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Microstructure refinement and mechanical properties improvement of HfB_2–SiC composites with the incorporation of HfC

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Abstract

HfB_2 and HfB_2–10 vol% HfC fine powders were synthesized by carbo/boronthermal reduction of HfO_2, which showed high sinterability. Using the as-synthesized powders and commercially available SiC as starting powders, nearly full dense HfB_2–20 vol% SiC (HS) and HfB_2–8 vol% HfC–20 vol% SiC (HHS) ceramics were obtained by hot pressing at 2000 °C/30 MPa. With the incorporation of HfC, the grain size of HHS was much finer than HS. As well, the fracture toughness and bending strength of HHS (5.09 MPa $m^{1/2}$, 863 MPa) increased significantly compared with HS (3.95 MPa $m^{1/2}$, 654 MPa). Therefore, it could be concluded that the incorporation of HfC refined the microstructure and improved the mechanical properties of HfB_2–SiC ceramics.

Keywords: Hot pressing; Mechanical properties; Hafnium diboride; UHTCs; Synthesis

1. Introduction

As a member of the ultrahigh temperature ceramics (UHTCs) family, transition metal carbides (MC, M = Hf, Zr) has a higher melting temperature and refractory.[1] Accordingly, the addition of MC to MB_2–SiC (one of the main systems of UHTCs) to form a ternary composite of MB_2–SiC–MC might adjust the microstructure and properties of MB_2–SiC composite. Recent years, a variety of research has been carried out on the ZrB_2–SiC–ZrC system, including the densification behavior, microstructures evolution, as well as the fabrication processing and properties.[2–6] Corresponding studies have confirmed that the MB_2–SiC–MC ceramics have superior resistance to ablation than the corresponding MB_2–SiC ceramics under an arc-jet environment.[7] To the best of the author's knowledge, studies on the HfB_2–SiC–HfC system are very limited. Monteverde studied the in situ synthesis of HfB_2–SiC–HfC by reactive hot pressing using Hf metal with B_4C and silicon as starting materials.[8] Licheri et al. studied the densification and microstructures of HfB_2–SiC and HfB_2–HfC–SiC composites by self-propagating high-temperature synthesis (SHS) followed by spark plasma sintering (SPS).[9] In the ZrB_2–SiC–ZrC system, Guo and Zhang pointed out that the addition of ZrC improved the densification and mechanical properties of ZrB_2–SiC ceramics evidently.[6] However, the effect of HfC addition on the microstructure development and the resulted different properties in the HfB_2–SiC system is still not clear.

On the other side, ultrafine powders have been widely demonstrated good sinterability and resulted in superior properties. In our previous study, HfB_2 was synthesized via carbo/borothermal reduction of HfO_2 with B_4C and carbon.[10] Combining the characteristics of carbo/borothermal reduction, HfB_2–HfC composite powders could also be synthesized by adjusting the starting powder ratio via carbo/borothermal reduction route. It is believed that the in situ synthesized HfB_2–HfC powders must lead to much more homogeneous distribution, which is much beneficial for the properties improvement of ceramics.

In this work, we aimed to investigate the effect of HfC on the microstructure and properties of HfB_2–SiC system. HfB_2 and HfB_2–10 vol% HfC powders were synthesized by boro/carbothermal reduction firstly. Then, HfB_2–20 vol% SiC (HS) and HfB_2–8 vol% HfC–20 vol% SiC (HHS) ceramics were

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hot pressed using as-synthesized HfB_2, HfB_2–10 vol% HfC and commercially available SiC as starting powders. The densification behavior, microstructure and mechanical properties of the hot pressed ceramics were investigated. The emphasis is put on the effects of HfC on the microstructure development and mechanical properties.

2. Experimental procedure

HfO_2 (purity 99.9%, main impurities include Zr 0.46%, specific surface area by BET about 11.3 m^2/g, particle size < 2 μm for 98%, Found Star Science and Technology Co., Ltd., Beijing, China), B_4C (D_{50} = 1.5 μm, purity 96%, Jingangzuan Boron Carbide Co., Ltd., Mudanjiang, China) and graphite (D_{50} = 1.5 μm, purity 99%, colloid chemistry Co., Ltd., Shanghai, China) were used as starting powders to synthesize HfB_2 and HfB_2–HfC. By adjusting the amounts of HfO_2, B_4C, and carbon in a desired molar ratio, HfB_2 and HfB_2–10 vol% HfC powders were synthesized at 1600 °C in vacuum (~5 Pa). The details of powder synthesis processing could be found in our previous work.[10]

Commercially available SiC powder (D_{50} = 0.45 μm, purity 98.5%, Changle Xinyuan Carborundum Micropowder Co. Ltd., Changle, China) was added to the synthesized HfB_2 and HfB_2–HfC powders to fabricate HfB_2–20 vol% SiC (HS) and HfB_2–10 vol% HfC–20 vol% SiC (HHS) ceramics, respectively. The starting mixtures were mixed for 24 h in plastic bottles using absolute ethanol and SiC balls as medium, and dried by rotary evaporation at 70 °C. After that, the mixed powders were sieved through a 200-mesh screen and then placed in a graphite die with a BN coating. Subsequently, the composites were hot pressed at 2000 °C for 1 h under a pressure of 30 MPa in an argon atmosphere with a heating rate of 10 °C/min. The hot pressed samples had dimensions of 37 mm × 30 mm × 4 mm.

