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Preparation of SiO_2–SiC composites with a precursor method

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Abstract

SiO_2–SiC composite particles were prepared through a hybrid sol–gel precursor process. Compacts were prepared by using a conventional sintering process. The techniques of DSC–TG, SEM and XRD were use to characterize the composite particles and the sintered compacts. It was found that a core–shell structure was constructed in the composite particles with cores of SiC and shells of amorphous SiO_2. Nucleation of SiO_2 occurred at about 1200 °C. The optimized sintering temperature for $30SiO_2$–70SiC (vol.%) composites was about 1400 °C with a relatively homogeneous microstructure. The maximum density was about 2.03 g cm^{-3}.

Keywords: SiO_2–SiC composite; Precursor; Hybrid sol–gel process; Crystalline

1. Introduction

In recent years, with the rapid development in scientific fields such as radar, microwave communication and electronic warfare, etc., the microwave absorbing materials have received considerable attention due to the special military position [1]. They can absorb electromagnetic energy and turn it into heat through energy dissipation due to the high dielectric properties. As a new kind of potential microwave absorbing materials, SiC shows unique performances, e.g., low density, high strength, anti-corrosive, semiconductivity, high thermal conductivity and high temperature stability. It can realize the unity of light weight, thin absorber layer, wide frequency range and multi-frequency bands. It was reported that very high dielectric constant appeared for SiC-based ceramic capacitors with the grain boundary of oxides insulation [2]. SiO_2–SiC composites are primising materials with potential applications in the microwave area. Several SiO_2–SiC related composites are investigated by surface processing technique [3–11]. Nevertheless, few detailed preparation processes of SiO_2–SiC composite have been reported.

In this work, a hybrid sol–gel method is used to prepare composite precursor. Thermogravimetry features of the composite particles are analyzed. Processes related to the preparation of SiO_2–SiC composites are discussed.

2. Experimental

α-SiC powders (~10 μm; China White Dove Group) were commercially available. SiO_2 was obtained by the hydrolysis of tetraethyl orthosilicate (TEOS: $Si(OC_2H_5)_4$) through a hybrid sol–gel process. The hybrid sol–gel process performed from a tetraethyl orthosilicate alcohol–water solution by sequentially using both HCl and ammonia as catalysts. A heterogeneous coating method was carried out to prepare SiO_2–SiC composite precursor. The ratio between SiO_2 and SiC was 30:70 in volumetric percentage. During the coating process, SiC particles were suspended in distilled water and ultrasonicated for 30 min to break down agglomerates. The pH value of the suspension was adjusted at about 2 by HCl. Tetraethyl orthosilicate in alcohol solution was then added to the suspension with stirring for 3 h. Then $NH_3{\cdot}H_2O$ was mixed into the suspension and the pH value was controlled at 10–11. The gel of SiO_2–SiC composite precursor was formed in a few minutes.

In the sol–gel process, two main types of reactions are involved: (1) silanol groups are formed by hydrolysis and (2) siloxane bridges are formed by a condensation polymerization reaction:

Hydrolysis:

$$Si{-}(OR)_4 + H_2O \rightleftharpoons Si{-}(OH)_4 + 4R{-}OH \quad (1)$$

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Condensation:

$$2Si{-}(OH)_4 \rightleftharpoons 2(Si{-}O{-}Si) + 4H_2O \quad (2)$$

The reaction process is strongly dependent on such factors as the concentration of individual reactants, temperature, mixing rate, etc. Excessive water will enhance the hydrolysis speed of TEOS, regardless of the catalyst of acid or alkali [12–14]. However, the excessive water can reduce the condensation rate due to the dilution effect. Therefore, the amount of excessive water should be carefully controlled for sol–gel transition.

The pH value is another important factor to influence the sol–gel process. Schaefer [15] reported that the quickest hydrolysis occurs at pH 1, while it will be the slowest at pH 7. The hydrolysis will become quicker at even higher pH value. The speed of condensation has the minimum value at pH 1.5. Hydrolysis and condensation can simultaneously be enhanced at pH value higher than 10. That is why the initial pH value was 2 and then adjusted over 10 for the hybrid sol–gel process in the present situation.

