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Short communication

Nanostructured HfC–SiC composites prepared by high-energy ball-milling and reactive spark plasma sintering

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ABSTRACT

A novel route combining the reactive spark plasma sintering (R-SPS) and $HfSi_2$-C powders was proposed for fabricating dense and nano-structured HfC–SiC composites. Ultra-fine and homogeneously distributed HfC (310 nm) and SiC (210 nm) grains were obtained after sintering at 1750 °C, which were attributed to the molecular-level homogeneity of Si and Hf in $HfSi_2$, the high-energy ball-milling of raw powders and low sintering temperature by R-SPS. The fracture toughness of the composites was improved up to 3 MPa $m^{1/2}$ because of the homogeneous distribution of HfC and SiC grains and consequent enhancement of crack deflection.

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1. Introduction

Hafnium carbide (HfC), belonging to a family of materials defined as the ultra-high temperature ceramics (UHTCs), has been considered as one of the potential candidates for thermal protection applications such as the leading edges and nose caps of hypersonic and re-entry space vehicles due to the high melting point (~3950 °C), high hardness (~20 GPa) and excellent chemical stability of HfO_2 which forms during oxidation [1,2]. However, because of its strong covalent bonding and low self-diffusion coefficients, high pressure (65–100 MPa) has been required for the densification of HfC ceramics by using hot pressing (HP) at 2200–2690 °C or spark plasma sintering (SPS) above 2400 °C, at which conditions grain growth occurs intensively [3–5]. The average grain sizes of dense HfC sintered without sintering additives have been reported to be 19–22 μm. The large grains are unfavorable for mechanical properties and thermal shock resistance [3,5,6].

In order to improve the sinterability and mechanical properties of HfC ceramics, sintering additives such as $MoSi_2$, $TaSi_2$ and SiC have been generally introduced [5–10]. Excellent mechanical properties of the resultant composites have been attributed to the fine grain size, low porosity and uniform distribution of the reinforcing phases [10,11]. SiC has been used as the secondary phase to improve the microstructure and properties of the UHTC composites because of its chemical stability, high hardness, and excellent oxidation resistance [10,12]. Liu et al. reported that SiC powder with fine particle size exhibits stronger grain refining effect of HfC matrix, higher efficiency for promoting densification and better mechanical properties of HfC–SiC ceramics than the coarse SiC powder [10].

Due to the combination of unique features such as fast heating/cooling rate, high applicable pressure and low sintering temperature, spark plasma sintering (SPS) is one of the most advanced sintering techniques, through which the densification of nanoparticles to near full density with minimum grain growth is possible [13,14]. Reactive-spark plasma sintering (R-SPS) has been recently introduced in order to densify UHTCs at relatively low temperature [15,16]. During R-SPS process, two or multi phases react to form new compounds. The heat which is generated during the reaction promotes densification [13]. The densification can be further enhanced through particle size refinement by high-energy ball-milling, which reduces the onset temperatures of sintering and decreases the temperature for intermediate and final stage sintering [17,18].

To our knowledge, HfC–SiC nano-composites with high density and homogeneous microstructure have not been reported yet. The preparation, microstructure and mechanical properties of the HfC–SiC composites were investigated. In addition, the relationships between the microstructure and mechanical properties were discussed.

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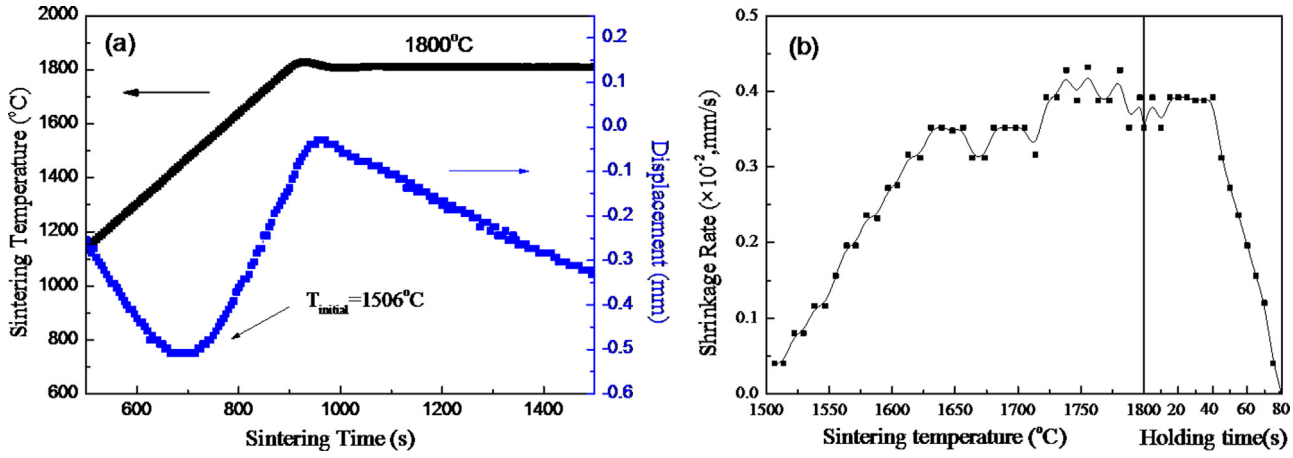

Fig. 1. Sintering behavior of the HfC–SiC composite sintered at 1800 °C by R-SPS. (a) The displacement of the lower electrode and (b) the shrinkage rate.

