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Effect of microstructure on mechanical, electrical and thermal properties of B_4C-HfB_2 composites prepared by arc melting

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ABSTRACT

B_4C-HfB_2 composites were prepared by arc-melting using B_4C and HfB_2 as raw materials. The eutectic composition of B_4C-HfB_2 system was $70B_4C$-$30HfB_2$ (mol%) with a lamellar eutectic microstructure. HfB_2 about 1 μm in thickness was dispersed in B_4C matrix uniformly of the eutectic composite, much smaller than raw powders. At the eutectic composition, the B_4C-HfB_2 composites showed the maximum Vickers hardness (31.2 GPa) and fracture toughness (5.3 MPa $m^{1/2}$) at room temperature, and maximum thermal expansion coefficient ($7.1 \times 10^{-6}\ K^{-1}$) from 293 to 1273 K. The electrical and thermal conductivity of B_4C-HfB_2 composites increased with increasing HfB_2 content. The electrical conductivity of B_4C-HfB_2 eutectic composites decreased from 8.94×10^4 to $7.43 \times 10^4\ Sm^{-1}$ with increasing temperature from 298 to 800 K, showing a metallic electrical behavior. The thermal conductivity of B_4C-HfB_2 eutectic composite was 16–18 $WK^{-1}\ m^{-1}$ from 298 to 973 K.

1. Introduction

Boron carbide (B_4C) and hafnium diboride (HfB_2) are excellent ultra-high temperature structural (UHTS) materials due to their extraordinary mechanical, electrical and thermal properties as shown in Table 1 [1–7]. The utilization of UHTS materials are greatly limited by their poor machinability due to high hardness. However, they may be machined precisely to be many kinds of complicated shape by electric spark cutting. Therefore, high electrical conductivity is a desirable property. Moreover, high thermal conductivity and low coefficient of thermal expansion are also beneficial to the improvement of thermal shock resistance by reducing temperature gradients and thermal stresses within the materials [8]. Previous studies revealed that the thermal conductivity of HfB_2 based materials involves the contribution of electronic mobility because of its high electrical conductivity, besides that of phonons [6,8].

In order to overcome the poor sinterability of HfB_2 and achieve the excellent combination properties of each component, B_4C-HfB_2 composites have been primarily prepared by conventional solid state sintering at high temperatures (2173–2473 K), such as hot-pressing (HP) [9], reactive hot-pressing (reactive-HP) [3,10] and pressureless sintering [4]. As shown in Table 1, their mechanical properties are usually reported whereas the electrical and thermal properties have been rarely concerned so far. Ordan'yan et al. [11] have reported that the B_4C-HfB_2 was a eutectic system with the eutectic composition of B_4C-(20–25 mol%) HfB_2 and the eutectic temperature of 2653 ± 30 K. However, no details of the experimental procedure were presented, nor were the microstructure and properties of the eutectic composites studied. Our research group has previously fabricated several carbide-boride eutectic composites using arc melting and floating zone melting, and investigated the effect of microstructure on some characters of B_4C-SiC [12], B_4C-TiB_2 [2], TiB_2-SiC [13] and ZrB_2-SiC [14]. These composites showed unique performance at the eutectic compositions, which may be resulted from their self-assembled microstructures by eutectic reaction [15]. The melting behavior and properties of B_4C-HfB_2 composites are expected to be similar to that of B_4C-TiB_2 composites since Hf belongs to the same family of Ti and Zr. Therefore, in the present study, the B_4C-HfB_2 binary composites were prepared by arc melting. The effects of the microstructure and composition on the mechanical, electrical and thermal properties were investigated.

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Table 1
Mechanical, electrical and thermal properties of B_4C, HfB_2 and B_4C-HfB_2 composites.

Material	Method	Sintering temperature (K)	Hardness (GPa)	Fracture toughness (MPa m$^{1/2}$)	Electrical conductivity (S m^{-1})	Thermal conductivity (W K^{-1} m^{-1})	Coefficient of thermal expansion ($\times 10^{-6}$ K^{-1})	Reference
B_4C		2813[a]	36.8	2.4 ± 0.2	8.79×10^3-8.04×10^2	10–28	5.5	[1–4]
HfB_2		3653[a]	28	3.8	9.1×10^6	104	7.15	[5–7]
B_4C-$11HfB_2$ (mol%)	Reactive hot pressing	2173	28.3	7.07				[3]
B_4C-$33HfB_2$ −7C (mol%)	Reactive hot pressing	2423	27	6				[10]
B_4C-$90HfB_2$ (mol%)	Hot pressing	2173–2273				114–131 (at RT) 87–93 (at 1273 K)		[9]
B_4C-$93HfB_2$ (mol%)	Pressureless sintering	2473	19.5	4.1				[4]

[a] Melting temperature.