After filtering, rinsing and drying at 100 °C for 10 h, the composite precursor was sieved and dehydrated at 400 °C in air for 2 h, to form the coated SiO_2–SiC composite particles. The heating rate was 10 °C min^{-1}. The coated SiO_2–SiC composite particles were dry pressed, and then sintered in air at 1100, 1200, 1300, 1400 and 1500 °C, for 2 h, respectively.

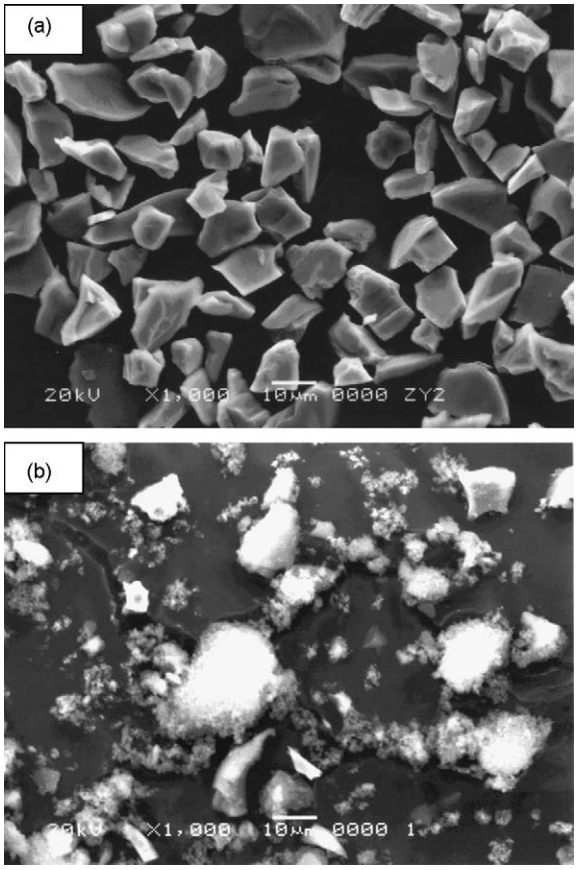

Fig. 1. Morphology of (a) SiC original particles and (b) SiC–SiO_2 composite particles.

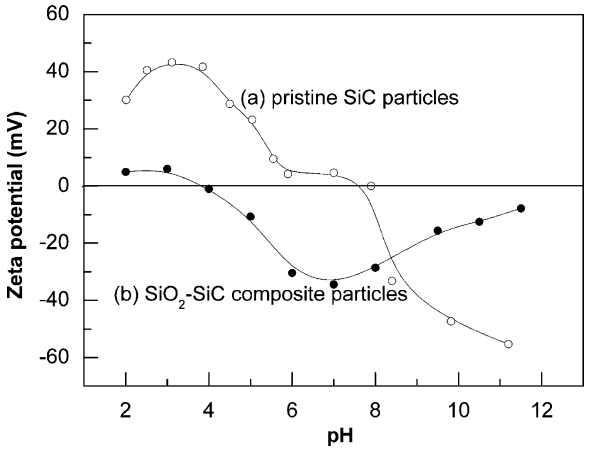

Fig. 2. Change in zeta potential versus pH of different samples: (a) SiC and (b) SiO_2–SiC.

