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Preparation of $SiC–SiO_2–CuO$ composites

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Abstract $SiC–SiO_2–CuO$ composite particles were prepared by double coating processes. SEM, DSC-TG, XRD techniques were carried out to characterize the coated composite particles and sintered compacts. It was found that a core-shell structure was constructed in the composite particles with the core of SiC and the shell of $SiO_2–CuO$. Cu–silicides were detected in hot-pressed compacts. SiO_2 might decompose at 1,300 °C. The decomposition product of Si would result in the transformation from $Cu_{6.69}Si$ into Cu_3Si.

Introduction

With the requirement of integration and miniaturization of instruments, it is necessary to fabricate the capacitors with high capacitance high reliability and small size [1]. Due to its superior material properties such as wide band-gap (3.26 V for 4-H SiC), high breakdown electric field (2.2×10^6 V/cm), high saturated electron velocity (2.0×10^7 cm/s) and high thermal conductivity (3.0~3.8 W/cm K) [2], silicon carbide (SiC) shows much potential applications in electronic devices.

SiC was normally considered not suitable for the application as capacitors due to its low intrinsic dielectric constant (~10) [3]. Nevertheless, a kind of SiC-based ceramic capacitor with unique grain boundary design showed huge dielectric constant of 2,910,000, which was much higher than that of titanates dielectrics [4, 5]. However, the high dielectric losses of the boundary phase of $Al_2O_3–MgO–SiO_2$ eutectic at room temperature would limit its practical applications.

In the present study, $SiO_2–CuO$ is selected to form the grain boundary phase. The thermodynamic behavior of $SiC–SiO_2–CuO$ composite particles is detected. Some physical and chemical changes of the composite particles are analyzed.

Experimental

Double coating processes were carried out to prepare composite particles. In the first step, SiO_2 was coated on SiC by sol–gel method. Then $Cu(OH)_2$ was deposited on $SiC–SiO_2$ composite particles by heterogeneous deposition. CuO was available during the sub-sequential heat treatment at 400 °C.

α-SiC particles (4~10 µm in diameter, China White Dove Group) were commercially available. The ratio of SiC phase to $SiO_2–CuO$ grain boundary phase was 75:25 (vol %). Tetraethylorthosilicate (TEOS) was used as source material for SiO_2. During the sol–gel process, SiC suspension was ultrosonicated for 30 min. A mixture of TEOS and ethanol (EtOH) was added into the suspension. The pH was adjusted at 1 for 2 h and then at 10, at which point the velocity of hydrolyzation and aggregation was fastest, respectively [6]. Then SiO_2-Sol was formed. After dried and calcined at 500 °C, $SiC–SiO_2$ composite particles were obtained.

During the second step, the aqueous suspension containing $SiC–SiO_2$ particles was ultrasonicated for 30 min and blended into saturated $CuSO_4$ solution. KOH solution was added to form a surface layer of $Cu(OH)_2$ on $SiC–SiO_2$

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particles. After 30 min, the final deposition of composite particles was filtered, rinsed and dried at 50 °C.

Phases in the coated particles were identified by X-ray diffraction analysis (XRD; Philips, PW1710X). The surface composition of different samples was confirmed through the zeta potential measurement (Zetaplus, Brookheaven, NY). During the measurement, a dilute solution of particle samples was prepared. Different zeta potential values were detected at different pH values. The microstructure was observed using the field-emission scanning electron microscopy (SEM; Quanta 200, FEI). The thermodynamic behavior of the SiC–SiO_2–$Cu(OH)_2$ composite particles was analyzed using differential scanning calorimetry (DSC) and thermogravimetry (TG; STA 449C, Netzsch, Bayern, Germany). The heating was conducted in flowing Ar gas (20 mL/min) with the heating rate of 10 °C/min. Al_2O_3 crucible was used as the reference material.

