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Short communication

Simultaneous high-frequency induction heated combustion synthesis and consolidation of nanostructured $HfSi_2$–SiC composite

Jeong-Hwan Park [a], Jin-Kook Yoon [c], Jung-Mann Doh [c], Byung-Soo Lee [b], In-Jin Shon [a,b,*]

[a] Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, 664-14 Deokjin-dong 1-ga, Deokjin-gu, Jeonju, Jeonbuk 561-756, Republic of Korea
[b] Division of Advanced Materials Engineering, the Research Center of Industrial Technology, Chonbuk National University, 664-14 Deokjin-dong 1-ga, Deokjin-gu, Jeonju, Jeonbuk 561-756, Republic of Korea
[c] Advanced Functional Materials Research Center, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 130-650, Republic of Korea

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Abstract

Dense nanostructured $HfSi_2$–SiC composite was synthesized by high-frequency induction heated combustion synthesis (HFIHCS) method in one step from powders of mechanically activated HfC and Si. Simultaneous combustion synthesis and densification were accomplished under the combined effects of an induced current and mechanical pressure. Highly dense $HfSi_2$–SiC was produced under simultaneous application of a 60 MPa pressure and the induced current. The average grain size and mechanical properties (hardness and fracture toughness) of the composite were investigated.

Keywords: A. Sintering; C. Hardness; Intermetallics; Nanostructures

1. Introduction

Interest in refractory metal silicides has increased significantly in recent years because of their potential application as high-temperature structural materials [1]. This class of materials has an attractive combination of properties, including high melting temperature, high modulus, high oxidation resistance in air, and a relatively low density [2,3]. Hafnium disilicide ($HfSi_2$) has one of the lowest resistivities and the highest melting point among refractory silicides [4]. However, as in the case of many intermetallic compounds, the current concern about these materials focuses on their low fracture toughness below the ductile–brittle transition temperature [5–7]. To improve their mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites [8–11]. An example is the addition of SiC to $HfSi_2$ to improve the properties. Silicon carbide also is one of the most attractive high-temperature materials under investigation because of its excellent creep resistance and oxidation behavior. Therefore, SiC may be the most promising additive as a reinforcing material for $HfSi_2$-based composites.

Many high-temperature dense composites are usually prepared in a multistep process [12,13]. However, the method of field-activated and pressure-assisted combustion synthesis has been successfully employed to synthesize and densify materials from the elements in one step in a relatively short period of time. This method has been used to synthesize a variety of ceramics and composites, including $MoSi_2$–ZrO_2, Ti_5Si_3 and its composites, WSi_2 and its composites, and WC–Co hard materials [14–19]. These materials are generally characterized by low adiabatic combustion temperature and cannot be synthesized directly by the self-propagating high-temperature synthesis (SHS) method. More recently, a new approach has been developed in which synthesis and densification can be effected simultaneously. This new process, referred to as the high-frequency induction heated combustion synthesis (HFIHCS), has been successfully used to synthesize and densify, in one step, some materials in a relatively short

* Corresponding author at: Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, 664-14 Deokjin-dong 1-ga, Deokjin-gu, Jeonju, Jeonbuk 561-756, Republic of Korea. Tel.: +82 63 2381; fax: +82 63 270 2386.
E-mail address: ijshon@chonbuk.ac.kr (I.-J. Shon).

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period of time [20,21]. The purpose of the present work is to produce dense nanophase $HfSi_2$–SiC composite within 1 min in one-step from mixtures of mechanically activated HfC and 3Si powders by using this method and to evaluate its mechanical properties.

2. Experimental procedure

Powders of 99.5% hafnium carbide (−325 mesh, Alfa Products) and 99% pure silicon (−325 mesh, Aldrich Chemical) were used as starting materials. Fig. 1 shows the scanning electron microscopy (SEM) images of the raw materials used. HfC and Si powder mixtures were first milled in a high-energy ball mill, Pulverisette-5 planetary mill with 250 rpm for 10 h.

Tungsten carbide balls (5 mm in diameter) were used in a sealed cylindrical stainless steel vial under argon atmosphere. The weight ratio of ball-to-powder was 30:1. Milling resulted in a significant reduction of grain size. The grain size and the internal strain were calculated by Stokes and Wilson's formula [22].

