactants released heat, which contributed to the densification. By the combination of the beneficial effects described above, the shrinkage stopped after 150 s at the stage of isothermal heating. The (Zr, Hf)B_2–SiC composite reached a dense state (R.D. 98.3%) after sintering at 1600 °C for 10 min under 40 MPa pressure. In contrast, a similar relative density value could be attained using as-synthesized nano-HfB_2 powder after SPS at 2100 °C for 35 min under 80 MPa.

Fig. 2 shows the XRD patterns of the starting powders and the sintered specimens. The XRD peaks of the HfB_2 powder used in this study were consistent with those in the PDF data file 89-3651 (Fig. 2(a)). However, peak broadening was found in Fig. 2(b) due to the refining of particle size by high energy ball milling. The calculation by Sherrer formula indicated the comminution of HfB_2 powder from 195 nm to 20 nm. The surface area of the crushed HfB_2 powder was 17.28 m^2/g, which was equivalent to the crystallite of 31 nm. The peaks of the crushed diboride shifted slightly, which indicated the change in lattice parameters by high energy milling. Mechanical alloying of the different constituents is believed to be a possible reason. The peaks of $ZrSi_2$ were still found in the mixed powders, which disappeared in the sintered

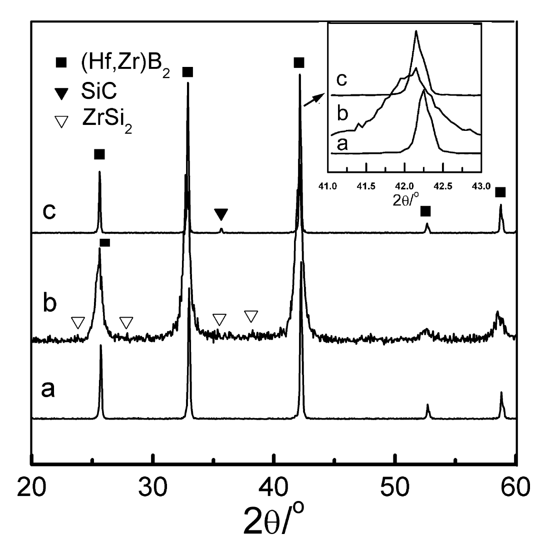

Fig. 2. XRD patents of (a) the synthesized HfB_2 powder, (b) the raw powder mixture after milling and (c) the sintered (Zr, Hf)B_2–SiC composites by RSPS.