A differential scanning calorimetry and thermogravimetry (DSC/TG; STA 449C, Netzsch, Germany) was used to investigate the thermogravimetric behavior of the SiO_2–SiC composite precursor and monolithic SiO_2 precursor, respectively. The heating was conducted in air at rate of 10 °C min^{-3}. Al_2O_3 crucible was used as the reference material. The density of the sintered compacts was measured using the Archimedes method. The morphology of samples was observed using a scanning electron microscopy (SEM, Model JEOL JSM-5610LV, Japan). Phases in the samples were identified by the X-ray diffraction analysis (XRD, Model Pw1700X, Holland). The surface condition of different samples was measured

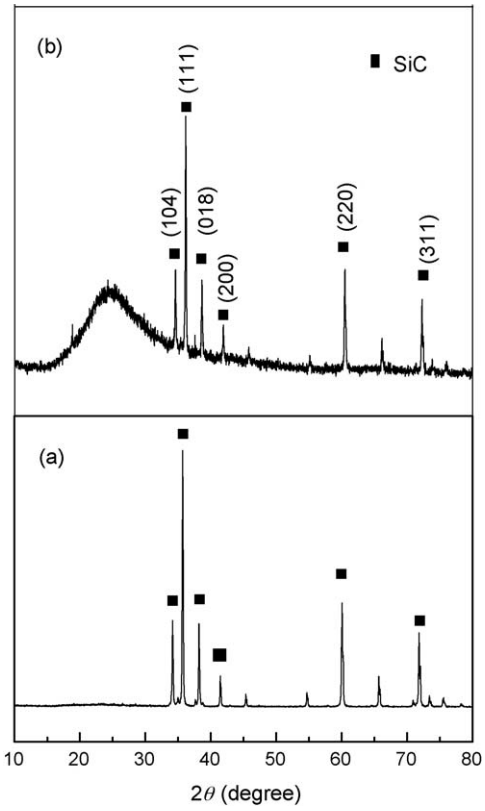

Fig. 3. XRD patterns of (a) raw materials and (b) coated composite particles.

through the zeta potential measurement (Zetaplus, Brookheaven, NYUSA).

3. Results and discussion

The morphologies of original SiC particles and SiO_2–SiC composite particles are shown in Fig. 1. Different from the well-defined original SiC particles in Fig. 1(a), adherent layer of SiO_2 is observed on the surface of SiC particles, indicative of a core–shell coating configuration, as shown in Fig. 1(b). According to the changes in zeta potential for original SiC particles and coated composite particles shown in Fig. 2, the isoelectric point of SiC is at pH 7.8, while that of SiO_2–SiC composite particles is at pH 3.5. Therefore, it is reasonable to say that a new surface of SiO_2 is formed on SiC particles.

Fig. 3(b) shows the XRD pattern of SiO_2–SiC composite particles. Compared to the XRD pattern of α-SiC raw particles in Fig. 3(a), there is an obvious broadened diffraction peak at about 23°, which is the typical characteristic of an amorphous material. Besides, diffraction lines corresponding to SiC are also detected. This represents that the SiO_2 layer appears as amorphous phase on the surface of SiC particles.

From the DSC–TG profiles of the SiO_2–SiC composite precursor and monolithic SiO_2 precursor shown in Fig. 4(a) and (b), an obvious weight loss is observed from 40 to 150 °C in Fig. 4(a), which refers to the removal of residual water and absorbed air. Correspondingly, an endothermic peak appears. The weight loss at 200 °C might be ascribed to the removal of organic solvent. As a result, an endothermic peak appears. At 400 °C, a weight gain of 0.1% is detected with an exothermic peak. Contrarily, no such weight gain appears at the same temperature through the DSC profile of the monolithic SiO_2 precursor shown in Fig. 4(b). This implies that oxidation of SiC particles might probably occur at 400 °C for SiO_2–SiC composites particles [16].

After sintering, phase changes in the sintered SiO_2/SiC compacts are illustrated in Fig. 5. It is noticed that amorphous SiO_2 appears for samples sintered at 1100 °C. At higher temperatures, SiO_2 crystallites tend to nucleate and grow. The diffraction line referring to quartz crystal appears, as shown in samples sintered above 1200 °C. The intensity of the diffraction peak for SiO_2 crystals increases with the increasing sintering temperature, which indicates the increasing content of crystalline SiO_2 within the sintered compacts [11]. Excess SiO_2 phase appears when the samples are sintered at 1500 °C due to the serious oxidation of SiC at such a high temperature.