Fig. 2 shows X-ray diffraction (XRD) patterns of raw powders and milled HfC + 3Si powder. The full width at half-maximum (FWHM) of milled powder is wider than that of raw powder due to internal strain and reduction of grain size. The average grain size of HfC measured by Stoke–Wilson equation was about 50 nm.

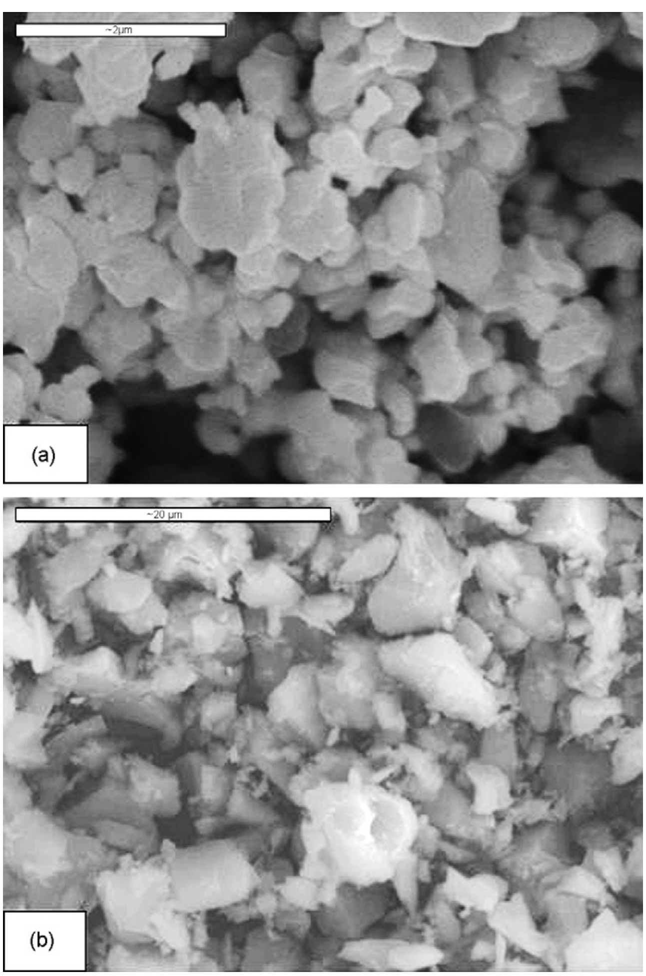

Fig. 1. Scanning electron microscope images of raw materials: (a) Hafnium carbide and (b) Silicon.

