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The effect of nanoscale SiC particles on the microstructure of Al_2O_3 ceramics

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Abstract

The hot-pressing temperature, matrix grain size, fracture mode and the distribution of SiC were studied to reveal the effect of SiC inclusions on the microstructure of Al_2O_3. Al_2O_3–SiC composite powder was prepared by the precipitation method. Nanoscale SiC particles were coated with Al_2O_3. After hot pressing, most of nanoscale SiC particles were randomly located within the Al_2O_3 grains. SiC inclusions raised the hot-pressing temperature, decreased Al_2O_3 grain size, and inhibited the abnormal grain growth of Al_2O_3. The intergranular fracture for Al_2O_3 was transformed to the intragranular fracture for Al_2O_3–SiC nanocomposites because of the addition of SiC. All those microstructure changes increased the mechanical properties of Al_2O_3-composites by 40%. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. Microstructure; B. Nanocomposites; D. Silicon carbide; D. Alumina (Al_2O_3); Precipitation (SiC)

1. Introduction

Al_2O_3 ceramics are widely used in many fields. However, the abnormal grain growth of Al_2O_3 that often occurs, result in the mechanical properties degradation, and make the application limited. There are several approaches to avoid the abnormal growth of the Al_2O_3 grains. One is through the purification of the starting powder, many researchers found if the starting powder was very pure (>99.99%), the abnormal grain growth of the Al_2O_3 ceramics did not happen when sintered at 1650°C for 1.5 h [1–3]. other way is through the addition of MgO [4–6], small amounts of MgO can effectively inhabited the abnormal growth of the Al_2O_3 grains. Another way is through the addition of the second phase particles [7,8]. Recently, Niihara et al. have found that the incorporation of small amounts of submicrometer (0.3 μm) SiC particles into Al_2O_3 could effectively enhance the strength [9,10], and inhibited the Al_2O_3 matrix grains growth. They called these materials "nanocomposites". In their experiments, SiC particles were mainly located within Al_2O_3 matrix grains. That was different from the conventional composites that second phase particles were mainly located on the boundaries. Many researchers have studied the "nanocomposites" in which ceramic matrices were reinforced with submicrometer ceramic particles [11–15], and also found that the second phase particles could decrease the Al_2O_3 grain size. However, there are few papers reported that nanoscale particles (<100 nm) inhibit the grain growth. Because of the small size and the large special surface, it is interesting to study the effect of nanoscale particles on the sintering procedure and the microstructure of the matrix. In our experiment, nanoscale SiC particles were uniformly dispersed in the starting powder by the precipitation method. Al_2O_3 will experience the transformation from the γ phase to the α phase at about 1200°C. The process of the grain growth would be different from that of the mixing method [16,17].

2. Experimental procedure

The precipitation method was used to prepare the starting powder. The processing steps for this method were outlined in Fig. 1. Nanoscale SiC particles (70 nm,

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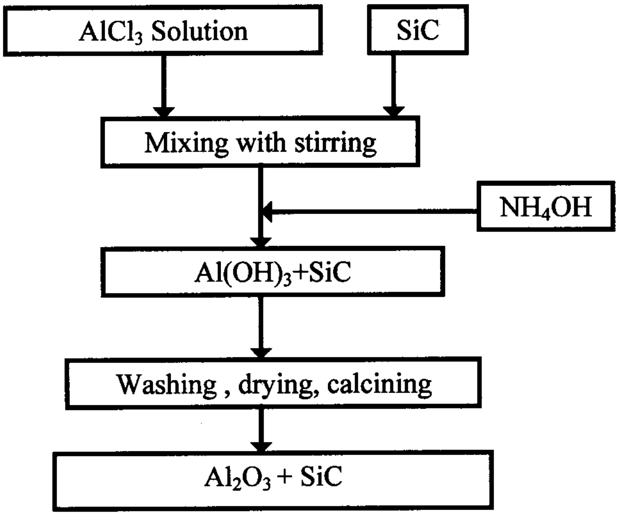


Fig. 1. Flow chart for the fabrication of Al_2O_3–SiC powder by the precipitation method.

Beijing Institute of Chemical Metallurge, CAS) were randomly dispersed into the $AlCl_3{\cdot}6H_2O$ solution. Adding ammonia and keeping pH between 9 and 10, the $Al(OH)_3$ precipitation including nano SiC particles were produced. After drying, calcining and wet-balling, the Al_2O_3–SiC powder could be achieved. The nearly full density samples could be got by hot-pressing (the pressure was 35 MPa) at temperatures between 1650 and 1750°C. Two kinds of SiC volume fraction (5 and 10 vol%) samples were prepared, and named after A5 and A10. In order to compare, superfine α-Al_2O_3 powder with a mean particle size of 0.15 μm was used to fabricate Al_2O_3 ceramics and named after A0.