Results and discussion

Figure 1 shows the changes in the zeta potential of original SiC and coated composite particles. The isoelectric point of SiC appears at 7.9. The isoelectric point of SiC–SiO_2 particles appears at pH 1.9, which is close to that of SiO_2 particles (about pH 2) [7] other than that of the original SiC particles. Since the zeta potential of a particle is determined by its surface composition, the measured results confirm that SiO_2 is coated on SiC particles. As for SiC–SiO_2–CuO composite particles, two isoelectric points appear at pH 7.4 and pH 11.3, respectively. The change in the zeta potential versus pH value is different from that of SiC–SiO_2 particles. The isoelectric point at pH 11.3 is close to that of CuO (about pH 10.8) [8], which indicates that a new surface of CuO might be formed on SiC–SiO_2 particles.

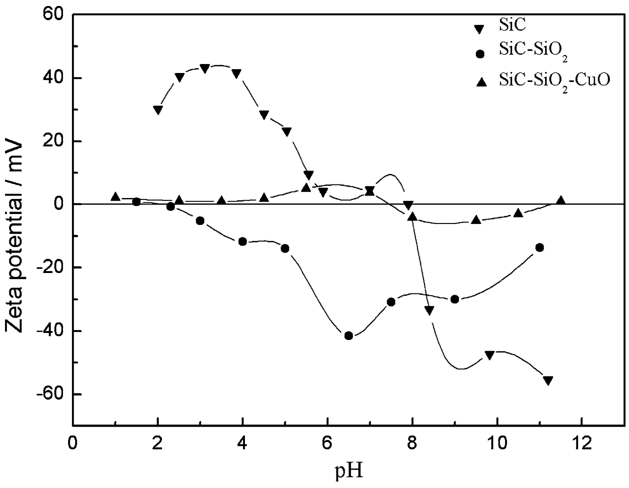


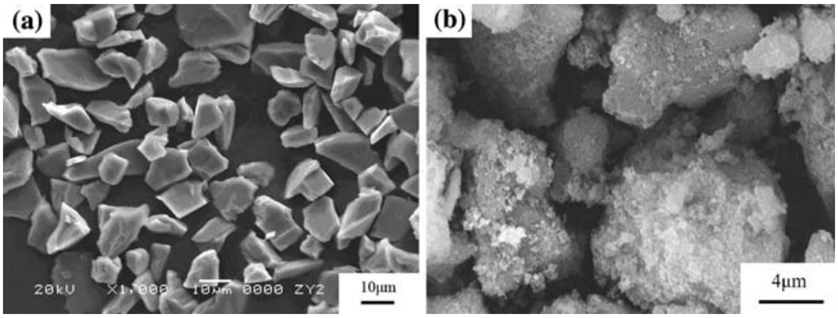
Fig. 1 Changes in zeta potential versus pH of different samples

The morphologies of SiC original particles and SiC–SiO_2–$Cu(OH)_2$ coated particles are shown in Fig. 2. Different from the original SiC particles in Fig. 2a, the surfaces of coated particles in Fig. 2b are rough. Very fine adherent SiO_2–$Cu(OH)_2$ crystallites appear on SiC particles. Such a core-shell structure shows much homogeneous dispersion between SiC particles and SiO_2–$Cu(OH)_2$ coatings.

Figure 3 shows the DSC-TG profiles of SiC–SiO_2–$Cu(OH)_2$ coated particles during the heating process. Four obvious weight losses are observed. The first one from 110 °C to 400 °C refers to the decomposition of $Cu(OH)_2$ with a weight loss of 1%. Correspondingly, an endothermic peak appears. The weight loss around 700 °C arises from the decomposition of CuO into Cu_2O, which leads to an endothermic peak [9]. At 970 °C, an obvious exothermic peak is observed, accompanied by a weight loss of 0.3%. This might be associated with the formation of the $Cu_{6.69}Si$ silicide. Such an assumption can be well evidenced through the XRD patterns shown in Fig. 4. At lower temperatures (<950 °C), no $Cu_{6.69}Si$ silicide is detected. As the temperature increases, CuO/CuO_2 will decompose into Cu, then the reaction between SiC and Cu will possibly occur. Cu is detected within samples sintered at 1,050 °C accompanied by the appearance of $Cu_{6.69}Si$. Detailed analysis about the silicide will be carried out in the following section in this paper.

An exothermic peak appears at 1,005 °C in Fig. 3, while no weight change is detected. This is ascribed to the melting of SiO_2–Cu_2O eutectic to form liquid phase [10].