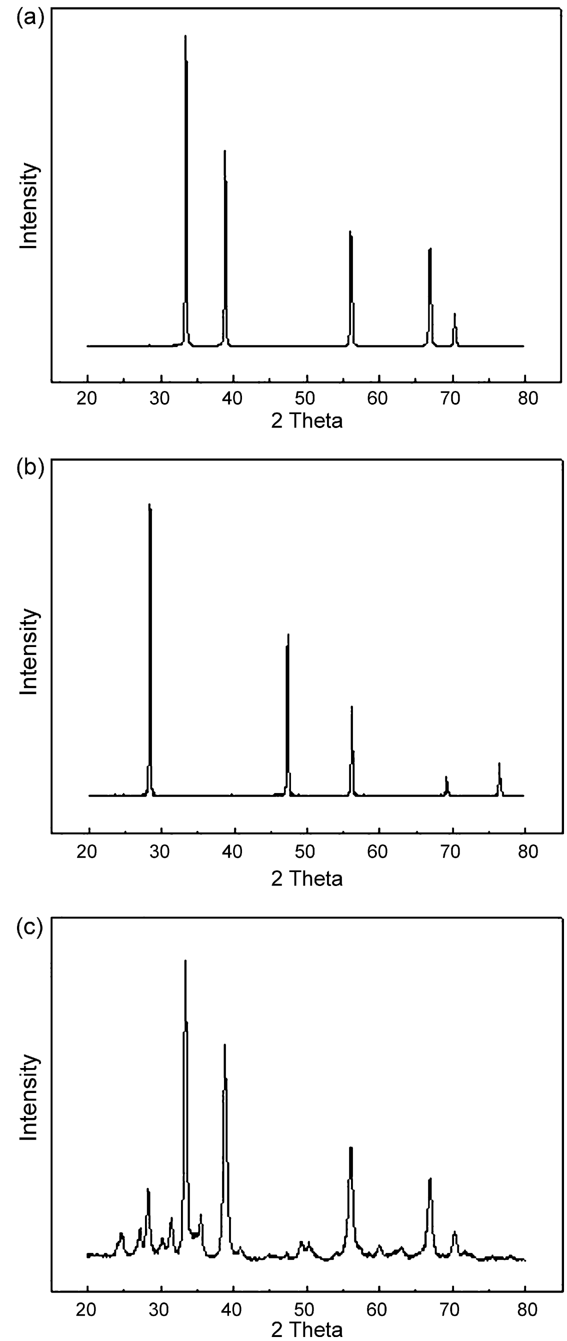

Fig. 2. XRD patterns of raw materials: (a) HfC, (b) Si and (c) milled HfC + 3Si.

After milling, the mixed powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the high-frequency induction heated combustion system, shown schematically in Fig. 3. The four major stages in the synthesis are as follows. The system was evacuated (stage 1). A uniaxial pressure of 60 MPa was applied (stage 2). An induced current (frequency of about 50 kHz) was then activated and maintained until densification

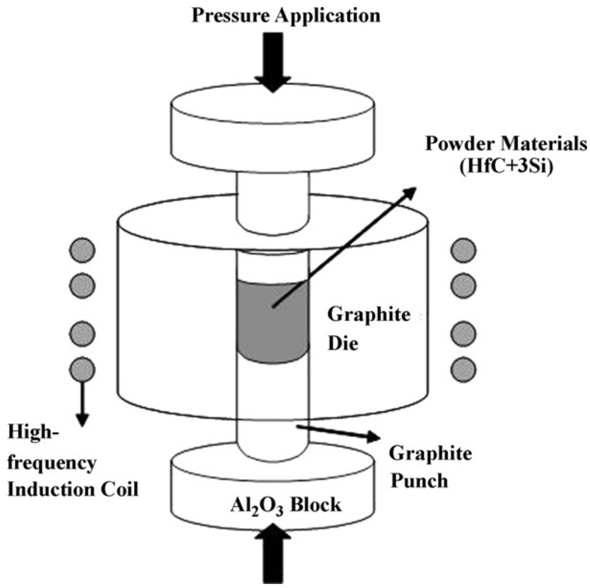

Fig. 3. Schematic diagram of apparatus for high-frequency induction heated combustion.

was attained as indicated by a linear gauge measuring the shrinkage of the sample (stage 3). Temperature was measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature (stage 4). The process was carried out under a vacuum of 40 mtorr.

