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SiC whisker reinforced ZrO_2 composites prepared by flash-sintering

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ABSTRACT

SiC whisker-reinforced ZrO_2 composite is prepared by flash sintering. The density of the composite obtained at the optimal conditions is close to the theoretical value. SEM observations reveal that the whiskers with well-preserved original morphology are uniformly distributed within the matrix and strongly bonded with ZrO_2. The composite exhibits a fracture toughness value higher than SiC–ZrO_2 (with 6 mol% Y_2O_3) made by conventional hot-pressing. These results clearly demonstrate that the flash-sintering can prepare SiC_w/ZrO_2 composites more effectively.

1. Introduction

Zirconia ceramic is one of the most important structural ceramics due to its high fracture toughness, resulting from the phase transformation [1,2]. However, the excellent properties only occur at ambient temperature and exhibit serious degradation with increasing temperature [3], which restricts the high-temperature applications of the material. One way to improve the mechanical properties of ceramic materials is to reinforce them with stronger whiskers [4]. For example, silicon carbide whiskers have been widely used to reinforce ceramics and achieved much better properties [5]. However, SiC whisker is rigid and has no volume shrinkage during the sintering. It is well-known that the shrinkage of the ZrO_2 matrix around the SiC whisker (SiC_w) leads to tensile hoop stresses and radial compressive stresses, which inhibit the densification of the composites [6,7]. Therefore, preparing whisker reinforced ceramic composites is not an easy job. Previously, SiC_w/ZrO_2 composites were prepared by hot-pressing at temperature of 1600 °C and pressure of 25 MPa [8,9].

Recently, a new sintering technique, electric field assisted flash sintering, has been developed [10]. Compared to other sintering techniques, flash sintering can densify ceramics at much lower furnace temperature and shorter time [10–15], even though the samples temperature can be very high due to Joule heating [16]. In general, flash sintering required two necessary conditions: (i) power dissipation must exceed a critical level; (ii) the furnace temperature must lie above a threshold value [17]. One unique advantage of flash sintering over conventional sintering is that the constraint effect occurring during sintering the composites could be reduced in flash sintering, likely due to the rates of volumetric and shear strains being equal to each other [18,19]. This unique feature of flash sintering may offer an opportunity to solve the constraint problem encountered in sintering ceramic composites.

In this paper, we report the preparation of SiC_w/ZrO_2 composites by flash sintering the corresponding powder compacts. We find that close-to-fully-dense composites can be obtained at 1000 °C (furnace temperature) for 60 s. The resultant composite exhibits fracture toughness higher than the materials prepared by conventional hot-pressing SiC_w/ZrO_2 [8,9]. The current results indicate that flash sintering is a very promising technique to prepare whisker reinforced ceramic composites.

2. Experimental procedure

The raw materials used in this study are 3 mol% yttria doped tetragonal zirconia powder of 20–50 nm (3YSZ, 99.9% purity, Beijing

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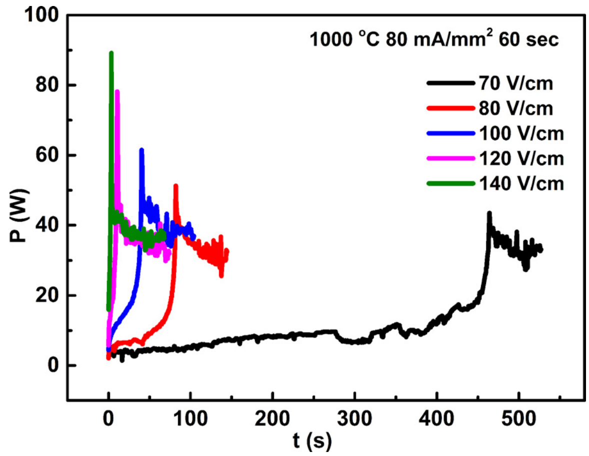

Fig. 1. Plots of power dissipation as a function of time for different applied fields.