Fig. 2 The morphologies of (**a**): SiC original particles; (**b**): SiC–SiO_2–$Cu(OH)_2$ composite particles



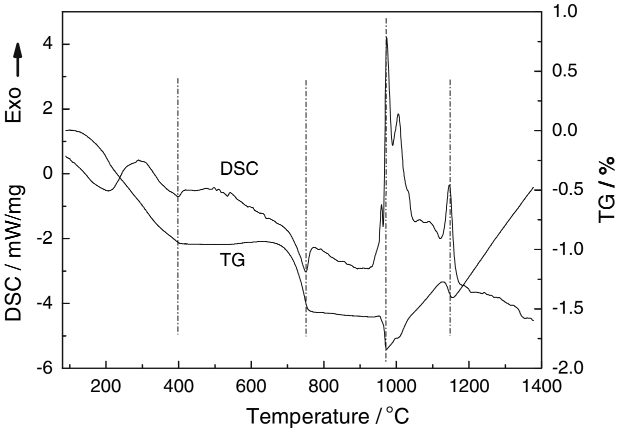


Fig. 3 The DSC-TG curves of the coated $SiC/SiO_2/Cu(OH)_2$ composite particles

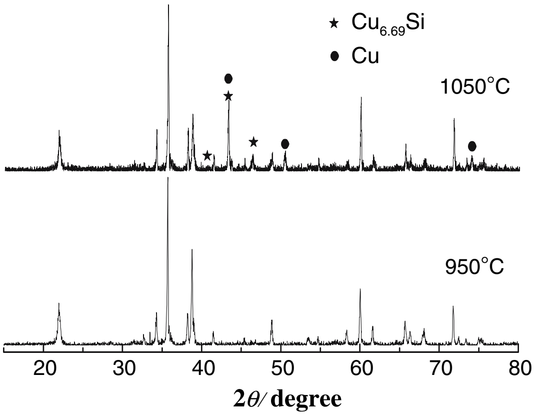


Fig. 4 XRD patterns of the composites sintered conventionally at 950 and 1,050 °C for 2 h in air

At higher temperatures, a sharp exothermic peak appears at 1,150 °C with a corresponding weight loss. It has been reported that SiC will decompose at high temperature [11]. So the weight loss may result from the following reaction:

$$SiC \rightarrow Si + C \tag{1}$$

$$C + CuO/Cu_2O \rightarrow Cu + CO_2 \tag{2}$$

In our previous work, Cu_3Si was detected at 800°C in SiC–Cu composites during the spark plasma sintering process [12]. In the present situation, Cu–silicides are also observed in $SiC–SiO_2–CuO$ composites prepared by hot press sintering. The XRD patterns of the composites sintered at different temperatures are shown in Fig. 5. At low temperature (1,000 °C), Cu is detected. At higher temperature of 1,100 °C, the peaks of Si and $Cu_{6.69}Si$ appear. As the temperature increases to 1,300 °C or above, Cu_3Si is detected. The peak intensity corresponding to Cu_3Si increases with the increasing temperature. Oppositely, the peak intensity of $Cu_{6.69}Si$ and SiO_2 decreases. And the peak of Si tends to disappear.

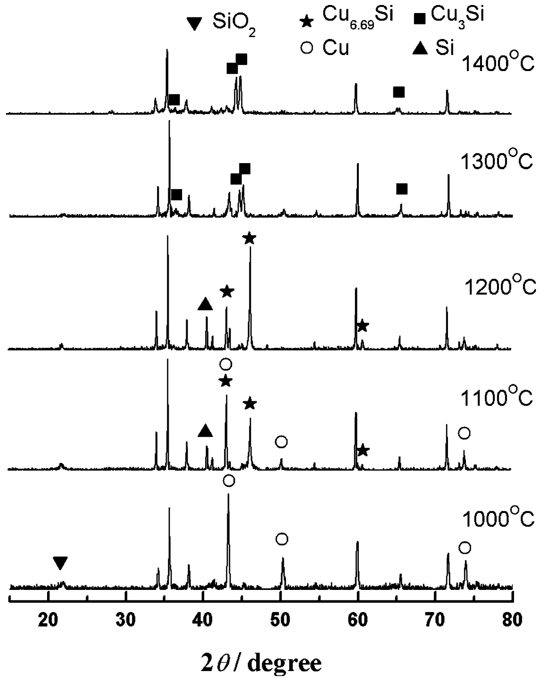


Fig. 5 XRD patterns of the composites sintered at different temperatures by hot pressing

