Crucial effect of SiC particles on in situ synthesized mullite whisker reinforced Al$_2$O$_3$-SiC composite during microwave sintering

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Abstract

Mullite whisker reinforced Al$_2$O$_3$-SiC composites were in situ synthesized by microwave sintering at 1500 °C for 30 min. The influence of SiC particle size on heating process and properties of Al$_2$O$_3$-SiC composite were investigated. The XRD and SEM techniques were carried out to characterize the samples. The thermal shock resistance and flexural strength of the samples were examined through water quenching and three-point bending methods, respectively. It was found that the bridging of mullite whisker appeared between Al$_2$O$_3$ and SiC particles which enhanced the thermal shock resistance. A so-called local hot spot effect was proposed dependent on the coupling of SiC particles with microwave, which was the unique feature of microwave sintering. The maximal thermal shock resistance and flexural strength were obtained for the samples with SiC particle size of ~5 µm.

Keywords: Al$_2$O$_3$-SiC composite, microwave sintering, mullite whisker, local hot spot effect

I. Introduction

Al$_2$O$_3$-SiC composite is a well-known material for high temperature structural applications due to its superior properties, such as high mechanical strength, excellent refractoriness, good chemical stability, high heat and creep resistance at high temperatures, and so on [1,2]. However, the oxidation of SiC at high temperature limits the application of Al$_2$O$_3$-SiC composite. Further, we found that coating of SiO$_2$ on SiC particles can effectively solve this problem, and facilitate the formation of mullite whisker between SiO$_2$ and Al$_2$O$_3$ at high temperature. Because of the bridging by mullite whisker, the interface bonding between SiC and Al$_2$O$_3$ can also be improved, resulting in the enhancement of thermal shock resistance. Due to its excellent thermal shock resistance and well resistance toward chemical attack, mullite whisker reinforced Al$_2$O$_3$-SiC composite is a promising material in the fields of refractories and ceramics [3–9]. Compared with other toughening methods such as phase transformation toughening, particle dispersion toughening and fibre toughening, the in situ synthesized whisker is cost-efficient, has higher toughness, better dispersion and without external whisker addition [10]. During fracture propagation process, the whisker would be pulled out and the cracks would be bridged or deflected, resulting in the absorption of energy, and the toughness of refractories or ceramics is thus improved [11].

The mullite whisker reinforced Al$_2$O$_3$-SiC composite can be prepared by pressureless sintering, hot pressing, microwave sintering etc. [5,8]. The sintering temperature of pressureless sintering or hot pressing is very high and the reaction between SiO$_2$ and Al$_2$O$_3$ is difficult to control. Microwave sintering, as a new heating method, has presently been investigated to prepare oxides and
other composites [12–15]. Furthermore, the microwave sintering has two significant advantages. One is volumetric energy absorption which will heat up the entire sample uniformly at the same time and overcome the temperature gradient of a conventional heat radiation method; the other is some unique properties of materials induced by microwave sintering due to the electromagnetic field [12,16]. There are also some remarkable characteristics of microwave sintering, such as the selective heating and local hot spot effect, which help reduce the sintering temperature and time, as well as improve the microstructure and mechanical properties of samples [17–19]. Due to significant influence of the microstructure on mechanical properties of any composite, it is very important to understand the aforesaid characteristics. Many researchers have studied the Al$_2$O$_3$-SiC composite with respect to different methods of synthesis and various mechanical properties [1,2,7,20–23]. However, the influence of SiC particle size on the heating process, microstructure and properties of Mullite whisker reinforced Al$_2$O$_3$-SiC composite has been seldom reported.

Therefore, in situ synthesized Mullite whisker reinforced Al$_2$O$_3$-SiC composite was prepared by microwave sintering in this research. The effect of SiC particle size on the heating behaviour, microstructure and properties was investigated. Additionally, the local hot spot effect mechanism was also discussed.