Sintered sample densities were measured using the Archimedes method. For the grain growth observation, samples were polished using diamond paste to a 1 μm finish. The Al_2O_3 and composite samples were respectively thermally etched in air and nitrogen at temperatures between 1400 and 1600°C. The etched surface and the fracture across section were examined using a scanning electron microscope (SEM), and the distribution of nanoscale SiC in the Al_2O_3 matrix was examined using a transmission electron microscope (TEM). Grain size was measured using the linear intercept method. Four micrographs (more than 200 grains) were taken in randomly selected area of each specimen. The average grain size, G, was then calculated using the relation

$$G = \frac{1.5L}{MN}$$

where 1.5 is a geometry-dependent proportionality constant, L the total test line length, M the magnification, and N the total number of intercepts.

For mechanical testing, the hot-pressed samples were cut and ground into rectangular bar specimens (4×3×30 mm). Fracture toughness was evaluated from the indentation fracture method [9]. Fracture strength was measured by the three-point-bending test at room temperature, and the crosshead speed of the bending machine was 0.5 mm min^{-1}.

3. Results and discussion

3.1. The dispersion of nanoscale SiC particles

It is very important to disperse nanoscale SiC particles homogeneously in Al_2O_3 because SiC particles are fine and easy to aggregate. There are three ways to avoid their agglomerates: (1) ultrasonic vibrating to open agglomerates, (2) regulating pH to make the zeta potential high, (3) adding dispersants. Since some carbon remains may be left after adding dispersants, only the first two ways were adopted to produce the good dispersion.

The relation between the zeta potential of SiC water solution and pH is shown in Fig. 2. The isoelectric point is located between pH 3 and 5. When the pH of SiC water suspension is far from this range, the charge of the particles is the same, and the SiC particles will repel each other for a static electric force. It is difficult for SiC particles to form agglomerates. For this reason, the pH for precipitation was controlled between 9 and 10. After ultrasonic vibration for 1 h and regulating the pH of the SiC water suspension to 9–10, SiC particles as shown in Fig. 3 can be obtained. The size range is between 60 and 100 nm.

After dripping the aqueous solution of $AlCl_3.6H_2O$ and ammonia into the SiC water suspension while keeping the pH between 9 and 10, the hydroxides of alumina [$Al(OH)_3$] were prepared with well-distributed SiC particles. Then calcining at 700°C for 1 h in air, the precipitate changed to the Al_2O_3–SiC powder as shown in Fig. 4. No single Al_2O_3 particles can be seen, and the SiC particles are dispersed in the channels or skeletons

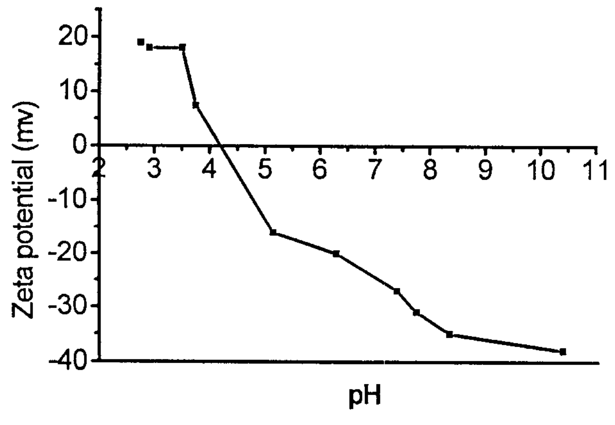


Fig. 2. The relation between the zeta potential of SiC and pH.

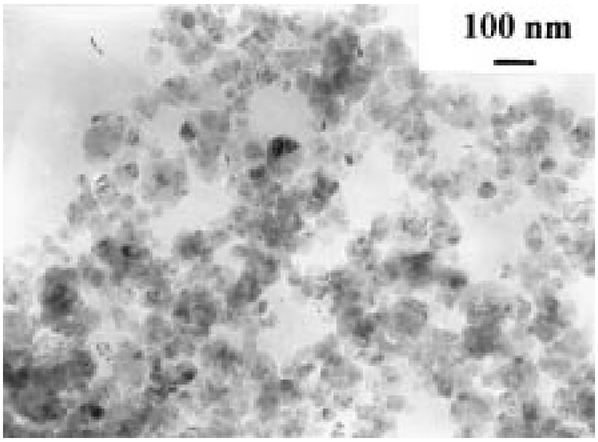


Fig. 3. TEM micrograph of nano SiC powder.