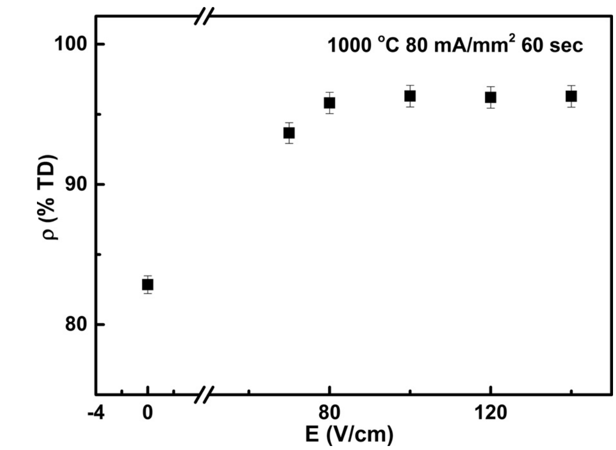

Fig. 2. Plots of the density of the resultant composite as a function of applied field.

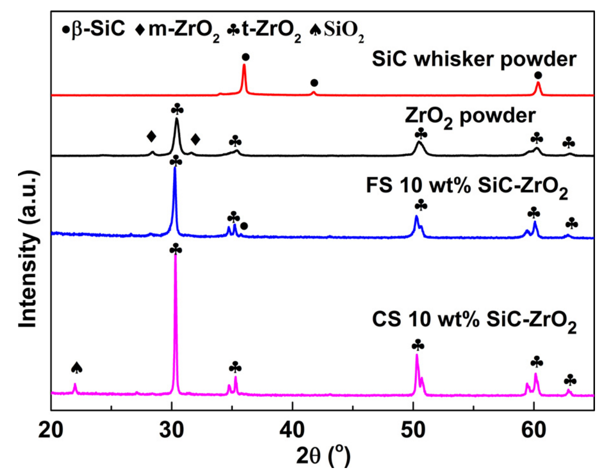

Fig. 3. XRD patterns of the SiC whisker, ZrO_2 powder, conventionally and flash sintered SiC_w/ZrO_2 composites, as labeled.

HWRK Chem Co., Beijing, China) in particle size and SiC whisker of 1.5 μm in diameter and 18 μm in length (99% purity, Alfa Aesar, MA, USA). First, 10 wt.% SiC whisker (corresponding to 17.5 vol.%) was mixed with the ZrO_2 powder by low speed ball milling for 12 h using water as the milling medium. The slurry was dried at 95 °C under constant magnetic stirring. The dried powder mixture was ground in an agate mortar, and subsequently pressed into dog bone-shaped compacts by uniaxial pressing at 10 MPa and cold isostatic pressing at 200 MPa. The compacts were pre-sintered at 800 °C for 4 h in air. A hole with a diameter of 1.6 ± 0.1 mm was drilled on each end of the sample for electric connection. Gauge section of green body was $3.34\,\text{mm} \times 1.16\,\text{mm} \times 20\,\text{mm}$.

The sample was threaded into hooks via the holes at the ends using platinum wires without paste, and hung into a box furnace (KSL-1700-A2; KJ Group, Anhui, China). The furnace was then heated to 1000 °C at 10 °C/min in air. A preset applied field was applied to the sample from a dc power source (Sorenson DLM-300, Sorensen, San Diego, CA). The maximum current density of the power source was set to be 80 mA/mm^2. After the current density reached the maximum value; the sample was held for an additional 60 s before the power to the specimen was disconnected. After disconnecting the power, the specimen was cooled down to room temperature at 5 °C/min. The sintering was carried out at five different applied fields of 70, 80, 100, 120 and 140 V/cm. For comparison, SiC_w/ZrO_2 composites were also prepared using the same power compacts by conventional sintering at 1400 °C for 2 h in a tube furnace.

The density of the sintered composites was measured using the samples cut from the gauge section by the Archimedes method with reagent-grade water as the medium. The crystal structure of the SiC whisker, ZrO_2 powder and sintered composites was characterized using X-ray diffractometer (Rigaku D/max-2400, Tokyo, Japan) using CuKa ($k = 1.54$ Å) radiation. The microstructure of the sintered composites was observed by scanning electron microscopy (SEM, S-4700; Hitachi, Tokyo, Japan) on polished and thermally etched surfaces. The hardness and fracture toughness were determined using indentation technique (HMV-G20ST; SHIMADZU, Tokyo, Japan) on the polished surface of the composite, using the indentation load of 19.6 N for 15 s. More than ten indentations were made on each sample to obtain reliable data. The indentation size and crack length were measured from SEM images.