II. Experimental

In this study, α-Al$_2$O$_3$ and α-SiC particles were used as raw materials. The α-Al$_2$O$_3$ particles were prepared by conventional pyrolysis of aluminium hydroxide precursor at 1300 °C for 30 min with a mean particle size less than 0.5 μm. The α-SiC particles with different sizes were commercially available. The selected SiC particle sizes were 500 nm, 5 μm, 50 μm, 150 μm, respectively. A sol-gel method was carried out to coat SiO$_2$ on SiC particles through the hydrolysis of tetraethyl orthosilicate. The volume ratio of SiO$_2$ and SiC was 1 : 5. Then the coated composite particles were mixed with α-Al$_2$O$_3$ particles. The ratio between α-Al$_2$O$_3$ and α-SiC particles was kept at 1 : 1 by volumetric fraction.

The mixed powders were uniaxially pressed into a cylindrical pellets (Ø 30 mm × 4 mm) at 10 MPa for 1 min. After being isostatically pressed at 100 MPa for 1 min, the green cylindrical pellets were sintered in a microwave chamber (TE666, WXD205-07, China Nanjing Sanle Microwave equipment). The frequency of microwave was 2.45 GHz with a maximum input power of 10 kW. The temperature was monitored by an infrared radiation thermometer (OI-T612B-1-type, GOID SUN, USA). A thermal insulation structure based on a hybrid heating mode was well designed with the wall materials of porous Mullite, Mullite fibres and aided heaters of SiC rods. The heating rate was controlled by tailoring the input power and the changes in reflected power were detected. According to the previous exploration, the optimum sintering temperature and holding time were 1500 °C and 30 min, respectively. The samples prepared with SiC powders having particle size of 500 nm, 5 μm, 50 μm and 150 μm, were denoted Al$_2$O$_3$-SiC-0.5, Al$_2$O$_3$-SiC-5, Al$_2$O$_3$-SiC-50 and Al$_2$O$_3$-SiC-150, respectively.

Phases of the samples were detected by X-ray diffraction (XD-3, Beijing Purkinje General Instrument Co. Ltd.). Morphology was observed by scanning electron microscopy (JEOL JSM-7001F, Japan). Density of the samples was measured by the Archimedes method. Thermal shock resistance of the samples was studied in terms of flexural strength retention on multiple water quenching cycles [24,25]. The selected thermal shock cycles were 0, 5, 10 and 15 times and the size of the sample 3 mm × 4 mm × 30 mm were used. For thermal shock resistance, the samples were heated to 1100 °C in a furnace (KSS, Luoyang Luwei Furnace Co. Ltd.), and then the samples were water quenched for 5 min followed by reheating at 1100 °C for 15 min. This cycle of 15 min heating and 5 min cooling was repeated and flexural strength was evaluated by three-point bending method (with a span of 16 mm and cross-head speed of 0.5 mm/min) using Universal Testing Machines (WD-P4504, Jinan Test Machine Co. Ltd.).

III. Results and discussion

Figure 1 shows the microwave heating profiles and corresponding changes in input power for Al$_2$O$_3$-SiC samples containing different SiC particle sizes. The input power of different samples is the same, and the initial display temperature of monochromatic optical fibre infrared thermometer is 600 °C.

As shown in Fig. 1a, it needs about 27 min and 139 min for the sample Al$_2$O$_3$-SiC-0.5 to heat to 600 °C and 1500 °C, respectively, and the heating rate is relatively slow. In Figs. 1b and 1c, heating to the same temperature takes about 21 min and 110 min for the sample Al$_2$O$_3$-SiC-5, while for the sample Al$_2$O$_3$-SiC-50, it takes about 24 min and 104 min, respectively. The sample Al$_2$O$_3$-SiC-150 should be heated 26 min to 600 °C and 103 min to 1500 °C (Fig. 1d). It can be seen from the heating profiles that the heating time initially decreases firstly and then increases with the increase of SiC particle size. By comparing the heating time of these samples at initial stage, it is evident that there is a minimum value for the sample Al$_2$O$_3$-SiC-5.

