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Short communication

$ZrSi_2$–SiC composite obtained from mechanically activated ZrC + 3Si powders by pulsed current activated combustion synthesis

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Abstract

Dense nanostructured $ZrSi_2$–SiC composite was simultaneously synthesized and consolidated by pulsed current activated combustion synthesis (PCACS) within 2 min in one step from mechanically activated powders of ZrC and 3Si. Highly dense $ZrSi_2$–SiC with relative density of up to 97% was produced under simultaneous application of a pressure of 60 MPa and the pulsed current. The average grain size and mechanical properties of the composite were investigated.

Keywords: A. Sintering; B. Nanocomposite; C. Mechanical properties; Solid state reaction

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]. 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 [4–6]. To improve their mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites [7–12]. One example of this is the addition of SiC to $ZrSi_2$. The isothermal oxidation resistance of metal silicide–SiC composite in dry air was found to be superior to that of monolithic metal silicide compact [13]. Therefore, SiC may be the most promising reinforcing material for $ZrSi_2$-based composites.

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties [14,15]. Since nanomaterials possess high strength, high hardness, excellent ductility and toughness, increasing attention has been paid to their application [16,17]. Recently, nanocrystalline powders have been developed by the thermochemical and thermomechanical process which is referred to as the spray conversion process (SCP), co-precipitation and high-energy milling [18–20]. However, the grain size in sintered materials is much larger than that in the pre-sintered powders due to the fast grain growth which occurs during the conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during the conventional sintering process [21]. Therefore, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering method which allows dense materials to be made within 2 min, has been shown to be effective in achieving this goal [22].

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The purpose of this work is to produce dense nanostructured $ZrSi_2$–SiC composite within 2 min in one step from mixtures of mechanically activated ZrC and Si powders at a ratio of 1–3 using the pulsed current activated combustion method and to evaluate its mechanical properties (hardness and fracture toughness).

2. Experimental procedure

Powders of 99.5% zirconium carbide (−325 mesh, Alfa Products) and 99% pure silicon (−325 mesh, Aldrich Products, Milwaukee, WI) were used as the starting materials. A mixture of the ZrC and Si powders at the ratio of 1–3 was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 10 h. Tungsten carbide balls (5 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of ball to powder was 30:1. Milling resulted in a significant reduction in the grain size. The grain size and the internal strain were calculated from the X-ray diffraction data according to Ref. [23]. The FWHM of the milled powder was wider than the raw powder due to the internal strain and reduction in the grain size. The average grain sizes of ZrC and SiC were about 56 nm and 40 nm, respectively.

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 a pulsed current activated combustion system (Eltek, in South Korea). The four major stages in the synthesis were as follows. First, the system was evacuated (stage 1) and a uniaxial pressure of 60 MPa was then applied (stage 2). A pulsed current was then applied and maintained until densification was attained as indicated by the shrinkage of the sample measured by a linear gauge (stage 3). The 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 relative densities of the synthesized sample were measured by the Archimedes method. Microstructural information was obtained from the product samples which were polished and etched using a solution of HF (15 vol.%), HNO_3 (25 vol.%) and H_2O (60 vol.%) for 10 s at room temperature. Compositional and microstructural analyses of the products were conducted through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). The Vickers hardness was measured by performing indentations at load of 10 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 the heating time during the processing of the ZrC + 3Si system are shown in Fig. 1. As the induced current was applied the specimen showed initially a small (thermal) expansion and the shrinkage displacement increased gradually with increasing temperature up to about

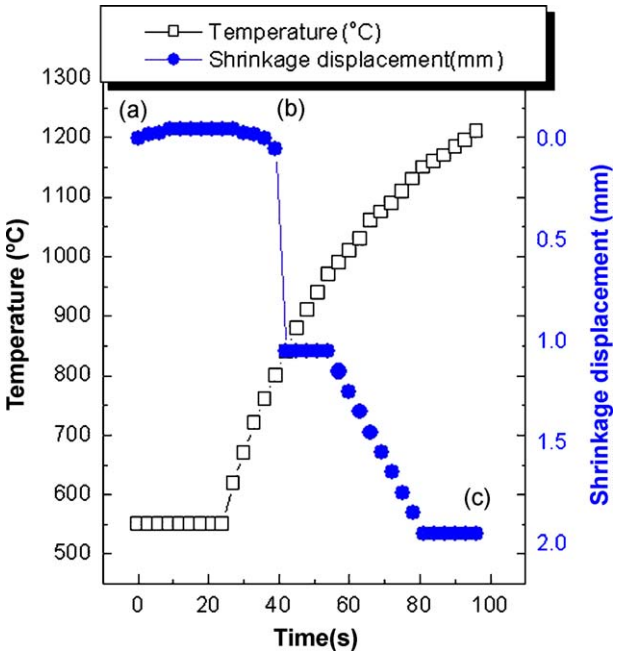

Fig. 1. Variations of temperature and shrinkage displacement with heating time during pulsed current activated combustion synthesis and densification of $ZrSi_2$–SiC composite.