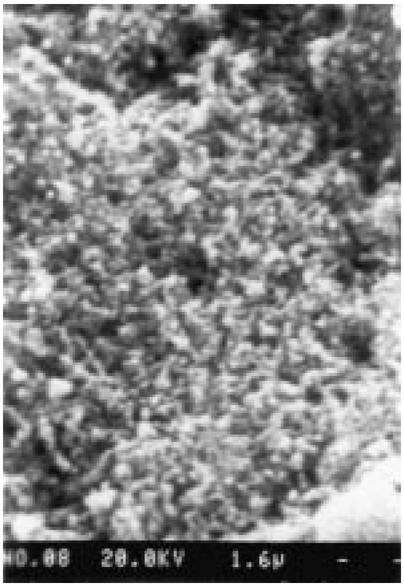


Fig. 4. SEM micrograph of Al_2O_3–SiC powder.

of porous γ-Al_2O_3. The surface area of the Al_2O_3–5 vol% SiC powder is 150 m^2/g.

3.2. The densification of nanocomposites

Fig. 5 shows the Al_2O_3 could get to nearly full densification at 1500°C. After adding 5 vol% nanoscale SiC particles, it become difficult to densify the composites, and the sintered temperature had to be increased to 1700°C to get full densification. After the SiC content increased to 10 vol%, the composites could get to full densification only above 1750°C. Because SiC particles were immobile and did not react with Al_2O_3 during the sintering temperature, they made the movement of the grain boundary difficult and inhabited the densification of Al_2O_3. Therefore, the sintering temperature had to be raised after adding nanoscale SiC powder.

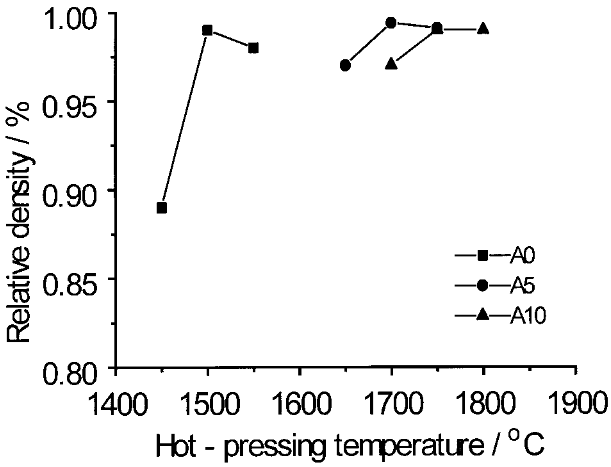


Fig. 5. The relative densities of the samples sintered at different temperatures.

3.3. The size of the matrix grains

Based on the Zener-type models, the secondary phase inhabited the growth of matrix grain. The limiting matrix grain size G can be got from Eq. (1):

