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Synthesis and densification of nano-crystalline hafnium carbide powder

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ABSTRACT

Ultra-fine hafnium carbide powder was synthesized by the carbothermal reduction of HfO_2 at 1600 °C using the modified spark plasma sintering (SPS) apparatus. The synthesized powder had a fine particle size of about 125 nm and a low oxygen content of below 0.5 wt%. The purity of the powder was >99.9% excluding Zr, and 99.6% when including Zr impurity. The intermediate reactions and particle growth were minimized due to the low synthesis temperature, fast heating/cooling rate and the effect of current during the modified SPS process. A relatively large amount of HfC powder could be synthesized by the new synthesis method (>175 g/day). HfC ceramics with high relative density (>96%) were obtained after sintering the synthesized powder without sintering additives at 2300 °C for 30 min under 100 MPa pressure by SPS. The average grain size of the obtained specimen was about 6 μm.

1. Introduction

Hafnium carbide (HfC) has been intensively investigated in recent years for its great potential in ultra-high temperature applications, due to its high melting point (about 3900 °C), phase stability, as well as good thermomechanical and thermochemical properties[1,2]. Therefore, the carbide is a promising material for cutting tools, rocket nozzles, space/air craft and thermal-field emitters [3–6]. Due to the strong covalent bonding of HfC, high temperature (>2200 °C) and pressure (65–100 MPa) have been required for the densification of HfC ceramics without sintering additives using hot pressing (HP) or spark plasma sintering (SPS) [3,7,8]. However, strong grain growth occurred because of the high sintering temperature. The average grain size of dense HfC sintered without sintering additiveshas been reported to be 19–22 μm. Large grains are unfavorable for some mechanical properties such as flexural strength and thermal shock resistance [7,8]. Since the sintering behavior of highly refractory materials is significantly affected by the characteristics of the raw powder, the synthesis of HfC powder with fine particle size is advantageous to obtain dense HfC ceramics at low temperatures.

Various processes for synthesizing HfC powder have been reported. Sacks et al. prepared fine HfC powders with an average particle size of 200 nm using organic compounds as precursors [9]. Liu et al. synthesized HfC powders with particle sizes of 380 nm or 200 nm by carbothermal reduction of HfO_2 with graphite and carbon black at 1800 °C, respectively [10]. Abdelkader et al. synthesized nano-HfC powder using electro-deoxidation in molten chloride bath [11]. HfC powders have been also synthesized by the reaction between carbon and pure metal hafnium (Hf), metal hydride (HfH_2) or metal oxide (HfO_2) [1,12]. Among the currently available preparation methods, the solid state carbothermal reduction of HfO_2 by Reaction (1) is the primary route for the commercial production of HfC powder because the process is cheap as well as reliable.

$$HfO_2 + 3C(s) = HfC(s) + 2CO(g) \quad (1)$$

$$\Delta G = 670.500 - 358.4T$$

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

High temperature (>1598 °C) is required for sustaining Reaction (1) under the standard condition (P_{co} = 1 atm) because of the low self-diffusion of carbon, which results in extended isotherms and the coarsening of particles. Ultrafine and highly pure HfC powder is thus difficult to be synthesized. In recent years, spark plasma sintering (SPS) has been widely used for the densification of refractory ceramics due to the combination of its unique features, such

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asfast heating rate and high pressure [13]. The SPS process has a potential advantage for powder synthesis compared with conventional heating methods, because the current which passes through the specimens during SPS was reported to increase the rate of compound formation and decrease the incubation time for the nucleation of the new phases [14]. In addition, the occurrence of unintended secondary reactions and growth of particles during the heating stage may be minimized due to the fast heating rate of SPS (>200 °C/min), low synthesis temperature and short holding time.

Nonetheless, the SPS process has not been commonly used for the synthesis of powders. In our previous work, amodified SPS process was used for synthesizing ZrB_2–SiC powder mixture, nano-HfB_2 powder, Al_4SiC_4 powder and Cr_2AlC powder [15–18]. A mold was specifically designed to prevent the application of a mechanical pressure to the starting powder during the synthesis [15].

In the present study, the synthesis of hafnium carbide powder by the carbothermal reduction of HfO_2 was investigated using the modified SPS apparatus. The effects of the synthesis parameters, such as the molar ratios of C/Hf, the synthesis temperature, the holding time and the heating rate, on the reaction yield of ultrafine HfC powder were investigated. The particle size, the morphology and the phase compositions of the as-synthesized HfC powder were also characterized. Furthermore, using the as-synthesized hafnium carbide powder, a monolithic HfC ceramics was densified without sintering additives by SPS.

