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High-frequency induction heated synthesis and consolidation of nanocrystalline B-SiC composite

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Metal matrix composites combine metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus), leading to greater strength in shear and compression and to higher service temperature capabilities. The attractive physical and mechanical properties can be obtained with metal matrix composites, such as high wear resistance, strength-to weigh ratio, fatigue strength, temperature stability and specific modulus. Nanopowders of Si and B_4C were fabricated by high energy ball milling. Highly dense nanostructured 4B-SiC composite was simultaneously synthesized and consolidated by high-frequency induction heating within three minutes from the mechanically activated powders. The microstructure, phases and mechanical properties (hardness and fracture toughness) were investigated using FE-SEM, XRD and Vickers hardness tester. The relative density of the composite was 98%, and the average grain sizes of B and SiC in composite are 60 and 75 nm, respectively. The fracture toughness of SiC can be improved by the addition of B to form a composite.

Key words: Rapid sintering, Composite, Nanomaterial, Mechanical properties, Synthesis.

Introduction

The continuous increase in the performance requirement of materials for aerospace and automotive applications has led to development of several structural composite materials. Among these, metal matrix composites refer to a kind of material in which rigid ceramic reinforcements are embedded in a ductile metal or alloy matrix. Metal matrix composites combine metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus), leading to greater strength in shear and compression and to higher service temperature capabilities. The attractive physical and mechanical properties that can be obtained with metal matrix composites, such as high wear resistance, strength-to weigh ratio, fatigue strength, temperature stability and specific modulus, have been documented extensively [1,2].

SiC has a low density, high hardness, chemical stability, low thermal expansion, and high strength at high temperatures. B has a low density and high melting point. Hence, composite consisting of SiC and B may be able to satisfy the good mechanical properties requirements of successful structural material.

Nanomaterials have received a good deal of attention recently as they possess high strength, high hardness, excellent ductility and toughness [3, 4]. In recent days, nanocrystalline powders have been developed by the thermochemical and thermomechanical process named as the spray conversion process (SCP), co-precipitation and high energy milling [5-7]. However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to a fast grain growth during conventional sintering process. So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the high frequency induction heated sintering method which can make dense materials within 2 min, has been shown to be effective in achieving this goal [8-10].

The purpose of this work is to produce nanopowders of Si, B_4C and synthesis and consolidation of nanocrystalline B-SiC composite within three minutes from mechanically activated powders (Si-B_4C) using this high-frequency induction heated sintering method. Microstructure and mechanical properties (hardness and fracture toughness) of the composite were also evaluated.

Experimental

Powders of 99% pure B_4C (< 60 μm, Alfa Aesar, Inc) and 99.5% pure Si (–325 mesh, Alfa Aesar Inc) were used as raw materials. The raw powders were milled by high energy ball milling for 10 hrs, by Pulverisette-5 planetary mill. The weight of the B_4C and Si powders was calculated, based on this equation ($B_4C + Si \rightarrow 4B + SiC$). With raw powders, Tungsten carbide balls (9 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. The milling

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was performed at a rotation velocity of 250 rpm, for 10 hrs.

The milled powder was placed in a graphite die (35 mm in outside diameter, 10 mm in inside diameter, 40 mm in height,), and sealed by upper and lower graphite punches. The high-frequency induction heated sintering system, made by Eltek in South Korea, is shown schematically in Ref. [11-13]. The four major stages in the sintering are as follows. The system was evacuated (stage 1), and a mechanically uniaxial pressure of 80 GPa was applied (stage 2). An induced current was then activated, and maintained to 1550 °C, and then turned off, without holding time (stage 3). The temperatures were measured, using 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 10 Pa.

The relative densities of the sintered sample were measured by Archimedes' method. Microstructural information was obtained from the 4B-SiC composite, which was polished. Compositional and micro-structural analyses of the products were made through X-ray diffraction (XRD), and scanning electron microscopy (SEM), with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured, by performing indentations on the sintered samples, at a load of 10 kg and a dwell time of 15 s. The grain size was calculated by Suryanarayana and Grant Norton's formula [14].