At lower temperatures, CuO and Cu_2O decompose or/and are reduced into Cu [12]. The carbon in the graphite die may enhance the reduction reaction (2). When the sintering temperature increases to 1,100 °C, Cu will react with SiC or Si to form Cu–silicides [13–16]. According to Rado et al. [13], when pure copper is in contact with silicon carbide, dissolution of SiC occurs with Si and C dissolved in Cu. An et al. [14] reported that Cu-silicide could be formed in Cu (180 nm)/3C–SiC specimens at 850 °C by the removal of the surface oxide SiO_2 of SiC particles. In our early work, substantial reaction in $SiC–Cu_2O–Cu$ composite powders was observed at above 950 °C [17]. In the present condition, due to the presence of SiO_2 coating layer, the $SiO_2–Cu_2O$ eutectic will melt to form a thin film, which limits the reaction between Cu and SiC. That is why no Cu–silicide is detected at temperatures lower than 1,100 °C. As the temperature increases, the flowing of the liquid is enhanced. Capillarity phenomena might appear which leads to the contact between Cu and SiC. As a result, the reaction occurs at 1,100 °C. At 1,300 °C or above, Si–O bonds are thermally broken [18]. More Si is formed to further the following reaction:

$$SiO_2 \rightarrow Si + O_2 \tag{3}$$

$$Cu_{6.69}Si + Si \rightarrow Cu_3Si \tag{4}$$

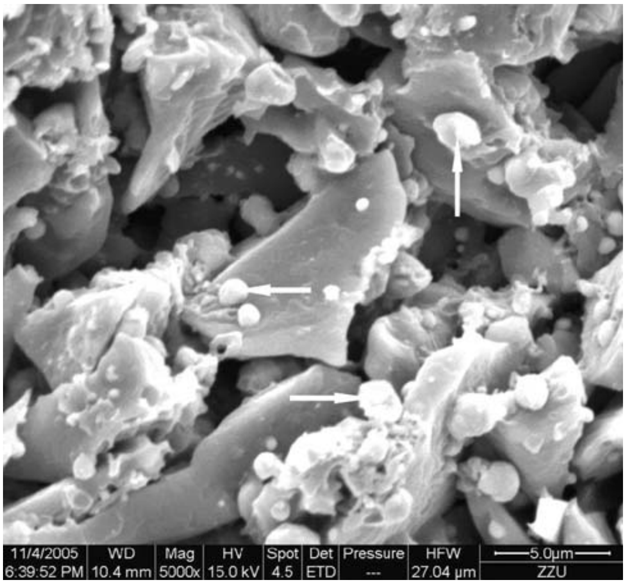


Fig. 6 SEM image of the composites sintered at 1,100 °C for 30 min by hot pressing

Normally, the interfacial wetting between Cu and SiC is very poor. According to Pelleg et al. [19], the contact angle of SiC by liquid Cu at 1,100 °C is 140°. And in the Cu/SiC composite system, no wetting at the interface occurs up to very high temperature, regardless of whether the production method is HIP or conventional powder metallurgy and sintering. The high surface tension will lead the copper atoms to coalesce in order to minimize the surface energy of the system as soon as atoms acquire sufficient mobility. Figure 6 shows the SEM image of the composites sintered by hot pressing at 1,100 °C. The spherical material is Cu, which indicates the aggregation of Cu. Rado has observed that SiC is well wetted by Cu–Si alloys [13]. So the formation of the Cu–silicides will decrease the amount of Cu atoms and lead to chemically-reacted interface to show uniform features [12].

Conclusions

SiC–SiO_2–CuO composite particles can be prepared by double coating processes. A good core-shell structure is constructed. SiC will decompose into Si and C at high temperature. Cu–silicides are detected in the hot-pressed compacts. $Cu_{6.69}Si$ will change into Cu_3Si at higher temperatures due to the decomposition of SiO_2.

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