2. Experimental

HfB_2 powder (48–75 μm, purity 99.0%; Alfa Aesar, Shanghai, China) and B_4C powder (1–10 μm, purity 98%; Aladdin, Shanghai, China) were used as starting materials. The powders were weighed and mixed in a high-energy planetary ball mill (PM100, Retsch, German) at a speed of 300 rpm for 45 min under the atmosphere of argon. A WC–10 wt% Co jar was employed as a milling container and zirconia balls together with a small amount of ethanol as grinding media. The ball to powder ratio (BPR) was around 3 in weight, i.e., 10 g powder using a mixture of 4, 30 and 50 zirconia balls 10, 5 and 3 mm in diameter, respectively. The homogenized slurry was dried under a vacuum condition at 333 K for 7 h. The powder mixture was isostatically pressed into disks with 15 mm in diameter and 5 mm in thickness at 30 MPa. The powder disks were melted twice by an arc-melting method and solidified on a water-cooled copper hearth in Ar atmosphere at 60 kPa.

The melting temperature of B_4C-HfB_2 composites was determined by monitoring the shrinkage curve of the powder compacts with a plasma activated sintering apparatus (PAS, ED-PAS III, Elenix, Japan). The temperature in the PAS equipment was measured using a pyrometer (IR-CA, CHINO, Japan) focused on a hole of $\phi 2 \times 5$ mm in the graphite mold wall of 10 mm in thickness. Due to the measured temperature (T) is different to the actual temperature (real melting point, T_m) in the mold, it was calibrated by the melting point of several standard materials, i.e., Cu, Ti and Al_2O_3 powders under the same conditions, as reported in the previous study [16]. The crystal structure was characterized using X-ray diffraction (XRD, Rigaku Ultima III, Japan) with Cu-$K\alpha$ radiation. The content of W and Zr impurity caused by milling container and balls in the B_4C-HfB_2 mixing powder was measured by inductively coupled plasma (ICP, Optima4300DV, PerkinElmer, USA) and that in the melted composite was examined by electron probe microanalysis (EPMA, JXA-8230, JEOL, Japan). The crystal orientation was determined by transmission electron microscopy (TEM, JEM-2100UHR, JEOL, Japan, at 200 kV). The microstructures were investigated by field-emission scanning electron microscopy (FESEM, FEI Quanta FEG250, USA). The hardness of B_4C-HfB_2 composites was measured by a Vickers micro-hardness tester (430SVD, Wolpert, USA) using a diamond indenter with a load of 9.8 N for 10 s on a polished surface perpendicular and parallel to the growth direction. The fracture toughness (K_{IC}) was evaluated by an indentation method and calculated by the following equations [3,17,18].

$$K_{IC} = 0.16 H_V a^{1/2} \left(\frac{c}{a}\right)^{-3/2} \quad (1)$$

$$K_{IC} = 0.0719 \left(P/C^{3/2}\right) \quad (2)$$

$$K_{IC} = 0.016 \left(\frac{E}{H_V}\right)^{1/2} \left(\frac{P}{C^{3/2}}\right) \quad (3)$$

where P is the indentation load (9.8 N), α is half of the average diagonal length of indentation (m), c is the indentation radial crack length (m), C is the average crack length from the center of the indent to the crack tip (m), E is the elastic modulus of composites calculated assuming a mixture rule ($E_{B_4C} = 460$ [19] and $E_{HfB_2} = 480$ [5] GPa) and H_V is Vickers micro-hardness (GPa). The reported hardness and fracture toughness values were an average of 10 points.

Electrical conductivity (σ) was measured by a commercial equipment (ZEM-3, Ulvac Riko, Japan) using a DC four-probed method for rectangular specimens ($3 \times 3 \times 10$ mm). Thermal conductivity (κ) was calculated from the thermal diffusivity (λ), specific heat (C_p), and density (d) using the relationship of $\kappa = \lambda C_p d$. The thermal diffusivity was tested by the laser flash method using the Netzsch LFA457 system for square specimens ($8 \times 8 \times 3$ mm). The specific heat (C_p) of each investigated composite was calculated according to the specific heat values from the HSC chemistry database [20] for each constituent phase, and its corresponding weight fraction by using the rule of mixtures. The densities of the bulk specimens were measured using the Archimedes' principle. The coefficient of thermal expansion (CTE) was determined by a thermo-mechanical analyzer (DIL402C, Germany) in the temperature range of 293–1273 K using rectangular specimens ($3 \times 3 \times 10$ mm). The change in dimensions of the specimens with increasing temperature was continuously recorded and the value of CTE (α) was calculated using the relation:

$$\alpha = \frac{\Delta L}{L_0 \Delta T} \quad (4)$$

where L_0 is the length of the specimens at ambient temperature, T_0 is about 293 K, ΔL and ΔT are the changes in the length and the temperature, with respect to their initial values, respectively.

3. Results and discussion

3.1. Crystalline phase of B_4C-HfB_2 composites

Fig. 1 shows the XRD patterns of composites on the cross section perpendicular to the growth direction at the composition of (a) $78B_4C$-$22HfB_2$, (b) $70B_4C$-$30HfB_2$, and (c) $65B_4C$-$35HfB_2$ (mol%). Only B_4C and HfB_2, without other phase, was identified, implying no chemical reactions between B_4C and HfB_2. In addition, the relative intensity of HfB_2 (100) in the B_4C-HfB_2 composite was significantly higher than that in raw powders, indicating HfB_2 (100) preferred orientation along growth direction. On the other hand, the impurity caused by the WC–10 wt% Co (jar) was almost zero and that by zirconia (balls) was less than 2 wt% although their hardness is

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