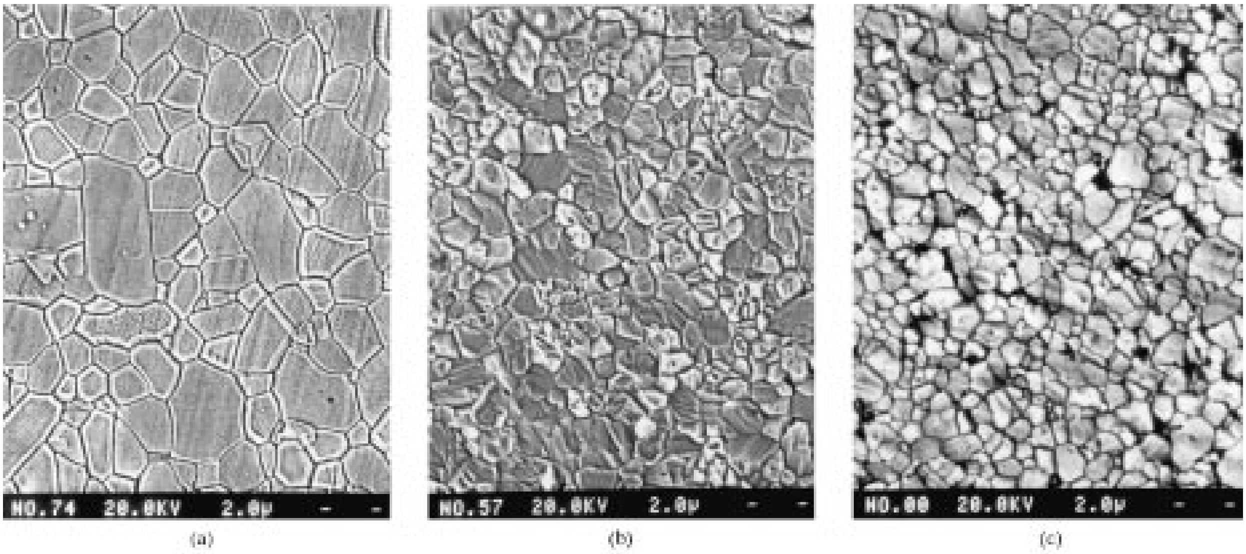
$$G = \frac{4r}{3f} \tag{1}$$

where r is the radius of the secondary particles, f is the volume fraction of the secondary phase. The equation shows that the size of the matrix grain decrease with the increase of the secondary phase.

Fig. 6 shows that the monolithic Al_2O_3 grains were large, and not uniform. Some Al_2O_3 grains grew abnormally. However, after adding SiC particles, the grain size of the composites was small, and decreased with an increase of the SiC volume fraction. Moreover, the grains of the composites were uniform.

The average grain size of A0, A5, A10 were calculated by the linear intercept method. The results were showed in Table 1. The Al_2O_3 matrix grain became smaller with the increase of the SiC content.

But the trend of the decrease was lower than expected. Based on Eq. (1), the ratio of the average grain size of A5 and A10, $G_{A5}/G_{A10}=2$. But the experiments showed $G_{A5}/G_{A10}=1.17$. The grain grow process of the samples prepared by the precipitation method was different from that of the samples prepared by the directly mixing of Al_2O_3 and SiC. In the former samples, Al_2O_3 transformed from the γ phase to the α phase at 1200°C [18], and most of the SiC particles were located in the Al_2O_3 grains. So the double of the SiC content did not mean the double of the SiC amount located on the boundary and pinning the boundary at the same time. The decrease trend of the grain size is lower than what were expected by the Zener model. Moreover, the rise of the sintering temperature with the addition of SiC reduced



(a) (b) (c)

Fig. 6. The grain size of the monolithic Al_2O_3 and the composites: (a) A0 without SiC (b) A5 with 5 vol% SiC: (c) A10 with 10 vol% SiC.

the grain decrease trend. The transforming procedure of A5 and A10 from the γ phase to the α phase was a nucleation-growth processing. The SiC particles gave the more centers of nucleation. So it decreased the grain size, made the grains uniform, and reduced the possibility of the abnormal growth of grains.

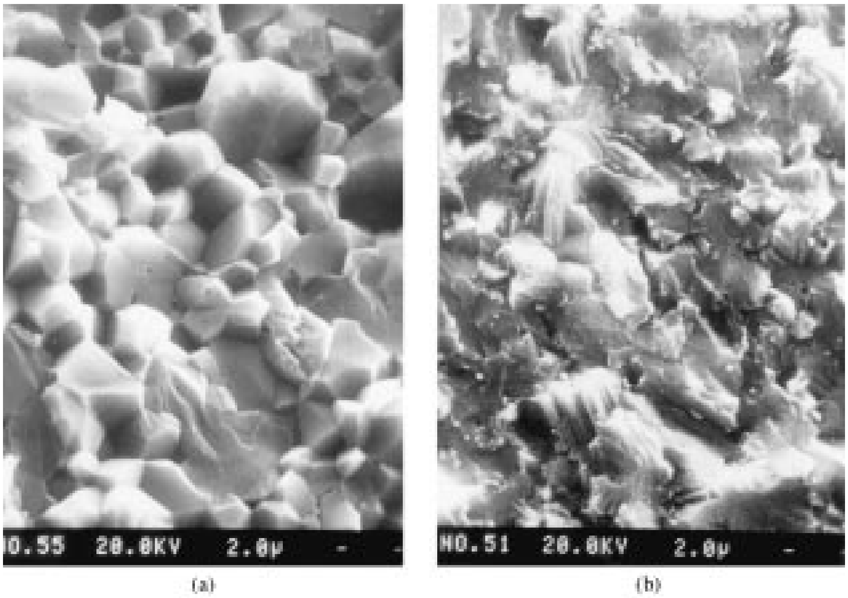
Table 1
The average grain sizes of samples calculated by the linear intercept method

Samples	SiC content (vol%)	HP temperature (°C)	Time (h)	The average grain sizes of Al_2O_3 (µm)
A0	0	1500	0.5	2.64
A5	5	1700	1	1.69
A10	10	1750	1	1.45

3.4. The fracture mode and the microstructure

Fig. 7 shows the SEM micrographics of the fracture across section of A0 (Fig. 7a) and A5 (Fig. 7b). The fracture mode of A0 was mainly intergranular fracture, and A5 was intragranular fracture. The addition of SiC particles made the fracture mode changed from intergranular to intragranular fracture.