800 °C, but then abruptly increased at about 900 °C. When the reactant mixture of ZrC + 3Si was heated to 800 °C under a pressure of 60 MPa, no reaction took place and no significant shrinkage displacement occurred as judged by the subsequent XRD and SEM analyses. Fig. 2 shows the SEM image of the powder (a) after milling and the specimen heated to (b) 800 °C and (c) heated to 1200 °C. Fig. 2(a) and (b) indicates the presence of the reactants as separate phases. The X-ray diffraction results, shown in Fig. 3(a) and (b) exhibit only peaks pertaining to the reactants ZrC and Si. However, when the temperature was raised to 1200 °C, the starting powders reacted with each other, producing highly dense products. The SEM image of the etched surface of the samples heated to 1200 °C under a pressure of 60 MPa is shown in Fig. 2(c). Complete reaction between these elements (ZrC and Si) took place under these conditions. These conclusions were supported by the X-ray diffraction patterns which contained peaks for the product phase, $ZrSi_2$ and SiC, as indicated in Fig. 3(c). The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density resulting from the change in the molar volume associated with the formation of $ZrSi_2$ and SiC from the reactants, ZrC and 3Si reactant and the consolidation of the product.

Fig. 4 shows plot of $B_r \cos\theta$ versus $\sin\theta$ for composite heated to 1200 °C, indicating that the intercept ($\kappa\lambda/L$) and slope (η) can be used to calculate the crystallite size (L) and lattice strain (η). The structure parameters, i.e. the average grain sizes of $ZrSi_2$ and SiC are obtained from Ref. [23] were 170 nm and 90 nm, respectively and the SiC particles were well distributed in the matrix, as confirmed by the SEM image shown in Fig. 2(c).

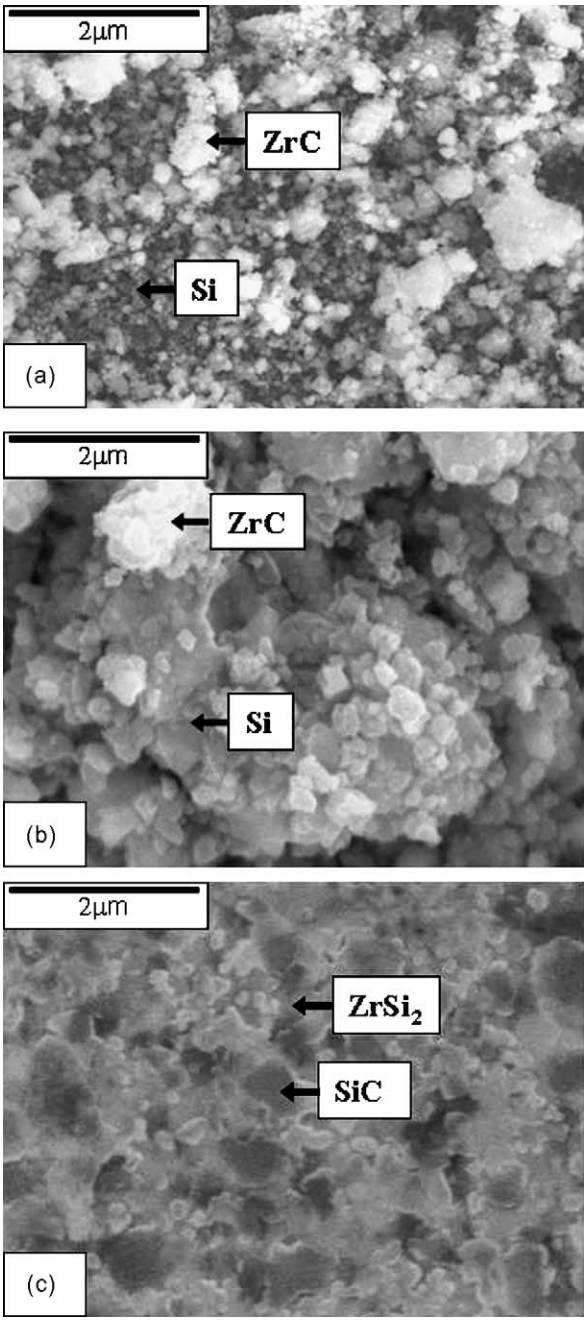

Fig. 2. SEM images of ZrC + 3Si system: (a) after milling, (b) before combustion synthesis, and (c) after combustion synthesis.