2. Experimental procedures

Commercially available $HfSi_2$ (particle size: 1–2 μm, purity: >99%; Alfa Aesar, MA, USA) and carbon black powders (surface area: 60–80 m^2/g, purity: 99.5%; Alfa Aesar, MA, USA) were used as the starting materials. Stoichiometric amount of $HfSi_2$ and carbon black powders were mixed for obtaining HfC–SiC (HSC) composites according to the Reaction (1).

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

The volume ratio of HfC and SiC obtained by Reaction (1) is 38.5:61.5. The theoretical density of the HfC–SiC composites calculated by the rule of mixture is 6.67 g/cm^3. The starting powders were mixed by high-energy ball-milling for 2 h in dry condition using a shaker mill (Spex D8000, Spex CertiPrep, Metuchen, NJ) with WC balls and jars. The ball-to-powder ratio by weight was 10. Milling program was composed of two cycles of 1 h milling – 1 h cooling schedule. In order to suppress the formation of oxides during the milling, the jars were sealed in a grove box under nitrogen atmosphere. After milling, the mixtures were granulated through a metallic sieve with 150 mesh size, then were loaded into a graphite mold (inner diameter 20 mm) in the glove box. The power mixtures were sintered at 1700–1900 °C (heating rate: 100 °C/min) by SPS (Dr. Sinter 2020, Sumitomo Coal Mining Co., Tokyo, Japan) for 10 min under a uniaxial pressure of 40 MPa in vacuum (~20 Pa). The temperature was measured by an optical pyrometer focused on the hole of the graphite mold. The sintering shrinkage of the specimen was analyzed by measuring the movement of the lower electrode (resolution 0.01 mm) which was connected to a computer. After grinding and polishing the surface of the sintered samples, the bulk densities were measured by Archimedes' method. Young's modulus was measured using an impulse excitation analyzer (RFDA MF professional, IMCE, Genk, Belgium). Hardness and fracture toughness of the samples were measured using a Vickers indenter (AVK-A, Akashi, Tokyo, Japan; loading condition: 1 kg, 10 s for hardness; 10 kg, 10 s for fracture toughness) according to the Anstis formula [19]. For each sample, 30 indentations were made and 60 diagonal lengths were measured to obtain a representative mean value of hardness. The phase compositions of the sintered specimens were determined by X-ray diffraction analysis (D/MAX 2500; Rigaku, Tokyo, Japan) using Cu Kα radiation. The microstructures of sintered specimens were analyzed by 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 grain size and chemical composition of the composites were further analyzed using a transmission electron microscope (TEM, JEM 2100F, JEOL, Tokyo, Japan) equipped with energy dispersive X-ray spectroscope (EDS, spot diameter: 1.0 nm).

3. Results and discussion

Table 1 summarizes the relative density of the HfC–SiC composites after sintering at various temperatures. Dense composites were obtained after sintering at 1750 °C, showing the low temperature densification of HfC–SiC composites. The densification curve during SPS indicated that the onset densification temperature was 1506 °C (Fig. 1(a)). The shrinkage rate increased till 1760 °C where the maximum value (0.43×10^{-2} mm/s) was observed, then decreased during the isothermal heating stage (Fig. 1(b)). The shrinkage rate became zero after 80 s during isothermal heating. Subsequently, thermal expansion was recorded (Fig. 1(a)). During SPS, the thermal expansion of the punches and spacers, as well as the sintering shrinkage of the powder, is recorded as the displacement. At the initial isothermal heating stage, the thermal expansion components offset the shrinkage of the powder. As a consequence, the displacement of the electrode stopped after certain time. When the final-stage sintering was mostly completed, the expansion overwhelmed the sintering shrinkage. The results indicated that the densification of the composites was mostly completed after sintering for 80 s.

Fig. 2 displays the XRD patterns of the starting powder after high-energy ball-milling and the HfC–SiC composites sintered at different temperatures. Peak broadening was observed in the XRD pattern. The crystallite size of the starting powder decreased from 2 μm to 8.6 nm after high-energy ball-milling according to the calculation by the Sherrer equation. The refinement of starting powder effectively promoted Reaction (1) by the decrease of diffusion distances [15]. In addition, the strong decrease in particle size promotes the densification of ultra-high temperature ceramics [20]. Carbon peaks were not observed because of the amorphous nature of carbon black. HfC and SiC peaks were not detected in the starting powder, indicating that Reaction (1) did not occur during the high-energy ball-milling process. Well defined HfC and SiC peaks were detected after the sintering at and above 1700 °C together with the complete disappearance of $HfSi_2$ peaks, which indicated that Reaction (1) was completed during R-SPS.

The average grain sizes of the HfC and SiC were 210 and 160 nm after sintering at 1700 °C, which increased to 480 nm and 390 nm at 1900 °C (Table 1). Despite the grain growth at 1900 °C, the sizes of HfC and SiC grains achieved in this research were much smaller than

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