3. Results and discussion

Fig. 1 plots the power dissipation as a function of time for different electric fields applied. The curves obtained at all five different fields show the characteristic behavior of flash sintering—existence of power dissipation surge, indicating that the composite can be flash-sintered within the range of applying field at the furnace temperature of 1000 °C. The curves also show that the incubation time (the time before the occurrence of the surge) for the composite quickly decreases with increasing the applied field, similar to yttria stabilized zirconia without SiC whiskers [20]. While the flash-sintering occurred at the furnace temperature of 1000 °C, the specimen temperature could be much higher than the furnace temperature due to Joule heating [16,21–24]. Here, the specimen temperature was estimated by using the model described in Ref. [16], to be 1400 °C, which is similar to the conventional sintering temperature for 3YSZ [25].

The effect of the applied field on the density of the resultant composites is shown in Fig. 2. It is seen that the density increases with increasing the field at beginning, and reaches the maximum value to be ~96% of the theoretical density at the applied filed = 100 V/cm. Further increasing the applied field, the density remained the same. The increased density is due to the accelerated mass transport with the applied field [16]. At the same current density limitation, the power spike increases with increasing the applied filed, leading to higher temperatures in the sample. The density of the sample prepared by conventionally sintering at 1400 °C for 2 h is also included Fig. 2, which is much lower than that for the flash sintered ones. The results clearly demonstrate that the flash-sintering is a promising technique to synthesize whisker reinforced composites.

Fig. 3 shows the XRD patterns of the SiC whisker, ZrO_2 powder, flash-sintered composite, and conventionally sintered composite.