The Vickers hardness measurements were made on polished sections of the $ZrSi_2$–SiC composite using a load of 10 kg and dwell time of 15 s. The calculated hardness value of the $ZrSi_2$–SiC composite was 1206 kg/mm^2. This value represents the average of five measurements. Indentations with large enough loads produced median cracks around the indent. The length of these cracks permits the estimation of the fracture toughness of the materials by means of the expression [24]. The calculated fracture toughness value for the $ZrSi_2$–SiC composite was approximately 3 MPa m$^{1/2}$. The mechanical properties (fracture toughness and hardness) of $ZrSi_2$–SiC composite are higher than those of monolithic $ZrSi_2$ which were reported as 834 kg/mm^2 and 2.3 MPa m$^{1/2}$ [25] due to addition of SiC.

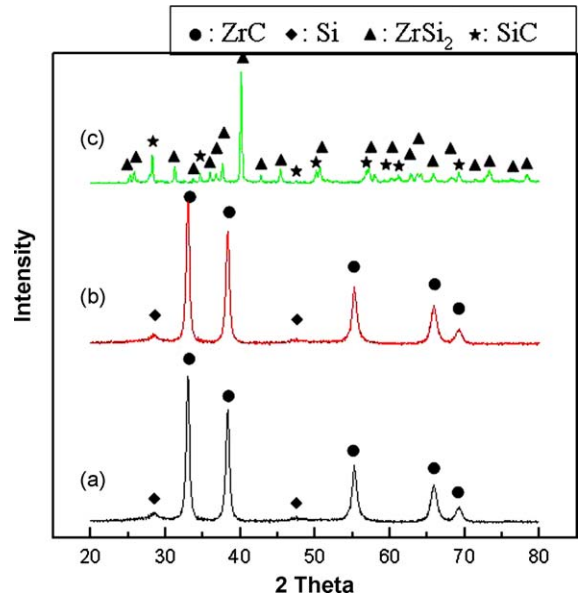

Fig. 3. XRD patterns of the ZrC + 3Si system: (a) after milling, (b) before combustion synthesis, and (c) after combustion synthesis.

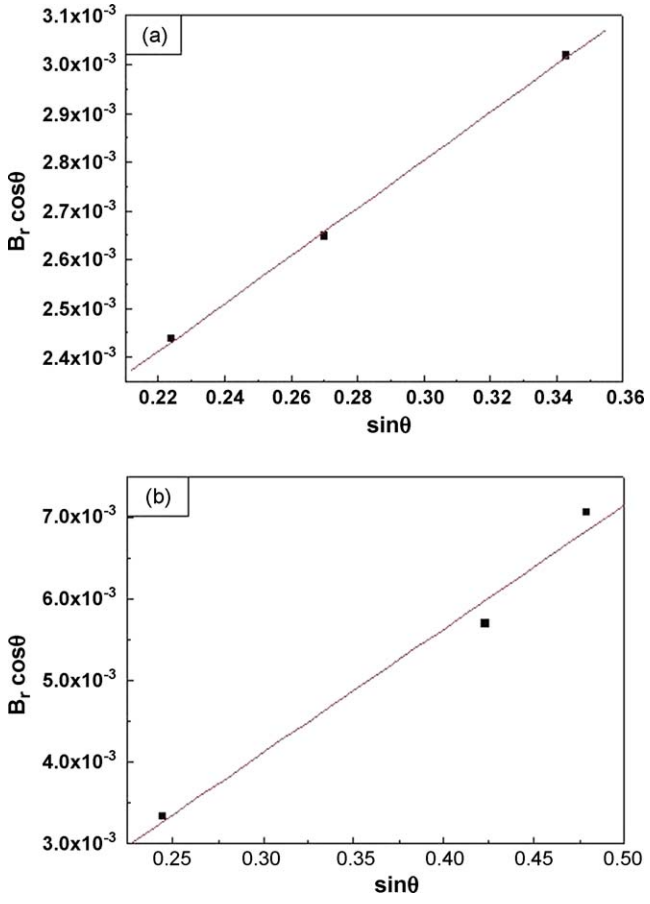

Fig. 4. Plot of $B_r \cos\theta$ versus $\sin\theta$, with (a) $ZrSi_2$ and (b) SiC.

4. Conclusions

Using the pulsed current activated combustion method, the simultaneous synthesis and densification of a nanostructured $ZrSi_2$–SiC composite was accomplished from mechanically activated powders of ZrC and 3Si. Complete synthesis and densification can be achieved in one step within duration of 2 min. The relative density of the composite was 97% when using an applied pressure of 60 MPa and the pulsed current. The average grain sizes of $ZrSi_2$ and SiC prepared by PCACS were about 170 nm and 90 nm, respectively. The average hardness and fracture toughness values obtained were 1206 kg/mm^2 and 3 MPa m$^{1/2}$, respectively. The present mechanical properties are higher than those of monolithic $ZrSi_2$.

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