Phase composition was determined by X-ray diffraction (XRD, D/max 2550 V, Rigaku Corporation, Japan) using Cu K_α radiation (λ = 1.54178 Å). The mass fraction of HfB_2 and HfC in the synthesized HfB_2–HfC powder was estimated based on the relative intensity of the strongest diffraction peak using K value method.[10,11] The mean diameter and particle size distribution of the synthesized powders were analyzed using a laser particle size analysis (Microtrac, Nikkiso Co. Ltd., Tokyo, Japan). The oxygen and carbon content of the as-synthesized powders were determined by nitrogen/oxygen determinator (TC600, LECO, St. Joseph, MI) and carbon determinator, respectively.

After removing the surface layer from the hot-pressed disks, the bulk density was measured using the Archimedes method with distilled water as the immersing medium, while the theoretical density was estimated with the rule of mixture. The microstructure characteristics of polished sections and fracture surfaces were observed by scanning electronic microscopy (SEM). Grain sizes of the as-sintered ceramics were determined with an average of 100 grains using an image analysis software package (Image-Pro). The Vickers' hardness and fracture toughness were determined by the indentation method (Wilson-Wolpert Tukon2100B, Instron, Norwood, MA), using a diamond indenter with a load of 5 kg for 10 s on a polished surface; the reported value was an average of 3 measurements. The fracture toughness was calculated by the following equation[12,13]:

$$K_{IC} = P\left[\pi\left(\frac{C_1 + C_2}{4}\right)\right]^{-(3/2)}(\tan\beta)^{-1} \quad (1)$$

where P is the indentation load (N), C_1 and C_2 are the measured diagonal crack length (m), and β is an angle constant (68°). Flexural strength was measured by a 3-point bending test (test bars 3 mm × 4 mm × 36 mm) with a span of 30 mm and the crosshead speed was 0.5 mm/min; the reported strength value was an average of 5 measurements. The Young's modulus (E) was also obtained from the bending test using the following equation:

$$E = \frac{L^3(P_2 - P_1)}{4BH^3(Y_{t2} - Y_{t1})} \quad (2)$$

where P_1 and P_2 are the initial and final load (N) of linear range respectively, L is the span (mm), B and H are the width (mm) and thickness (mm) of samples respectively, Y_{t1} and Y_{t2} are the deflection (mm) when load are P_1 and P_2 respectively.

3. Results and discussion

3.1. Synthesis of HfB_2 and HfB_2–HfC powders

HfB_2 was synthesized based on the following carbo/borothermal reduction reaction:

$$HfO_2 + 0.5B_4C + 1.5C = HfB_2 + 2CO \quad (3)$$

Thermodynamic calculation showed that the above reaction became favorable at ~1500 °C in the standard state. And it could be reduced to below 1000 °C at $P_{CO} \sim 10$ Pa by thermodynamic calculation. However, previous studies showed that 1500–1600 °C was needed to ensure reaction to completeness. Therefore, 1600 °C was chosen as the reaction temperature in this work. Compared with reaction (3), previous studies have shown that HfO_2 could react with B_4C at lower temperatures:

$$HfO_2 + \tfrac{5}{7}B_4C = HfB_2 + \tfrac{5}{7}CO + \tfrac{3}{7}B_2O_3 \quad (4)$$

At the same time, the produced B_2O_3 would continue to react with HfO_2 and carbon to form HfB_2.

$$HfO_2 + B_2O_3 + 5C = HfB_2 + 5CO \quad (5)$$

If all the produced B_2O_3 reacted with HfO_2 and carbon, the reaction (3) could be derived by combining the above two reactions (4) and (5) with the molar ratio 1:0.5 of HfO_2 and B_4C. However, B_2O_3 had a high vapor pressure and vaporized rapidly above 1100 °C. Accordingly, vaporization of B_2O_3 would induce an excess of HfO_2 and C, which resulted in the formation of HfC based on reaction (6):

$$HfO_2 + 3C = HfC + 2CO \quad (6)$$

Therefore, HfC was presented in the final product synthesized from a stoichiometric ratio of the starting materials according to reaction (3) owing to the vaporization of B_2O_3. And early results showed that the content of HfC was 14.8 wt%. By adjusting