Fig. 6 shows the density of compacts sintered at different temperature. The density increases with the sintering temperature, and reaches the maximum density of 2.03 g cm^{-3} at about 1400 °C. At lower temperatures, the presence of amorphous SiO_2 leads to local melting at the interface between SiO_2 and SiC grains. The densification of the composites will proceed via a so-called transient viscous sintering [17]. Maximum densification might be achieved at about 1400 °C with the

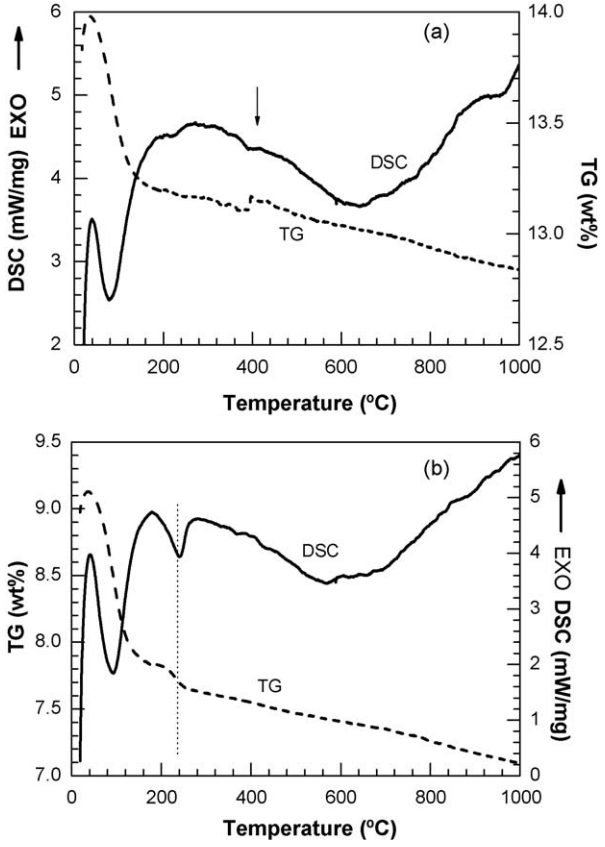

Fig. 4. DSC–TG curve of (a) SiO_2–SiC composite precursor and (b) SiO_2 precursor.

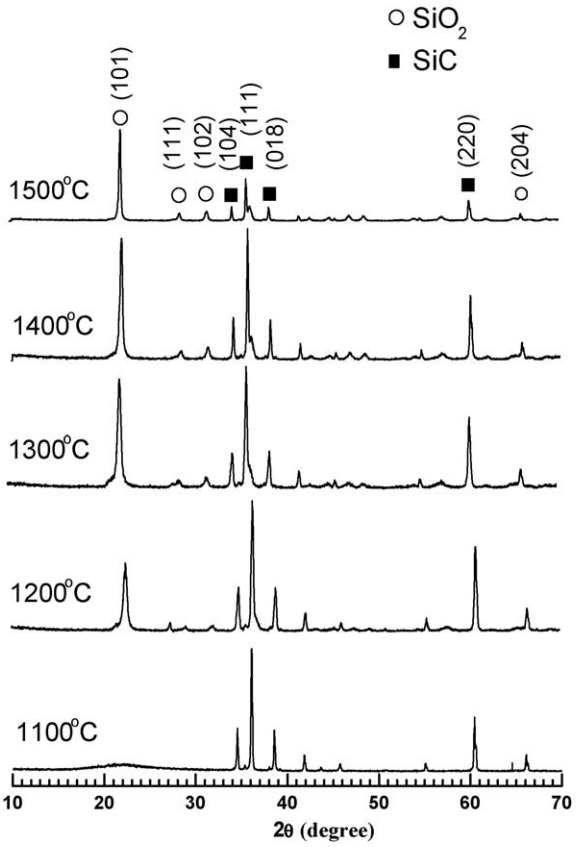

Fig. 5. XRD patterns of SiO_2–SiC composites sintered at different temperatures.