2. Experimental procedure

Hafnium dioxide (HfO_2, purity 99% (metals basis), 325 mesh; Alfa Aesar, Ward Hill, MA) was used as the starting powder in this work. A phenolic resin (Phenolite, Kangnam Chemical Co., Seoul, Korea) with char yield of 49 wt% was used as the carbon source [16]. To determine the optimized parameters for obtaining fine and pure HfC powder, the molar ratio and heating conditions were controlled as shown in Table 1. HfO_2 powder and phenolic resin were mixed in a polyethylene bottle for 4 h using yttria-stabilized ZrO_2 balls and ethanol as the mixing media. Subsequently, the slurries were dried at 120 °C for 12 h, crushed by vibration mill machine, and granulated through a 100-mesh sieve. The obtained powder mixtures were compacted into disks with a diameter of 30 mm under a uniaxial pressure of 5 MPa in order to improve the particle contact for promoting the reaction and to suppress the scattering of the powder in vacuum. The disks were placed in a graphite crucible and heated under vacuum using a modified SPS apparatus (Dr. Sinter 2020; Sumitomo Coal Mining Co., Tokyo, Japan). Fig. 1 shows the schematic of the modified SPS apparatus for powder synthesis. A graphite crucible with two caps was designed to prevent the pressure applying to the raw powder mixture, which can ensure that the powders can be synthesized without densification [15]. The synthesis temperature was between 1500 and 1650 °C under vacuum (below 20 Pa) with the heating rate of 50–300 °C/min. The holding time was 30–90 min at the desired temperature. Subsequently, rapid cooling was performed by turning the furnace power off. The temperature of the specimens was measured by an one color optical pyrometer which was focused on the hole through the graphite crucible. For comparison, the raw powder mixture was heated at 1600 °C for 1 h using a conventional furnace with a heating rate of 10 °C/min in vacuum (below 20 Pa). The weight loss of the heat treated powder mixtures was measured after the synthesis in order to estimate the completion of the reaction. The obtained powder was crushed using a mortar and was collected for characterization.

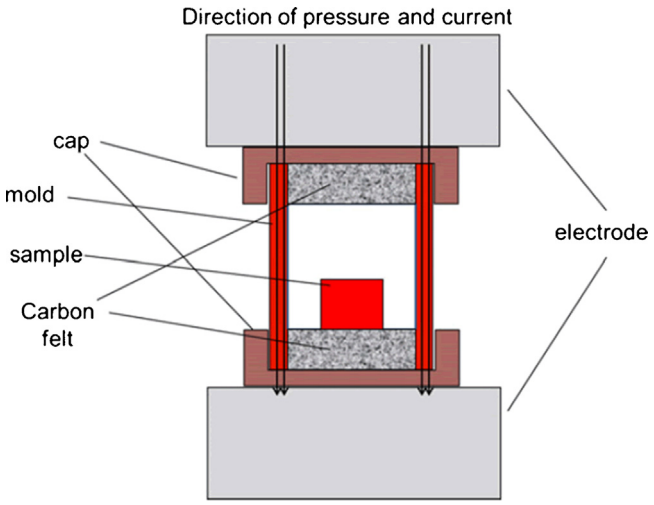

Fig. 1. Schematic of modified SPS apparatus for powder synthesis.

The phase compositions of the synthesized powders were determined by X-ray diffraction analysis (XRD, CuKα, D/MAX 2500; Rigaku, Tokyo, Japan). The morphology and particle size of the synthesized powders were analyzed using field emission scanning electron microscopy (JSM-6700F; JEOL, Tokyo, Japan) and transmission electron microscopy (JEM-2100; JEOL) equipped with selected-area electron diffraction (SAED) and energy dispersive spectrometer (EDS). An image analysis program (Nano measurer, China) was used to precisely analyze the size of particles and grains. At least 300 grains per specimen were measured for the deter-

Table 1
Chemical compositions and heating conditions.

Synthesized powders	Weight per batch(g)	Molar ratios (C/Hf)	Temperature (°C)	Holding time (min)	Heating rate (°C/min)
HC1	3	3.3	1600	60	100
HC2	3	3.4	1600	60	100
HC3	3	3.5	1600	60	100
HC4	3	3.6	1600	60	100
HC5	3	3.6	1500	60	100
HC6	3	3.6	1550	60	100
HC7	3	3.6	1650	60	100
HC8	3	3.6	1600	30	100
HC9	3	3.6	1600	45	100
HC10	3	3.6	1600	90	100
HC11	3	3.6	1600	60	50
HC12	3	3.6	1600	60	200
HC13	3	3.6	1600	60	300
HC14	35	3.6	1600	90	200
[a]HC15	3	3.6	1600	60	10

[a] Synthesized using a conventional furnace.