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Effects of high-energy ball milling and reactive spark plasma sintering on the densification of HfC-SiC composites

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ABSTRACT

The combined effects of high-energy ball milling (HEBM) and reactive spark plasma sintering (R-SPS) of $HfSi_2$ and C powder mixture on the densification and microstructure of nanostructured HfC-SiC composites were investigated. HEBM significantly promoted the densification and improved the microstructure of the HfC-SiC composites. In contrast, the reactions between $HfSi_2$ and C did not directly promote the densification of the HfC-SiC composites. While the reaction was mostly completed at 1300 °C, the onset temperature of significant densification was 1610 °C. Fine and homogeneously distributed HfC and SiC particles formed by HEBM and R-SPS were the key factors for promoting the densification of the HfC-SiC composites. The fine particles had high surface energy, which provided enough driving force for densification. In addition, the homogeneously distributed SiC particles effectively suppressed the growth of HfC matrix grains during densification.

1. Introduction

Hafnium carbide (HfC) has been considered as one of the potential ultra-high temperature ceramic (UHTC) materials for the application in hypersonic aviation field because of its high melting point (~3900 °C), hardness (26.5–32.9 GPa), elastic modulus (424 GPa) and chemical stability [1,2]. Consequently, researches have been performed for the production of HfC ceramics with high relative density, fine microstructure and good mechanical properties [3,4]. However, due to the strong covalent bonding and low self-diffusion coefficients, pressure-assisted sintering at high temperature is required for the densification of monolithic HfC ceramics by hot pressing (HP) at 2200–2690 °C or spark plasma sintering (SPS) above 2400 °C under a pressure of 65–100 MPa [3,5,6]. As a consequence, strong grain growth (average grain size: 19–22 μm) deteriorated the flexural strength of the UHTC materials.

SiC particles promote the densification and improve the microstructure, mechanical properties and oxidation resistance of the UHTC composites [7–9]. Especially, SiC powder with fine particle size exhibited stronger grain refining effect of HfC matrix, higher efficiency for promoting densification and better mechanical properties of the resultant HfC-SiC ceramics than the coarse SiC powder [7].

Reactive spark plasma sintering (R-SPS) has been recently introduced to obtain the UHTC with high density and fine microstructure because of its unique features such as fast heating/cooling rate, high applicable pressure and low sintering temperature [10–12]. During R-SPS process, two or more constituent phases of the powders mixture used as raw material react to form new compounds without significant grain growth.

The sinterability of highly refractory ceramics can be enhanced by decreasing the particle size due to the increase of surface area and the reduction of the diffusion distance of chemical species [13]. The particle size refinement, uniformity improvement and the increase of contact area between components can be achieved by high-energy ball milling (HEBM) [14]. Commercially available ZrB_2 powders have been pre-processed by HEBM for obtaining fine starting powders in order to improve the SPS kinetics, reduce the onset temperatures of sintering and decrease the intermediate and final sintering temperature [15–17].

In our previous work, dense and nanostructured HfC-SiC composites (grain size – HfC: 310 nm, SiC: 210 nm) were prepared by HEBM and R-SPS. The sinterability of the HfC-SiC composites were significantly improved by the combination of the processes [12]. However, the effects of HEBM and R-SPS on the densification and microstructure of nanostructured HfC-SiC composites have not been precisely analyzed yet.

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In the present research, the effects of HEBM and R-SPS on the densification and microstructure of HfC-SiC composites were systematically investigated. For that purpose, the phase formation, microstructure and densification behavior of the $HfSi_2$-C powder mixture were analyzed at different temperatures. Based on the analysis, the sintering mechanism of dense and nanostructured HfC-SiC composites was proposed.

2. Experimental procedures

Commercially available $HfSi_2$ (particle size: 30 μm; purity: >99%, Alfa Aesar, MA, USA), nano-SiC (size: 45–55 nm; purity: >97.5%, GRANDKOREA Corp., KOREA), carbon black (surface area: 60–80 m^2/g; purity: 99.5%, Alfa Aesar, MA, USA) and a synthesized HfC (mean particle size: 125 nm; metal basis purity except Zr: 99.92%) were used as the starting materials. The synthesis condition of the HfC powder was reported elsewhere in detail [18]. Stoichiometric amounts of $HfSi_2$ and carbon black powders were mixed for obtaining the HfC-SiC (here after termed HSC) composites according to reaction (1).

$$HfSi_2 + 3C = HfC + 2SiC \quad (1)$$

$$\Delta G = -167385 - 7.456T$$

where ΔG: Gibbs' free energy (J/mol), and T: Temperature (K).

The volume fractions of HfC and SiC phases formed in the sintered specimen were 38.5 and 61.5%, respectively.

