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Fabrication of finegrained Al_2O_3 ceramic at low sintering temperature①

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Abstract: A research on fabrication of finegrained Al_2O_3 ceramic at lower sintering temperature was carried out. Al_2O_3 powder with 50 nm in diameter is compounded with 11.24% Al and 4.75% Fe(mass fraction) by high-energy ball-milling. Al is got from Al powder which is a component of the materials being milled and Fe from steel milling balls and milling jar during the milling. In this way, nearly no impurity is brought into the composite powder during milling. With hot pressing of the composite powder and pure Al_2O_3 powder, it is proved that Al_2O_3 powder can be densified at lower sintering temperature when the powder is compounded in this way. Al_2OC and AlFe form during sintering process of the composite powder. With the reactive sintering and multiphase sintering mechanisms, finegrained Al_2O_3 ceramic is fabricated at low sintering temperature.

Key words: finegrained Al_2O_3 ceramic; sintering; nanometer Al_2O_3-Al-Fe composite powder; high-energy ball-milling; strength; toughness

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1 INTRODUCTION

Al_2O_3 ceramic has many super properties. It is widely used in many fields[1]. While usually the sintering temperature of it is very high(about 1 550 - 1 950 ℃). Al_2O_3 grains grow rapidly at so high temperature, which will make the mechanical properties of the ceramic, especially toughness and strength, decrease. So a considerable effort has been made on how to fabricate dense finegrained Al_2O_3 ceramic at lower sintering temperature[2-4]. But until now, this problem hasn't been solved very well. Multiphase sintering is a popular technique that has been developed on this. Some phases, such as MgO, SiC, Y_2O_3 and $AlFe_x$, have been found to be good second phases for the sintering. But usually people just mix these powders into Al_2O_3 powder and sinter them[5-8]. Some impurities usually are brought into the powders in the process of mixing[9], and the sintering result can't satisfy them enough. In order to solve this problem, Al_2O_3 powder and Al powder were milled with steel milling balls in steel milling jar using high-energy ball-mill here. Then some amount of Fe that broke away from milling balls and milling jar came into the powders being milled and nanometer Al_2O_3-11.24% Al-4.75% Fe(mass fraction) composite powder was prepared. In this way, nearly no impurity was brought into the composite powder. The intermetallic compound, $AlFe_x$, was expected to form when the composite powder was sintered. Then reactive sintering and multiphase sintering mechanisms would give effect to the sintering process at the same time, which could accelerate the sintering rate and be beneficial to fabricating finegrained Al_2O_3 ceramic.

2 EXPERIMENTAL

The Al_2O_3 powder used here has an average particle size of 50 nm and the industrial aluminium powder of 75 - 150 μm. In preparing the Al_2O_3-Al-Fe composite powder, SPEX 8000 high-energy ball-mill with rotation speed of 875 r/min, steel milling jar and milling balls were used. The mass ratio of ball to powder for the milling was 10∶1 and the milling time was 13.5 h. After the milling, the final compositions of the powder were Al_2O_3-11.24% Al-4.75% Fe(mass fraction). The ferrum came from the milling balls and milling jar. The pure Al_2O_3 powder and the composite powder were put into die respectively without cold pressing and

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sintered. Three samples were obtained. The sintering conditions for the samples are listed in Table 1. The powder morphologies were observed with PHILIPS EM420 TEM and the impact fracture microstructures of three samples with PHILIPS XL30 SEM. Japanese D/max-2500PC XRD was used to identify the phases of the powders and the samples. The densities of the samples were determined using Archimedes method.

Table 1 Sintering conditions for samples

Sample No.	Powder	Material of die	Sintering temperature/ ℃
1	Pure Al_2O_3	Graphite	1 300
2	Composite	Graphite	1 300
3	Composite	Graphite	1 300

Sample No.	Holding time/ h	Pressure/ MPa	Sintering atmosphere
1	2	50	Argon
2	1	50	Argon
3	2	50	Argon

3 RESULTS AND DISCUSSION

3.1 TEM research

The morphologies of the pure Al_2O_3 and the Al_2O_3-Al-Fe powder being milled for different times are presented in Figs. 1(a)-(f) respectively. From these images we can see that, during the high-energy ball-milling, Al_2O_3 particulates wedge themselves into Al particulates first. As milling goes on, the composite powder is homogenized and smashed. Fe particulate isn't seen in the images. The possible reason is that Fe particulates are very fine when they break away from milling jar and milling balls. They come into Al particulates too during the milling. Finally, fine homogeneous Al_2O_3-Al-Fe composite powder is obtained.