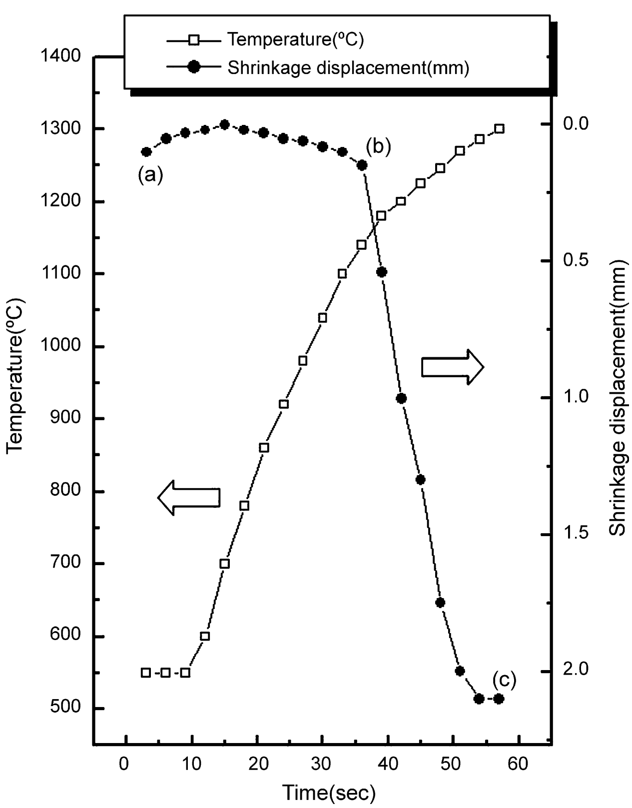

Fig. 4. Variation of temperature and shrinkage displacement with heating time during high-frequency induction heated combustion synthesis and densification of $HfSi_2$–SiC composite (under 60 MPa, 90% output of total power capacity).

The relative densities of the synthesized sample were measured by the Archimedes method. Microstructural information was obtained from product samples which were polished and etched using a solution of HF (30 vol.%), HNO_3 (30 vol.%) and H_2O (40 vol.%) for 10 s at room temperature. Compositional and microstructural analyses of the products were made through XRD and SEM with energy dispersive X-ray analysis (EDAX).

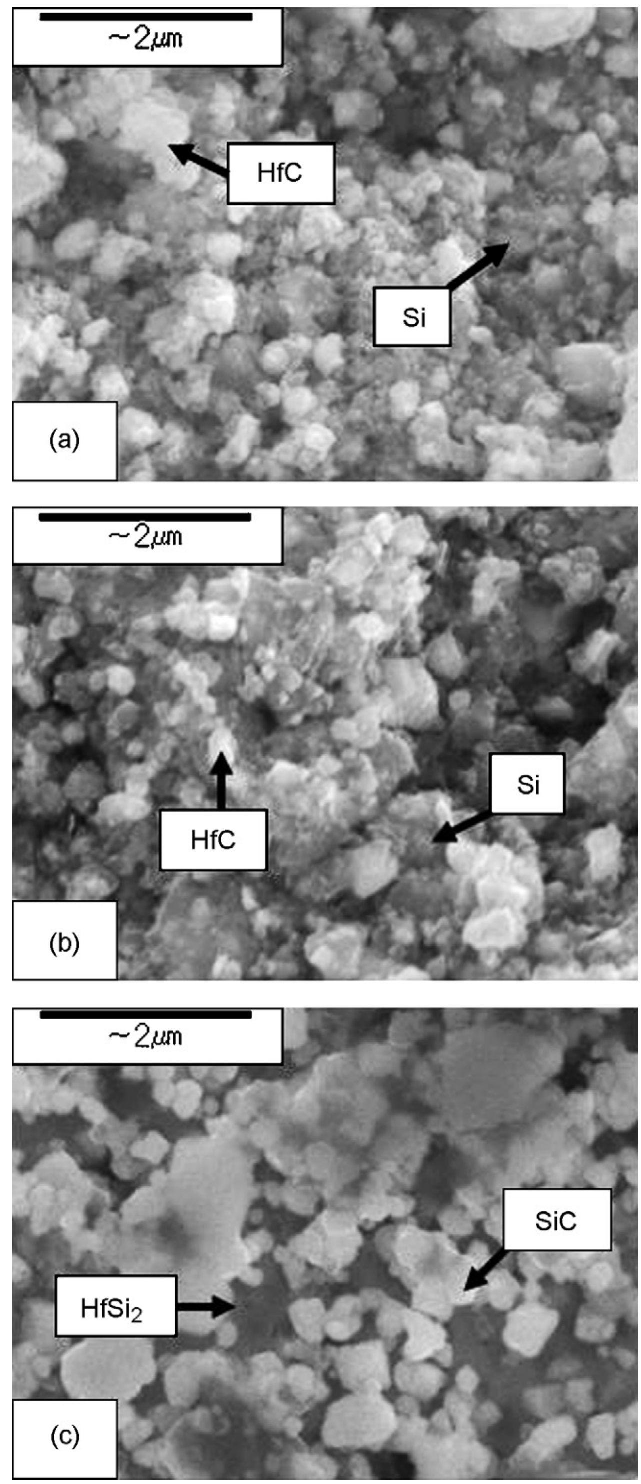

Fig. 5. Scanning electron microscope images of HfC + 3Si system: (a) after milling, (b) before combustion synthesis, and (c) after combustion synthesis.