In the temperature range of 600–1500 °C, the heating profiles exhibit remarkable zigzag characteristics and the heating rates are unstable, except for the sample Al$_2$O$_3$-SiC-5. Heating duration from 600 °C to 1500 °C takes 112 min for the sample Al$_2$O$_3$-SiC-0.5, while for the samples Al$_2$O$_3$-SiC-50 and Al$_2$O$_3$-SiC-150 it needs 80 min and 77 min, respectively. The heating profile of the sample Al$_2$O$_3$-SiC-5 is relatively smooth and the heating time from 600 °C to 1500 °C is 89 min at the
heating rate of 10 °C/min. In contrast to other three samples, the heating rate of the sample Al$_2$O$_3$-SiC-0.5 is too slow, which leads to the high energy consumption during microwave sintering. Yet, the heating rates of Al$_2$O$_3$-SiC-50 and Al$_2$O$_3$-SiC-150 samples are too fast and the mullite grain has not enough time to grow, resulting in the insufficient growth of mullite whisker. Only the heating rate of the sample Al$_2$O$_3$-SiC-5 is stable, which facilitates the reaction between Al$_2$O$_3$ and SiO$_2$ and the growth of mullite whisker.

Figure 2 shows the XRD patterns of Al$_2$O$_3$-SiC samples containing different SiC particle sizes. It can be clearly seen from Fig. 2 that the phases of microwave sintered samples are all composed of Al$_2$O$_3$, SiO$_2$, SiC and mullite. For the sample Al$_2$O$_3$-SiC-0.5, the phases are mainly Al$_2$O$_3$, SiO$_2$ and SiC and the intensity of mullite diffraction peak is relatively weak. While for the sample Al$_2$O$_3$-SiC-5 the phases of SiC and mullite are predominant and the intensity of Al$_2$O$_3$ and SiO$_2$ diffraction peaks are relatively weak. This phenomenon can be attributed to the increase of heat generated by the dielectric loss of SiC particles in microwave field with the increase of SiC particle size. Thus, the reaction between Al$_2$O$_3$ and SiO$_2$ to form mullite is enhanced. As the SiC particle size increases, more mullite is formed around SiC particles. The peak height referring to mullite increases firstly and then decreases versus the SiC particle size. For the sample Al$_2$O$_3$-SiC-50 the diffraction peak intensity of mullite phase is slightly weaker than that of SiC phase. While for the sample Al$_2$O$_3$-SiC-150 the diffraction peak intensity of mullite phase is obviously weaker than that of SiC phase because of the consumption of SiO$_2$ coated on SiC particles. Due to the very short heating time in the mullite formation temperature range (600–1500 °C) for the samples containing larger SiC particle size, the growth of mullite whisker is insufficient. So the maximum amount of mullite whisker appears in the sample Al$_2$O$_3$-SiC-5.

Figure 3 shows the SEM images of fracture surface
of the Al$_2$O$_3$-SiC samples containing different SiC particle sizes. Obviously, many of pores can be found in the sample Al$_2$O$_3$-SiC-0.5 after microwave sintering, as shown in Fig. 3a. The SiO$_2$ coated on SiC particles fuses, but the good interface bonding between SiO$_2$ and Al$_2$O$_3$ particles is not accomplished. This may be ascribed to the too small size of SiC particles and the insufficient heat concentration at the particle surface, so the temperature rise of samples mainly depends on the aided heaters of SiC rods and the self-heating of samples is difficult to be realized. Therefore, the growth of mullite whisker is slow with the weak interface bonding between Al$_2$O$_3$ and SiC particles. With the increase of SiC particle size, there are fewer pores in the sample Al$_2$O$_3$-SiC-5, as shown in Fig. 3b. Furthermore, the needle-like mullite whisker can be found in samples. With further increase of SiC particle size, the mullite whisker can also be found in the sample Al$_2$O$_3$-SiC-50, but the length-to-diameter ratio of mullite whisker is relatively small [26] and there are lots of pores in samples (Fig. 3c). This can be ascribed to the fast heat concentration and low heat diffusion at the particle surface during microwave sintering with larger SiC particle size in samples. With even further increase of SiC particle size, instead of needle-like mullite whisker the short rod-like mullite whisker and lots of pores appear in the sample Al$_2$O$_3$-SiC-150, as shown in Fig. 3d. It is because of the too large size of SiC particles and too fast temperature rise in samples, hence there is not enough time for the mullite grain to grow in one direction. With the coexistence of solid and gas phases, the anisotropic growth of mullite grain is limited to a certain degree [26], thus the growth of mullite grain in every direction is fast, resulting in the short rod-like mullite. Compared with the short rod-like mullite, the needle-like mullite whisker is more effective in bridging the microcracks.