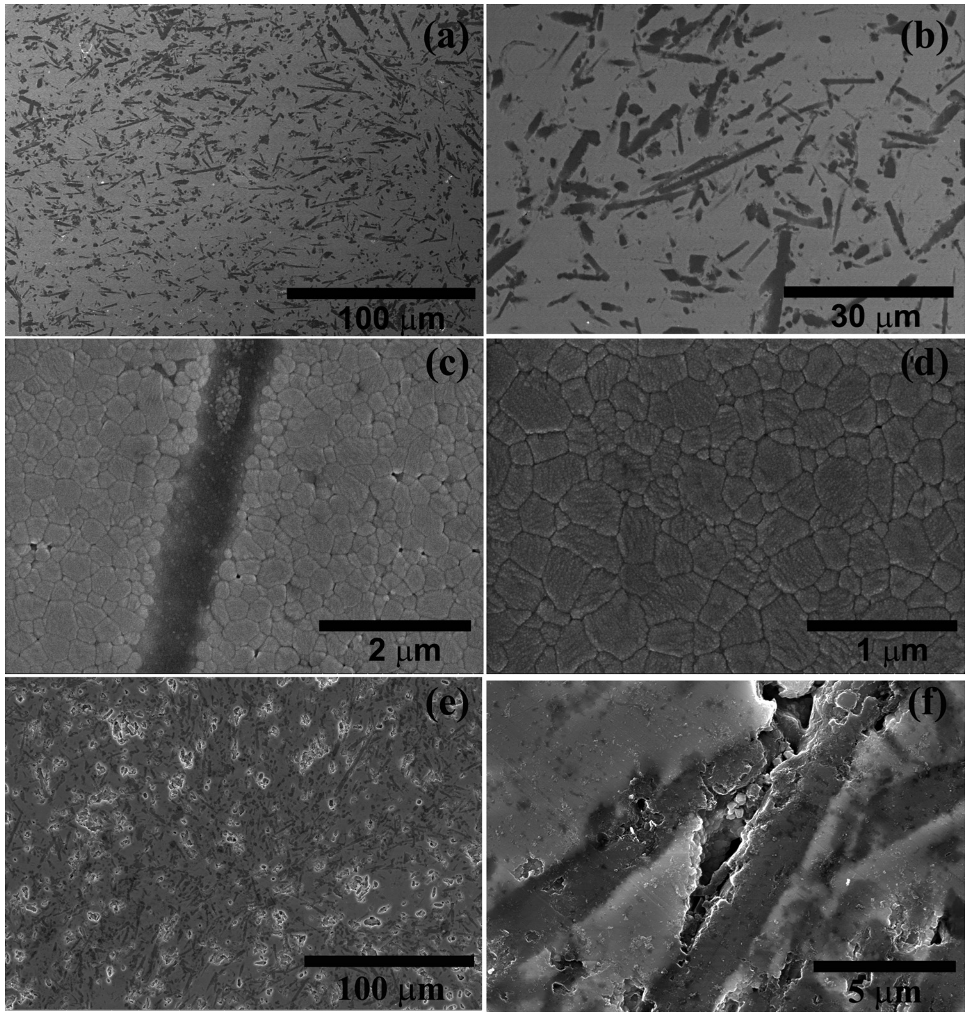

Fig. 4. Typical microstructure of SiC_w/ZrO_2 composite prepared (a)–(d) by flash sinerting at following conditions: applied filed = 100 V/cm, limit current density = 80 mA/mm^2, holding time = 60 s, and furnace temperature = 1000 °C; and (e)–(f) by conventonally sintered at 1400 °C for 2 h.

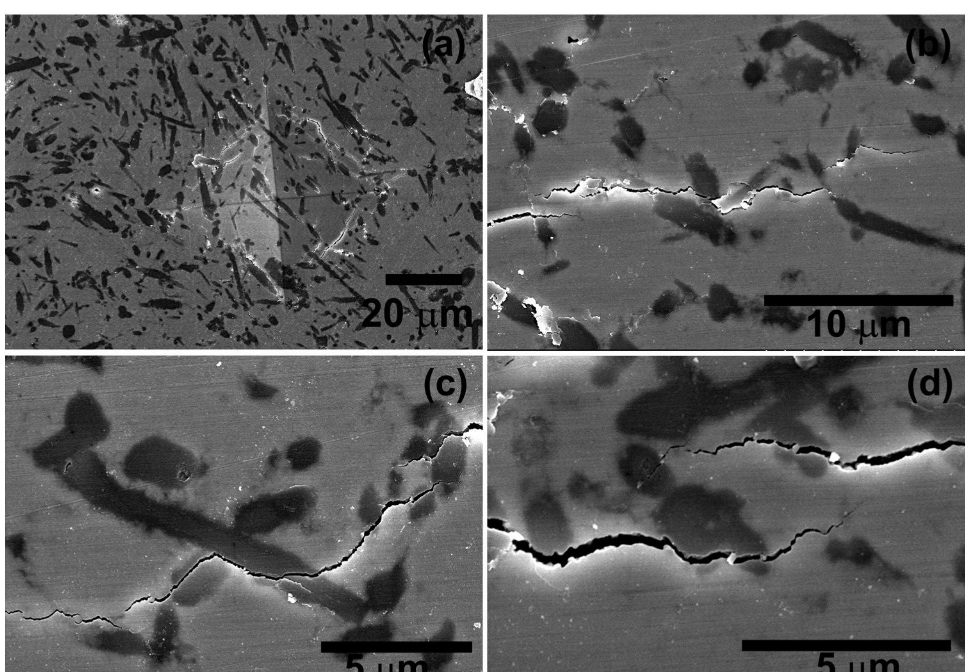

Fig. 5. Typical indentaion morphologies formed on the flash sintered SiC_w/ZrO_2 composite.

According to the XRD patterns, the SiC whisker is pure β-SiC, while the ZrO_2 powder contains the minor m-ZrO_2 phase and major t-ZrO_2 phase. The pattern of the flash-sintered composite reveals that the material contains all these three phases without any other detectable phase, suggesting that the sintering process did not damage any phase. Comparing the XRD patterns of the pure ZrO_2 and the composite reveals that the relative intensity of the diffraction peaks corresponding to m-ZrO_2 phase becomes weaker within the composite, indicating some of the m-ZrO_2 transformed to t-ZrO_2 during the sintering. On the other hand, besides the three major phase, the composite prepared by conventional sintering also contains detectable SiO_2 phase, likely due to the oxidation of SiC whisker during air sintering. Therefore, flash-sintering can lead to pure SiC_w/ZrO_2 composite, which is difficult to obtain by conventional pressureless sintering in air. It is likely due to the extreme short sintering time in flash sintering.