3.2 XRD research

XRD pattern of the composite powder is shown in Fig. 2(a), from which, the components of the composite powder obtained are confined to be Al_2O_3, Al and Fe. Using the XRD technique, the phases of sample 2 and sample 3 are revealed to be the same: Al_2O_3 + AlFe + Al_2OC. The XRD pattern of sample 3 is shown in Fig. 2(b). Fig. 2 (a) shows that no phase transformation and reaction about aluminium and alumina occur during the milling process. The reactions occuring upon sintering are as follows:

$$Al + Fe \rightarrow AlFe \quad (1)$$

$$Al + Al_2O_3 + C \rightarrow Al_2OC \quad (2)$$

where the carbon mainly comes from the graphite dies.

3.3 Density

The relative densities of sample 1, sample 2 and sample 3 are determined to be 73%, 79% and 93%, respectively.

3.4 SEM research

Figs. 3(a), (b) and (c) present the fractured surface images of samples 1, 2 and 3, respectively. As presented in Fig. 3(a), there are many pores with tens to hundreds nanometers in diameter in sample 1 and no regular polyhedron Al_2O_3 grain can be seen in it.

There are many pores in sample 2 too, but exact Al_2O_3 grain morphology can't be seen in its fractured surface because the grain surface is covered with many whiskers with about 100-200 nm in length and many particulates with about tens of nanometers in diameter distributing among the whiskers, which can be seen in Fig. 3(b). According to the XRD pattern (Fig. 2(b)) and the morphology, the whiskers are confirmed to be Al_2OC and the particulates to be AlFe. Some reactions about Al and Fe occur and Al_2OC and AlFe form during sintering.

Fig. 3(c) shows the fractured surface image of sample 3, from which sample 3 is found to be much denser than the other samples and the Al_2O_3 grain morphology in it to be regular polyhedron. The microstructure of the sample is mixed type of intergranular and intragranular fracture. Al_2OC whiskers with 100-400 nm in length locate interlacedly at Al_2O_3 grain boundaries (as shown by arrow 1 in Fig. 3(c)). The whiskers are the ones that the Al_2OC grains in sample 2 grow up to be. The addition of Al_2OC can increase the material toughness and strength. The toughening and strengthening mechanisms are mainly interface debonding, crack deflection and whisker pullout. In the sample, AlFe grains with about tens of nanometers in diameter can be seen in some Al_2O_3 grains or at grain boundaries (as shown by arrow 2 in Fig. 3(c)). The particulates can improve the toughness of the material too. The toughening mechanisms are mainly interface debonding and crack deflection. The chemical combination about Al_2OC and AlFe releases energy which accelerates Al_2O_3 grain boundary diffusion and bulk diffusion and increases densification rate.

Some formation models about AlFe and Al_2OC in the material are conceived as follows. After the high-energy ball-milling, Al_2O_3 particulates are coated with a certain amount of Al and Fe. When the composite powder is sintered, AlFe and Al_2OC form on the surface of Al_2O_3 particulates. Al_2OC whisker is a long-cycle modulation crystal and