Fig. 8 shows the TEM micrographics of the A5 samples. It can be seen that the size of the Al_2O_3 matrix grains was about 1–2 µm, and the boundaries were



(a) (b)

Fig. 7. SEM micrographs of the fracture surfaces of A0 and A5 samples: (a) A0; (b) A5.

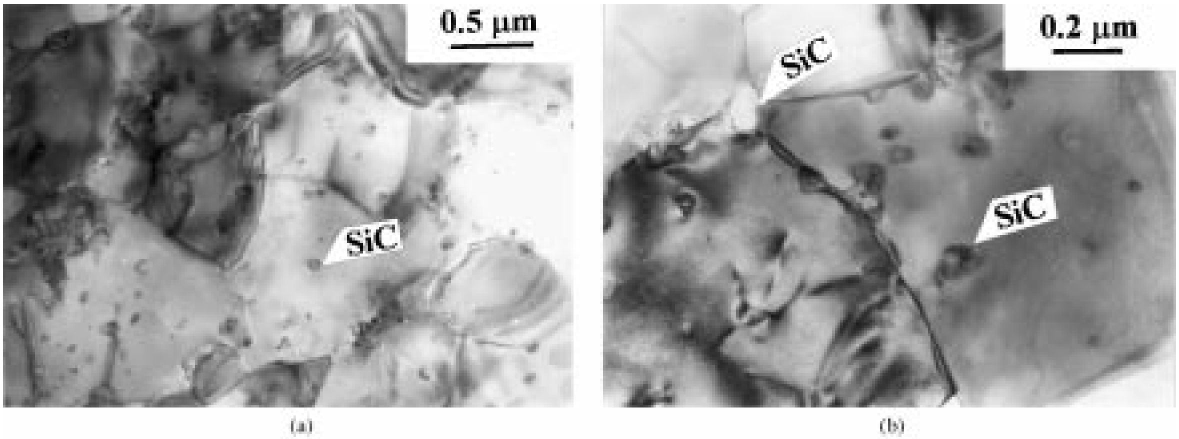


Fig. 8. TEM micrographs of A5 sample: (a) shows SiC particles were mainly located in the Al_2O_3 grains; and (b) shows few large particles were located on the boundaries or junctions.

tortuous. Nanoscale SiC particles were distributed throughout the Al_2O_3 matrices. It should be noted that most of SiC particles were present inside the Al_2O_3 grains, only few large particles were located on the boundaries or junctions of grains. According to Niihara's classification [10], it is called 'intragranular-type nanocomposites' if nanoscale particles are predominantly dispersed in matrix grains. It proved that the near intragranular nanocomposites could be obtained by the precipitation method. This type microstructure was believed to be advantageous to strengthening grain boundaries, and resisting the crack propagation [9,10]. Meanwhile, the SiC particles located on the boundaries inhabited the movement of boundaries, and decreased the grain size. Such a microstructure was effective to improved the mechanical properties. The strength of A5 was 467 MPa and toughness was 4.7 $MPam^{1/2}$. Compared with A0 (strength: 350 MPa, toughness: 3.25 MPa $m^{1/2}$), both strength and toughness were improved by 40%. That should result from intragranular microstructure and finer matrix grains. The strength of A10 was 415 MPa and toughness was 3.8 MPa; $m^{1/2}$, they were higher than those of A0 and lower than those of A5. The reason may be that the SiC content of A10 was beyond the optimum content (some researchers believed it was between 3.5 and 5 wt%) [19].

4. Conclusions

After ultrasonic vibrating and regulating the pH of the SiC water suspension, nanoscale SiC were randomly dispersed in the $AlCl_3$ solution. Nearly full densification of Al_2O_3–SiC nanocomposites could be achieved although the starting Al_2O_3–SiC powder produced by the precipitation method was porous. Most SiC particles were located within the Al_2O_3 grains because of the transformation of Al_2O_3 from the γ phase to the α phase. Nanoscale SiC particles inhibited the grain growth of Al_2O_3, made the matrix grains smaller, and raise the sintered temperature. The fracture mode of Al_2O_3–SiC nanocomposites were mainly intragranular fracture compared to the intergranular fracture of the monolithic Al_2O_3 ceramic. The strength and toughness of the Al_2O_3–SiC nanocomposites increased by 40% than the Al_2O_3 ceramics because of the addition of nanoscale SiC particles.

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