Fig. 4 shows typical SEM images of the composite flash sintered at optimal conditions and that conventionally sintered. The low magnification images (Fig. 4a and b) reveal that the composite contains very few pores, suggesting that it has very high desnity, consistent with the density measurement. The images also reveal that the SiC whiskers were uniformly dispersed in the ZrO_2 matrix. The SiC whisker morphology was well preserved in the composites with the mean diameter and length of SiC whisker similar to those of the raw powder. Closer examination (Fig. 4c) reveals that the interface between the SiC whisker and the ZrO_2 matrix takes serrate morphology, suggesting a good bond between them. Fig. 4d shows that the ZrO_2 matrix consists of equiaxed grains with the average grain size of 230 nm. These results further confirm that flash-sintering is a very promising technique to effectively prepare whisker reinforced composites. It seems that the whisker related constraint effect did not limit the densification process in flash sintering. Jha and Raj [19] suggested that electric fields can help to reduce the reinforcing-phase caused constraint effect, because in flash sintering the vacancy and interstitials generated within the grains migrate to grain boundaries and pores so that both volumetric and shear strain are at equal rates. On the other hand, the sample conventionally sintered at 1400 °C (which is similar to the specimen temperature estimated for the optimal flash sintering conditions) contains pores around the SiC whisker and the poorly bonded interfaces between the SiC whisker and ZrO_2 matrix (Fig. 2e and f), clearly showing the constraint effect. Therefore, flash sintering is much more effective and promising for sintering the SiC_w/ZrO_2 composite.

To further examine the quality of the flash-sintered composite, the mechanical properties were measured by indentation technique on the sample obtained at the optimal conditions. Fig. 5a shows a typical indentaion morphology. The hardness (H) of the ceramic was estimated using the following equation,

$$H = \frac{1.8544P}{d^2} \tag{1}$$

where P is the indentation load and d is the indentation diagonal measured from the SEM images. The measured value is 11.0 ± 0.3 GPa.

There are two types of cracks: Palmqvist cracks and median cracks, classified by the crack-to-indent ratio. The crack with the ratio in the range of 0.25–2.5 is classified as Palmqvist cracks [26]; while the crack with the ratio >2.5 is classified as median cracks. For the current material, the crack-to-indent ratio was measured to be about 1.2. Thereby, the equation proposed for Palmqvist cracks were used to estimate the fracture toughness (K_{IC}) of the composite [26,27]:

$$K_{IC} = k\left(\frac{E}{H}\right)^{2/5}\left(\frac{P}{al^{3/2}}\right) \tag{2}$$

where E is the Young's modulus of the material, a half the indentation diagonal, l the crack length, and k the dimensionless constant determined experimentally. The measured toughness for the composite is 9.7 ± 0.3 MPa m$^{1/2}$. This value is much higher than that (4.8 ± 0.5 MPa m$^{1/2}$) of the SiC_w–ZrO_2 (with 6 mol% Y_2O_3) composites made by hot pressing; but lower than that (16.3 ± 1.1 MPa m$^{1/2}$) of the SiC_w/ZrO_2 (with 2 mol% Y_2O_3,) composites [8,9]. It was reported that the high Y_2O_3 content promoted the formation of interfacial amorphous layers, which strengthened the interfacial bonding and resulted in low fracture toughness [8,9]. The cracks were closely examined under SEM (Fig. 5b and d). Crack deflection, transgranular fracture, and bridging can be clearly observed along the crack wake, which, together with transformation toughening are likely responsible for the observed toughness [8,9,28].

4. Summary

ZrO_2-matrix ceramic composite reinforced with 10 wt.% SiC whiskers was flash-sintered at different applied electric fields. The composite obtained at the optimal condition (applied field = 100 V/cm, current density = 80 mA/mm^2, hold time = 60 s, furnace temperature = 1000 °C) exhibited a density close to the theoretical value and well-bonded interfaces between the SiC whisker and the ZrO_2 matrix. The original morphology of the whiskers was well preserved in the flash sintering sample. The hardness and fracture toughness of the composite were measured by indentation technique to be 11.0 ± 0.3 GPa and 9.7 ± 0.3 MPa m$^{1/2}$, respectively. This work clearly demonstrates that flash sintering is a very promising technique to prepare whisker reinforced ceramic composites.

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