From Fig. 4, it can be clearly seen that the density of the Al$_2$O$_3$-SiC samples increases firstly and then decreases with the increase of SiC particle size (in Fig. 4, $D$ is the diameter of SiC particles). Moreover, the density of the samples Al$_2$O$_3$-SiC-0.5 and Al$_2$O$_3$-SiC-5 have the minimum and maximum value, respectively. This can be attributed to the improvement of heat concentration at the SiC particle surface with the increase of the SiC particle size. SiO$_2$ in samples fuses to form flowing glass phase, then the pores are filled and the porosity of samples decreases, resulting in the increase of density. With continuous increasing of the SiC particle size from $\sim$5 $\mu$m to $\sim$150 $\mu$m, the density of samples decreases after microwave sintering, as shown in Fig. 4.

**Figure 3.** SEM images of fracture surface of Al$_2$O$_3$-SiC samples containing different SiC particle sizes: a) 500 nm, b) 5 $\mu$m, c) 50 $\mu$m and d) 150 $\mu$m

**Figure 4.** Density of Al$_2$O$_3$-SiC samples containing different SiC particle sizes
According to the analysis of SEM images in Fig. 3, the too large size of SiC particles in samples and the insufficient heat diffusion at the SiC particle surface during microwave sintering lead to the formation of pores in samples. As a consequence the high porosity and loose structure result in the low density of samples. With the increase of SiC particle size from \( \sim 500 \text{ nm} \) to \( \sim 150 \text{ \( \mu \text{m} \)} \), the maximum density of the samples is 2.13 g/cm\(^3\).

Flexural strength of the Al\(_2\)O\(_3\)-SiC samples containing different SiC particle sizes after 0, 5, 10 and 15 thermal shock cycles were plotted in Fig. 5. It can be seen that the flexural strength of all Al\(_2\)O\(_3\)-SiC samples increases firstly and then decreases with the increase of SiC particle size after the same thermal cycles, and the flexural strength of the sample Al\(_2\)O\(_3\)-SiC-5 reaches its maximum value. Because of the increasing size of SiC particles, the amount of mullite whisker increases as well as the enhancement of thermal shock resistance of samples. The flexural strength of samples decreases with further increasing of the SiC particle size from \( \sim 5 \text{ \( \mu \text{m} \)} \) to \( \sim 150 \text{ \( \mu \text{m} \)} \). This can be ascribed to the too large size of SiC particles, fast temperature rise of samples and insufficient reaction between Al\(_2\)O\(_3\) and SiO\(_2\). So the thermal shock resistance of samples decreases without the sufficient reinforcement of mullite whisker.

From Fig. 5 the highest flexural strength value of the Al\(_2\)O\(_3\)-SiC samples is 110 MPa. Compared with the flexural strength of other corundum-mullite refractory materials, 60 MPa [8] and 48 MPa [27], this Al\(_2\)O\(_3\)-SiC composite is a good candidate for the applications of refractories. The flexural strength of the sample Al\(_2\)O\(_3\)-SiC-150 retains only 20% of its initial flexural strength after 5 cycles. The flexural strength of the samples Al\(_2\)O\(_3\)-SiC-0.5, Al\(_2\)O\(_3\)-SiC-5 and Al\(_2\)O\(_3\)-SiC-50 all retain approximately 40% of their initial flexural strength after 5 cycles. After 15 cycles, the flexural strength retention of the samples Al\(_2\)O\(_3\)-SiC-0.5 and Al\(_2\)O\(_3\)-SiC-50 are only 20% and 25%, respectively. While after the same number of thermal cycles, the flexural strength of the sample Al\(_2\)O\(_3\)-SiC-5 can still retain 30% of its initial flexural strength. As a result, it is obvious that the sample Al\(_2\)O\(_3\)-SiC-5 preserves the excellent thermal shock resistance. From the above analysis, we can find that the thermal shock resistance of mullite whisker reinforced Al\(_2\)O\(_3\)-SiC composite is much better than the Al\(_2\)O\(_3\)-SiC composite without mullite whisker.