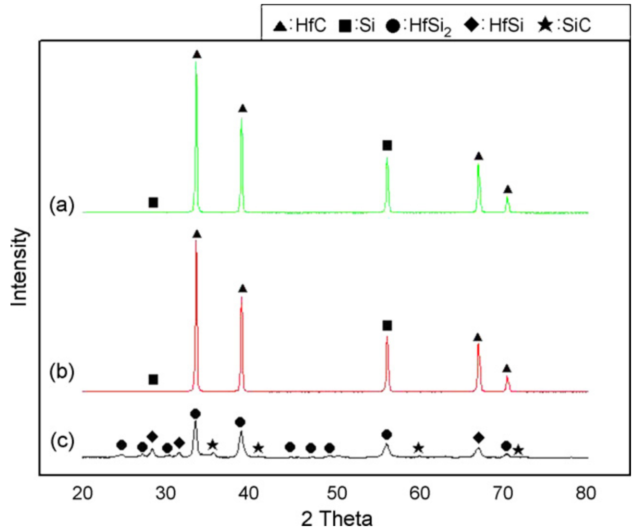

Fig. 6. XRD patterns of the HfC + 3Si system: (a) after milling, (b) before combustion synthesis, and (c) after combustion synthesis.

Vickers hardness was measured by performing indentations at load of 5 kg and a dwell time of 15 s on the synthesized samples.

3. Results and discussion

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the processing of HfC + 3Si system are shown. Figs. 4 and 5 show the secondary electron microscope (SEM) image of a powder (a); after milling, a specimen heated to 1100 °C (b); and heated to 1300 °C (c), respectively. Fig. 5(a) and (b) indicates the presence of the reactants as separate phases. X-ray diffraction shows in Fig. 6(a) and (b) peaks pertaining to the reactants HfC and Si. However, when the temperature was raised to 1300 °C, the starting powders reacted producing highly dense products. A complete reaction between these elements (HfC and Si) has taken place under these conditions. These conclusions were supported by SEM images (Fig. 5c) and X-ray diffraction analyses with peaks of the product phase, $HfSi_2$ and SiC phase (Fig. 6c). A minor phase (HfSi) has been observed by X-ray diffraction analyses, as shown in Fig. 6(c). The presence of the minor phase suggests a deficiency of Si.

The structure parameter, i.e. the average grain size of silicide ($HfSi_2$) obtained from Stokes and Wilson's formula [22] was about 100 nm and the SiC particles were well distributed in matrix, ascertained by SEM image (Fig. 5c).

Vickers hardness measurements were made on polished sections of the $HfSi_2$–SiC composite using a 5-kg load and 15-s dwell time. The calculated hardness value of $HfSi_2$–SiC composite was 1060 kg/mm^2. This value represents an average of five measurements. Indentations with large enough loads produced median cracks around the indent. The length of these cracks permits an estimation of the fracture toughness of the materials by means of the expression suggested in Ref. [23]:

$$K_{IC} = 0.204\left(\frac{c}{a}\right)^{-3/2} H_v a^{1/2}$$

where c is the trace length of the crack measured from the center of the indentation, a the half of average length of two indent diagonals, and H_v is the hardness. The calculated fracture toughness value of $HfSi_2$–SiC composite is about 3.4 MPa m$^{1/2}$. The fracture toughness is higher than that of the SiC phases reported as 1.8 MPa m$^{1/2}$ [7]. The toughness value is the average of measurements on five measurements.

4. Summary

Using the high-frequency induction heated combustion method, the simultaneous synthesis and densification of $HfSi_2$–SiC composite was accomplished using powders of mechanically activated HfC and Si. Complete synthesis and densification can be achieved in one step within duration of 1 min. The average grain size of $HfSi_2$ prepared by HFIFCS was about 100 nm. The average hardness and fracture toughness values obtained were 1061 kg/mm^2 and 3.4 MPa m$^{1/2}$, respectively. The fracture toughness is higher than that of the SiC phase.

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