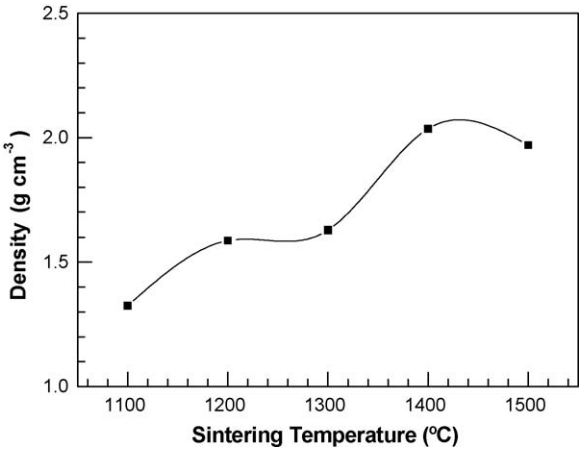

Fig. 6. Change in density versus sintering temperature for the conventional sintered SiO_2–SiC composites.

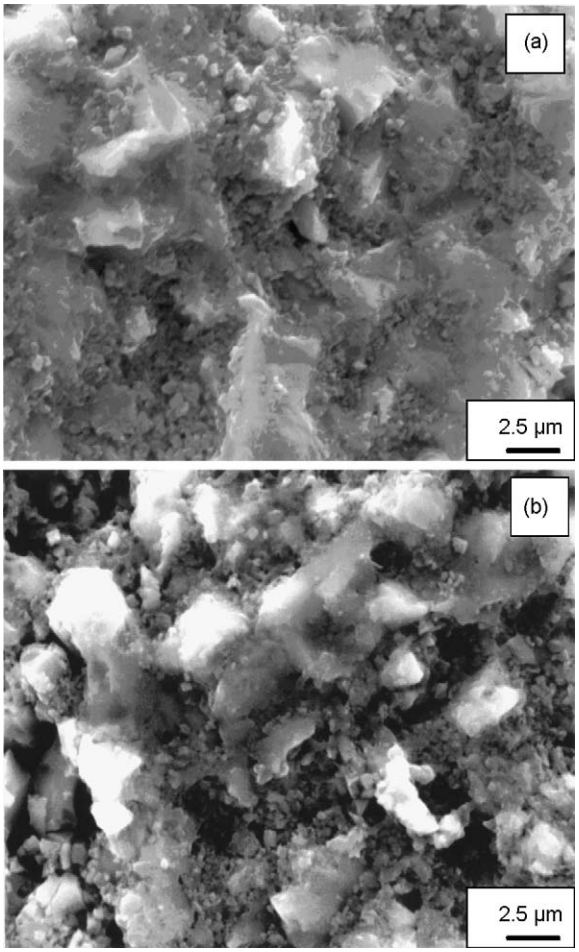

Fig. 7. SEM image of SiO_2/SiC composites sintered at (a) 1400 °C and (b) 1500 °C for 2 h in air.

full crystallization of SiO_2 and the initial oxidization of SiC. The oxidization of SiC at such high temperatures leads to the formation of new amorphous SiO_2. At 1500 °C, successive oxidation of SiC to form CO and/or CO_2 leads to the decrease in the density of the samples. From the SEM image shown in Fig. 7(a), it is observed that relative dense microstructure can be realized within the SiO_2/SiC compacts at the sintering temperature of 1400 °C. Whereas, local pores appear at samples sintered at 1500 °C, as shown in Fig. 7(b). Therefore, it can be considered that the optimized sintering temperature of SiO_2–SiC composites is about 1400 °C.

4. Conclusions

A hybrid sol–gel method has been applied to prepare SiO_2–SiC composite particles with a core–shell structure. Compacts have been prepared by using a conventional sintering process. Nucleation of SiO_2 occurred at above 1100 °C. The optimized sintering temperature for $30SiO_2$–70SiC (vol.%) composites was about 1400 °C with a relatively homogeneous microstructure, and the maximum density was about 2.03 g cm^{-3}.

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