Figure 6 presents the schematic of mullite growth during microwave sintering. With the temperature rise of the Al\(_2\)O\(_3\)-SiC samples, the aided heaters of SiC rods in thermal insulation structure absorbed microwave to produce heat because of the high dielectric loss of SiC and the heat transmission is outside-in. Meanwhile, the SiC particles in the samples preferentially absorbed the microwave energy and elevated the local temperature instantaneously, which led to the local hot spot effect during microwave sintering. The local heat spreads from the inside to the outside and SiO\(_2\) coated on SiC particles is heated to form the fused glass phase, resulting in the formation of mullite whisker between Al\(_2\)O\(_3\) and SiO\(_2\). Therefore, there are two kinds of heat in microwave hybrid heating mode. With continuous increasing of the input power, the local hot spot effect is constantly enhanced, which promotes the anisotropic growth of mullite whisker. As a result, along one-dimensional direction the mullite grain grows faster to give large length-to-diameter ratio whisker between Al\(_2\)O\(_3\) and SiO\(_2\) [28].

Through the analysis of microwave heating behaviour
the Al₂O₃-SiC samples, with the increase of the SiC particle size from ~500 nm to ~150 µm the time for samples to reach 600 °C firstly decreases and then increases. The slow-fast-slow phenomenon can be found for samples heated up to 600 °C. The explanation for this phenomenon is that at the initial stage of microwave heating the temperature rise of samples mainly depends on the local hot spot effect induced by the coupling of SiC particles with microwave. With too small (~500 nm) SiC particle size in the Al₂O₃-SiC samples, the dielectric loss of SiC particles absorbing microwave is lower than the heat diffusion of SiC particle surface. Accordingly, the desirable heat concentration is difficult to reach, resulting in the slow heating rate and limited amount of mullite. With too large (~150 µm) SiC particle size in samples, the dielectric loss of SiC particles absorbing microwave is higher than the heat diffusion of SiC particle surface, but the heat on the SiC particle surface is too high. Although the reaction between Al₂O₃ and SiO₂ to form mullite can be promoted by a higher heat concentration, the anisotropic growth of mullite whisker is limited, resulting in the small length-to-diameter ratio of mullite whisker [14]. So there is a critical particle size (~5 µm) which keeps the balance of heat concentration and heat diffusion. When the SiC particle size dispersed in samples is in the range of critical particle size, the dielectric loss of SiC particles absorbing microwave is equal to the heat diffusion of SiC particle surface, which facilitates not only the fast temperature rise of samples at low temperature but also the formation of bridging mullite whisker with large length-to-diameter ratio between SiC and Al₂O₃ particles (Fig. 7).

IV. Conclusions

In situ synthesized mullite whisker reinforced Al₂O₃-SiC composite containing different SiC particle sizes was prepared by hybrid microwave sintering at 1500 °C for 30 min. The optimum SiC particle size for mullite whisker reinforced Al₂O₃-SiC composite is ~5 µm, which corresponds to the maximum amount of mullite whiskers in Al₂O₃-SiC composite and optimum properties among the four groups of samples. The critical SiC particle size is ~5 µm, in which the dielectric loss of SiC particles absorbing microwave is equal to the heat diffusion of the SiC particle surface, so the anisotropic growth of mullite whisker with large length-to-diameter ratio is promoted. Just as important, the local hot spot effect of SiC particles is the unique heating feature of microwave sintering which promotes the one-dimensional growth of bridging mullite whisker between SiC and Al₂O₃ particles.

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