Results and Discussion

Fig. 1 shows SEM images of raw powders of B_4C and Si. The powders have a angular shape. The X-ray diffraction patterns of raw powders and mechanically high-energy ball milled powders are shown in Fig. 2. In Fig. 2(c), the peaks of reactants (B_4C and Si) were detected and the peaks of products (B and SiC) were not observed. The full width at half-maximum (FWHM) of the diffraction peak in Fig. 2(c) is more broad than that in Figs. 2(a) and (b) due to the refinement of powders and strains. Fig. 3 indicates a plot of $B_r\cos\theta$ versus $\sin\theta$, to calculate the grain size of B_4C and Si in milled powders. The average grain sizes of B and SiC are 67 and 68 nm, respectively from the X-ray data in Fig. 2 by Suryanarayana and Grant Norton's formula [14].

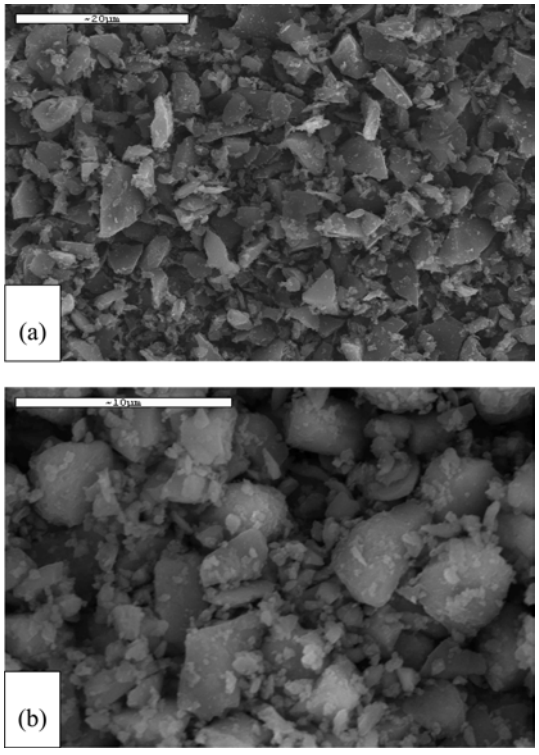

Fig. 1. Fe-SEM images of raw materials. (a) B_4C, (b) Si.

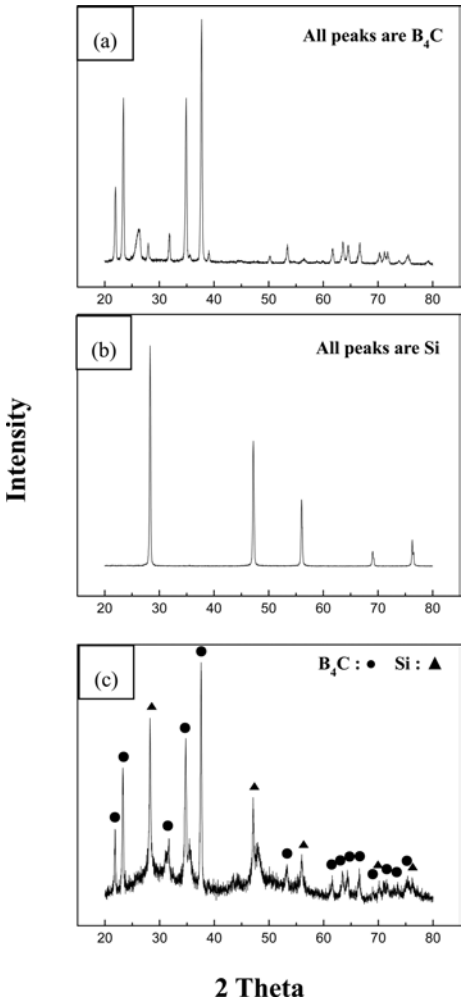

Fig. 2. XRD patterns of raw materials. (a) B_4C, (b) Si, and (c) mechanically milled powders.

The application of the induced current resulted in shrinkage, due to consolidation and synthesis. Fig. 4 shows the variations in shrinkage displacement and temperature with heating time, during the sintering of the milled powders. As the induced current was applied, the shrinkage displacement is nearly constant with temperature, up to about 1000 °C. Afterwards, shrinkage displacement abruptly increased and then is