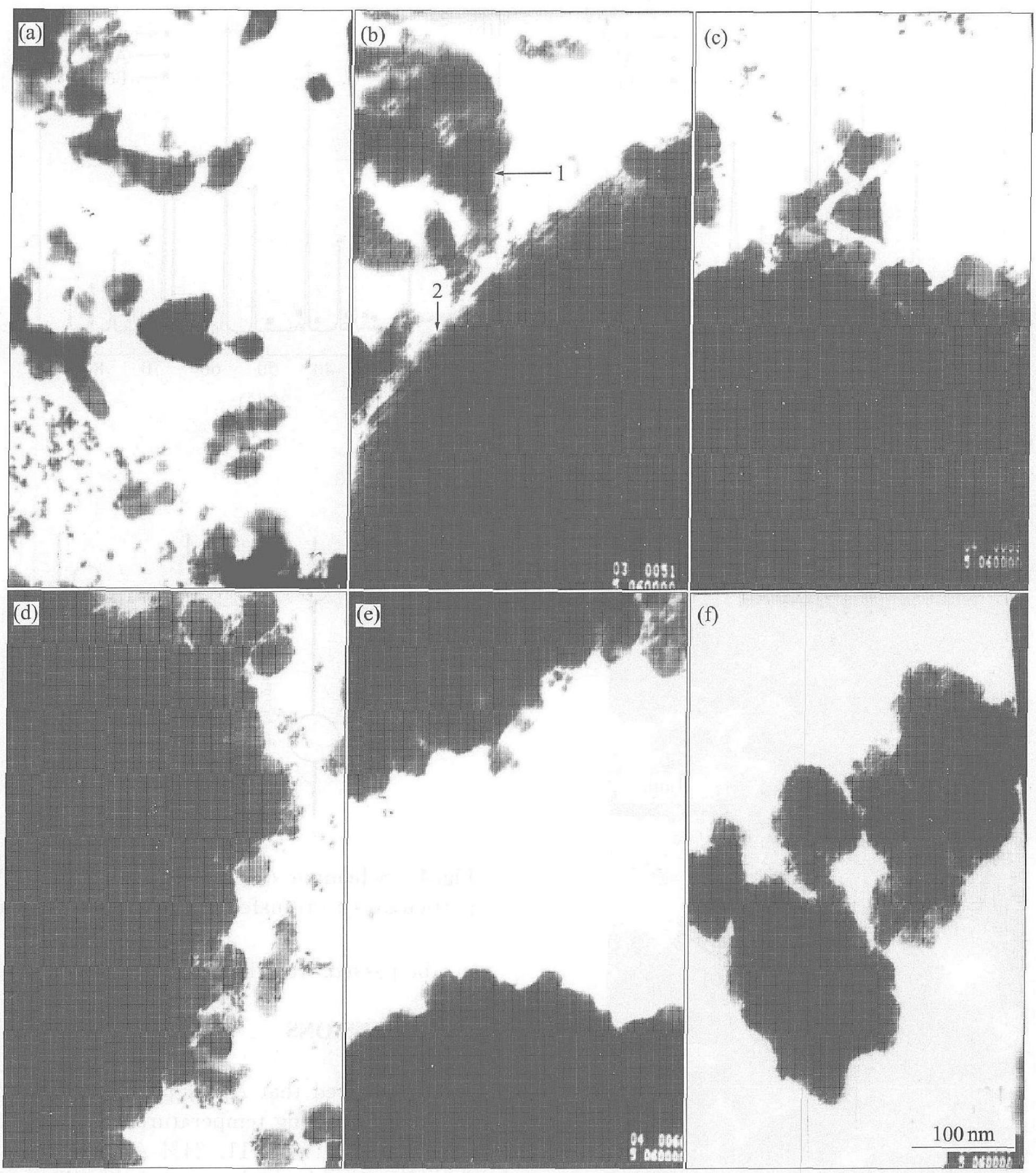

Fig. 1 TEM images of powders
(a) —Pure Al_2O_3 powder; (b)−(f) —Composite powder milled for 0 min, 1 min, 20 min, 120 min and 810 min respectively
(Arrow 1 —Al_2O_3 particulate; Arrow 2 —Al particulate)

composed of Al_2O_3 and Al_4C_3, which connects with Al_2O_3 grain tightly in the material. The strength of Al_2OC is high. It can hinder crack in its extending[10]. With this phase in the ceramic, the toughness and strength of the material can be increased. At the beginning of sintering, tiny AlFe particulates and Al_2OC whiskers exist on the surface of Al_2O_3 particulates. As sintering keeps on, Al_2OC whiskers and AlFe particulates can grow up through Al_2O_3 grain boundary diffusion or surface diffusion.

The growth process of Al_2O_3 grains is the transfer process of Al_2O_3 grain boundaries, so only when the transfer driving force is higher than the resistance of AlFe particulates and Al_2OC whiskers at Al_2O_3 grain boundaries can the Al_2O_3 grains grow up. The maximal resistance, F_{max}, that AlFe particulate can give to the transfer of Al_2O_3 grain boundary, is approximately expressed as[11]

$$F_{max} = \pi r \gamma_b \quad (3)$$

where r is the radius of AlFe particulate; γ_b is the Al_2O_3 grain boundary energy per unit area.

So, as shown in Fig. 4, only the AlFe particulates small enough can be passed by Al_2O_3 grain boundary and come into Al_2O_3 grain and the bigger particulates are kept at the boundary. AlFe partic-