In order to investigate the effects of HEBM and R-SPS on the densification and microstructure of HSC, raw powder mixtures with different mixing methods and chemical compositions were prepared as listed in Table 1. The starting powders were mixed by HEBM for 2 h using a shaker mill (SpexD8000, Spex CertiPrep, Metuchen, NJ) loaded with WC balls and jars. The ball-to-powder ratio was 10:1 by weight. In order to analyze the effect of oxidation during the milling, part of the jars were milled without sealing. In the other cases, the jars were sealed in a glove box with a nitrogen atmosphere. After milling, the powder mixtures were granulated through a metallic sieve with a #150 mesh size and were directly loaded into a graphite mold (inner diameter 10 mm) in the glove box. In order to analyze the effect of HEBM, part of $HfSi_2$ and C powders (HSC3) were mixed using ultra-sonication for 30 min in ethanol. Then the slurry was dried at 80 °C using a rotate evaporator. After granulizing through a metallic sieve with a #150 mesh size, the powder mixtures were also loaded into a graphite mold.

The power mixtures were sintered at 1750 °C by SPS (Dr. Sinter 2020, Sumitomo Coal Mining Co., Tokyo, Japan) for 10 min at a uniaxial pressure of 40 MPa in vacuum (~20 Pa). In order to analyze the reaction process and densification mechanism, the powder mixtures of HSC1 and HSC3 were heated with changing temperature by SPS under 40 MPa pressure without isothermal heating. The sintering temperature was measured by an optical pyrometer focused on the hole of the graphite mold. The heating rate was set at 100 °C/min. The sintering shrinkage of the specimen was analyzed by measuring the displacement of the lower electrode (resolution 0.01 mm) which was connected to a computer.

After grinding and polishing the surface of the sintered specimens, the bulk densities were measured using Archimedes' method. The theoretical densities of HfC and SiC are 12.2 g/cm^3 and 3.21 g/cm^3, respectively, and the values of the composites were calculated according to the rule of mixtures [18]. The hardness of the specimens was measured using a Vickers indenter (AVK-A, Akashi, Tokyo, Japan; loading condition: 1 kg, 15 s). The phase compositions and microstructures of the specimens were determined using X-ray diffraction (XRD, Cu Kα, D/MAX 2500; Rigaku, Tokyo, Japan) and field emission scanning electron microscopy (JSM-6700F, Tokyo, Japan). An image analysis program (Nano measurer, China) was used to precisely measure the grain size. At least 200 grains per specimen were measured for the determination of average grain size. The microstructures and chemical compositions of the composites were further analyzed using a transmission electron microscope (TEM, JEM 2100F, JEOL, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS, spot diameter: 1.0 nm).

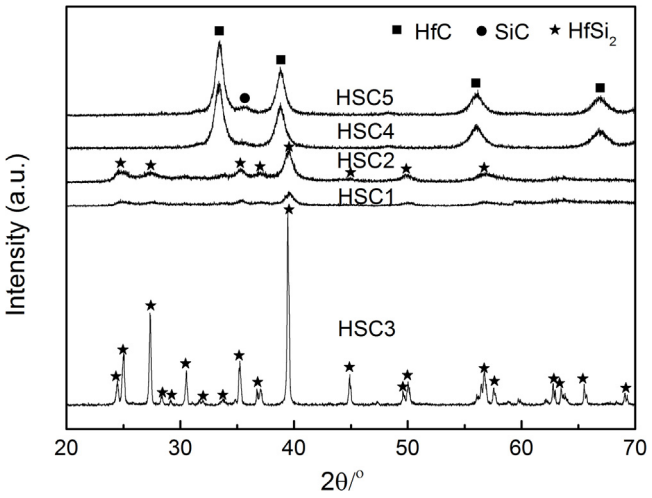

Fig. 1. XRD patterns of the different starting powders after mixing.

3. Results and discussion

3.1. Characterizations of the starting powders

Fig. 1 shows the XRD patterns of the different starting powders after mixing. The peak broadening of the $HfSi_2$ was clearly observed in HSC1 and HSC2, which indicated the reduction of the crystallite size induced by HEBM. The initial particle size of $HfSi_2$ was 30 μm, while the average particle size after HEBM was calculated to be 8.6 nm by Sherrer equation. Carbon black was not detected by XRD because of its amorphous state. The peaks of HfC and SiC were not identified in HSC1 and HSC2, which indicated that reaction (1) did not actively occur during the HEBM process. After milling in air using HEBM, oxide peaks were not detected in HSC2 because of the amorphous structure of the oxides [19]. Peak broadening was observed in HSC4 and HSC5, indicating the effective refinement of HfC and SiC particles by HEBM. The average particle size of HfC decreased from 125 nm to approximately 7 nm after milling.

Fig. 2 shows SEM images of the starting powders after mixing. Coarse $HfSi_2$ (30 μm) and fine carbon black (20 nm) with extremely nonuniform distributions were observed in HSC3 after ultra-sonication (Fig. 2(a)), which was attributed to the significant difference of density between $HfSi_2$ (8.02 g/cm^3) and carbon black (2.27 g/cm^3) as well as the particle size difference. However, fine and homogeneously intermixed particles were observed in HSC1 and HSC5 after HEBM (Fig. 2(b) and (c)), although some particles were strongly agglomerated because of the cold welding during milling process. Therefore, HEBM greatly reduced the crystallite size and improved the uniformity of powder mixture [15].

3.2. Phase compositions and microstructures of the sintered specimens

Fig. 3 shows the phase compositions of HSC after sintering at 1750 °C for 10 min. The peaks of HfC and SiC were detected in all cases. Residual $HfSi_2$ was not detected in HSC1, HSC2 and HSC3,

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