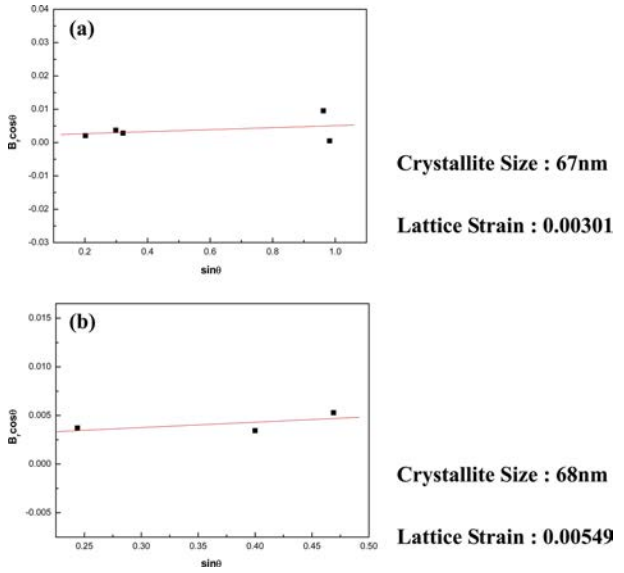

Fig. 3. Plot of Br (B crystalline + B strain) cosθ versus sinθ for (a) B4C and (b) SiC in the milled powders.

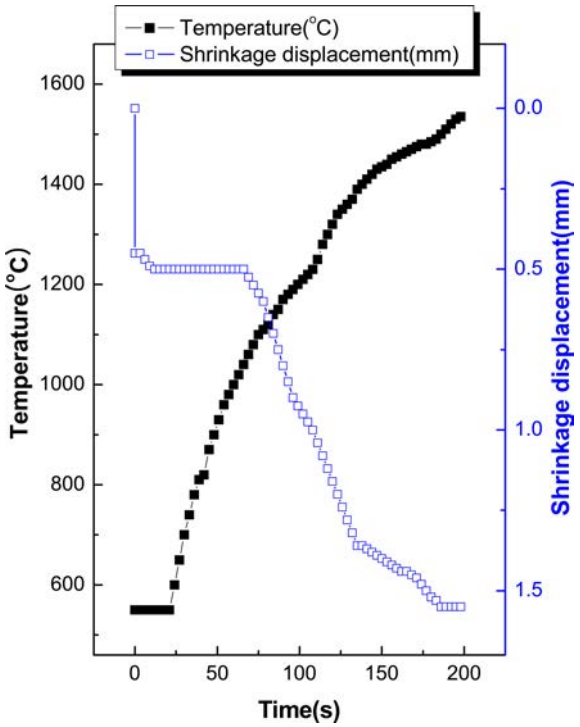

Fig. 4. The variation of temperature and shrinkage displacement with heating time during the sintering of milled powders.

almost linearly to 1500 °C, at which the consolidation terminates. The longer the induced current was applied, the more the specimens shrunk. The shrinkage curve suggests that the consolidation terminates in three minutes. Fig. 5 shows XRD pattern of the high-energy ball milled powders heated to 1550 °C, in which B and SiC peaks are mainly detected. This indicated that the reaction of solid state replacement was established during the induced current heating. From above result, the interaction between B_4C and Si is thermodynamically

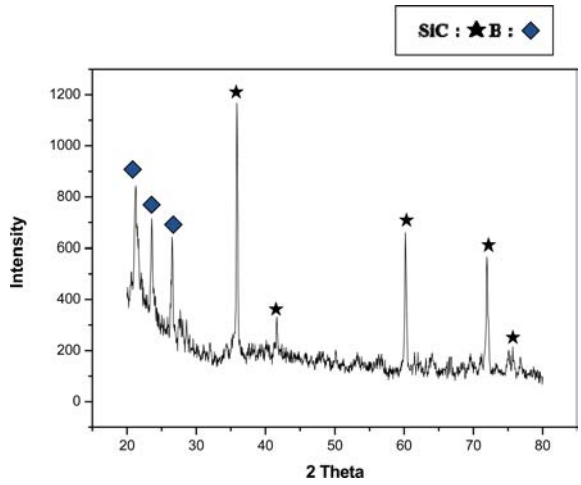

Fig. 5. X-ray diffraction pattern of the 4B-SiC composite heated to 1550 °C.