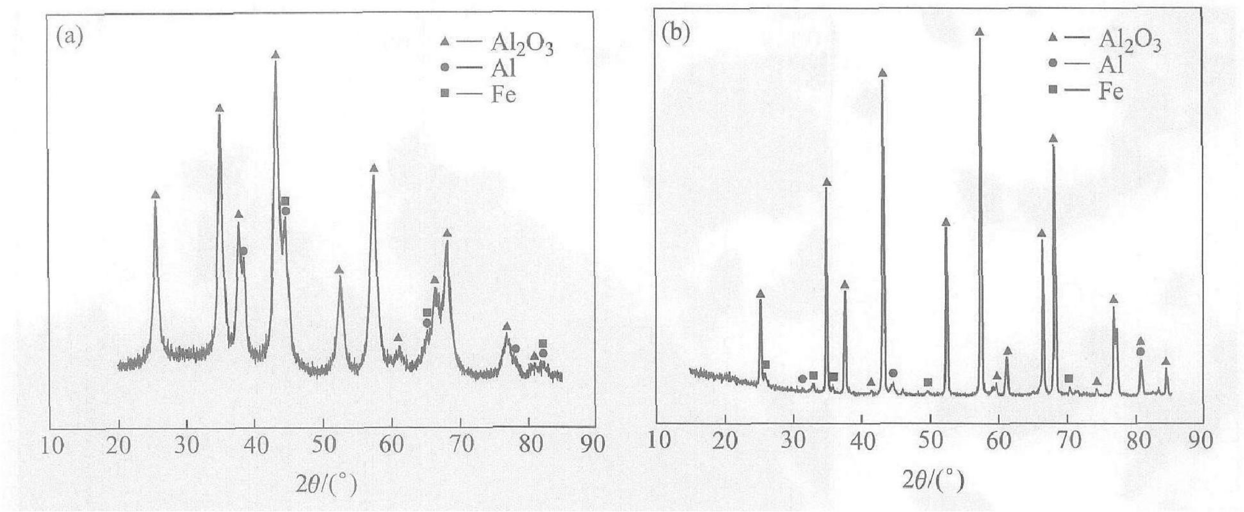

Fig. 2 XRD patterns of samples
(a) —Composite powder; (b) —Sample 3

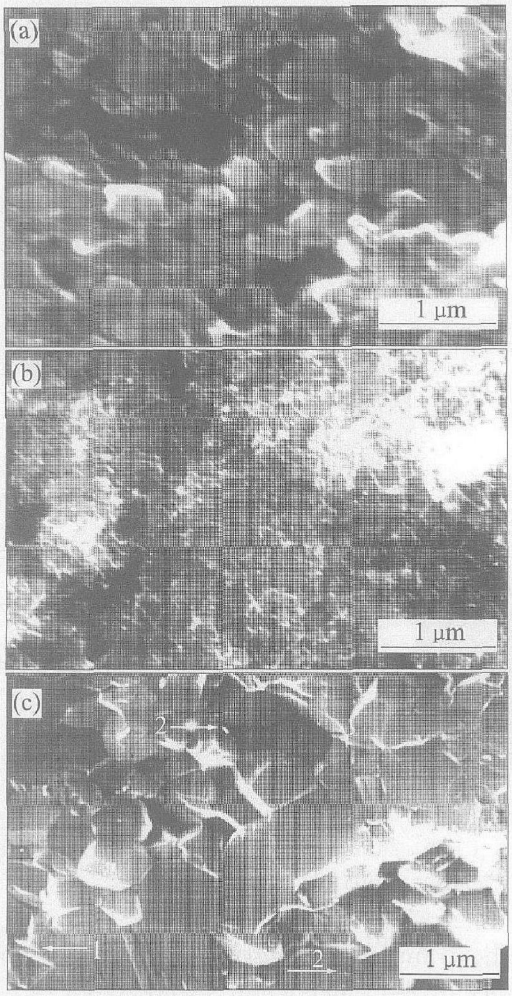

Fig. 3 Fracture SEM images of samples
(a) —Sample 1; (b) —Sample 2; (c) —Sample 3
(Arrow 1 —Al_2OC; Arrow 2 —AlFe)

ulate in Al_2O_3 grain decreases the strength of Al_2O_3 grain and is beneficial to the happening of intragranular fracture, which improves the mechanical properties of the material[12-14]. Al_2OC whisker has high length-to-diameter ratio. It gives higher resistance to the transfer of Al_2O_3 grain boundary than AlFe particulate. Al_2OC whisker

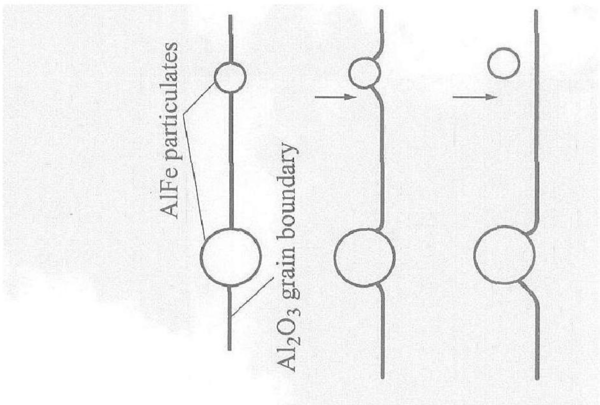

Fig. 4 Schematic diagram of resistance of AlFe particulates to transfer of Al_2O_3 grain boundary

can't be passed. It is kept at the boundary.

4 CONCLUSIONS

It is proved that Al_2O_3 powder can be densified at low sintering temperature when the powder is compounded with 11.24% Al and 4.75% Fe (mass fraction) by high-energy ball-milling. In the Al_2O_3-Al-Fe composite powder, Fe comes from steel milling balls and milling jar during the milling and Al from Al powder, a component of the materials being milled. In this way, nearly no impurity is brought into the composite powder during milling. Al_2OC and AlFe form during the sintering process of the composite powder. With the reactive sintering and multiphase sintering mechanisms, finegrained Al_2O_3 ceramic is fabricated at lower sintering temperature.

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