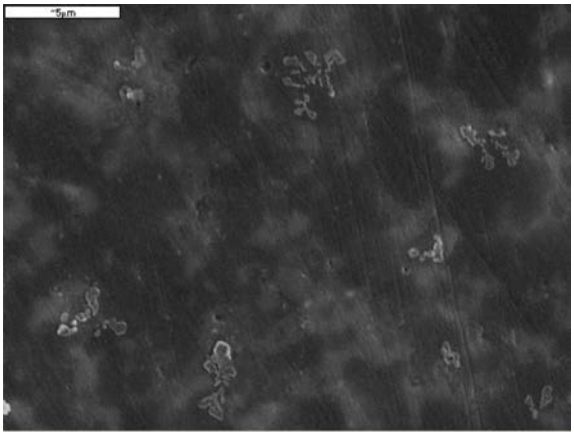

Fig. 6. FE-SEM image of the 4B-SiC composite heated to 1550 °C.

feasible according to equation (1).

$$B_4C + Si \rightarrow 4B + SiC \quad (1)$$

A FE-SEM image of the sample heated to 1550 °C is shown in Fig. 6. In SEM image, dark area and grey area are B and SiC from the mass contrast, respectively. From the figure, it is apparent that the grain sizes of B and SiC consist of nanograins. The structural parameters, i.e. the average grain sizes of B and SiC in composite heated to 1550 °C, are 60 and 75 nm, respectively from the X-ray data in Fig. 5 by Suryanarayana and Grant Norton's formula [14]. Thus, the average grain sizes of the sintered B and SiC are not much larger than those of the initial powders, indicating the absence of grain growth during sintering. This retention of the grain size is attributed to the rapid heating and the relatively short-term exposure of the powders to the high temperature. The corresponding relative density of the 4B-SiC composite was 98%. It is considered that the reasons for the high density of the composite obtained at low temperature are as follows. Firstly, the application of

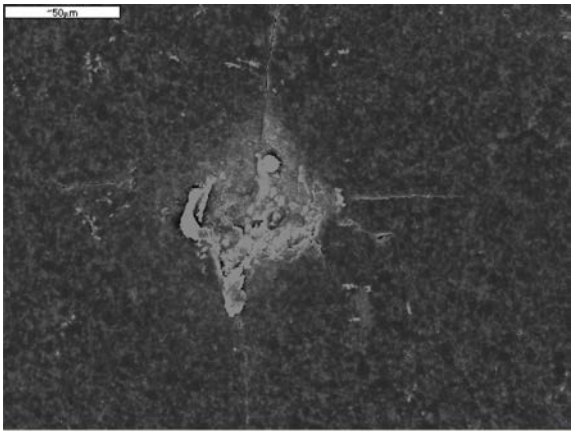

Fig. 7. Vickers hardness indentation in a 4B-SiC composite heated to 1550 ºC.

pressure during initial stage sintering adds another term to the surface energy driving force [15]. Secondly, the effects of the current on sintering have been interpreted in terms of the rapid heating rate due to Joule heating, surface cleaning of powders due to the presence of plasma, the enhancement of wettability under the electric field and the fast mass transport due to electromigration [16-18].

Vickers hardness measurements were made on polished sections of the 4B-SiC composite, using a 10 kg_f load, and 15 s dwell time. The calculated hardness value of 4B-SiC composite sintered at 1550 ºC from high energy ball milled powders was 1590 kg/mm^2. This value represents an average of five measurements. Indentations with large enough loads produced median cracks around the indent. Fig. 7 shows Vickers indentation in the 4B-SiC composite heated to 1550 ºC. One to three additional cracks were observed to propagate from the indentation corner. The length of these cracks permits an estimation of the fracture toughness of the material. From the length of these cracks, the fracture toughness values can be determined, using the method of Niihara et al. [19]. As in the case of the hardness values, the toughness values were derived from the average of five measurements. The toughness value of composites obtained heated to 1550 ºC is 9 MPa · m$^{1/2}$. The fracture toughness is higher than that of the SiC phases reported as 1.8 MPa · m$^{1/2}$ [20]. This is believed to suggest that B and SiC in the composite may deter the propagation of cracks.

Conclusions

The nanopowders of B_4C and Si were made by high-energy ball milling method. Using HFIHS, the nanostructured 4B-SiC composite was simultaneously synthesized and consolidated within three minutes from the milled powder. The relative density of the composite was 98%, and the average grain sizes of B and SiC in composite are 60 and 75 nm, respectively. The hardness and fracture toughness of the composite were 1590 kg/mm^2 and 9 MPa · m$^{1/2}$, respectively. The fracture toughness of SiC can be improved by the addition of B to form a composite.

Acknowledgments

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