

## Alumina phase transition and morphology development in a flux by adding silica

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Well developed plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  particles were obtained in NaCl-KCl by sintering at 1000 °C for 4 h, using  $\text{Al}(\text{OH})_3$  powder as the starting material. The influence of silica on the phase transition and morphology development were examined. When silica was added, the main phase was  $\gamma$ - $\text{Al}_2\text{O}_3$  in the sample by sintering at 1000 °C, and mullite,  $\text{SiO}_2$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  phases were observed in the sample by sintering at 1200 °C. Some abnormal particles were observed in the sample with Si added by sintering at 1000, 1100 and 1200 °C.

**Key words:** Flux, Preparation, Plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$ , Silica.

### Introduction

Alumina is one of the most important materials in the ceramic industry because of the unique chemical, electrical and mechanical properties [1]. Alumina particles have a strong tendency of anisotropic growth as platelet growth is underway under an unconstrained environment. Highly developed anisotropic ceramic particles are used as reinforcements of metal, ceramics and resin to improve their mechanical properties such as the elastic modulus, toughness and strength. Ceramic platelets are easy to disperse into a matrix phase, compared with whiskers or short fibers [2]. Also, whiskers and fibers pose a health hazard similar to asbestos due to their high aspect ratio [3].

Investigations have shown that plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  particles can increase the fracture toughness more significantly than spherical particles because the plate-like grains can easily crack bridge in a ceramic matrix [4, 5]. Plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  particles also lead to significant increases in mechanical strength and toughness of a glass [6, 7]. Moreover, alumina platelets are also much easier to disperse in an epoxy resin and are less expensive, compared to alumina nano-particles. The tensile strength, elastic modulus and fracture toughness of an epoxy were improved by selecting alumina platelets as the reinforcement, where the platelets were coated using 3-glycidoxypropyltrimeth-oxysilane [8]. On the other hand, highly textured alumina ceramics have been fabricated using alumina platelets as a seed [9].

For these reasons, the preparation of plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  particles has been given much attention in the last decades. There are mainly three methods for the preparation of plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  particles, which are

wet-chemical [3], a solid-state reaction and a molten salt method [1]. Compared with the conventional solid-state reaction, the preparation temperature and time of the molten salt method can be significantly reduced because of the high diffusivity of the components in the molten salt [1]. Compared with the wet-chemical method, the molten salt method can be simple to obtain well-crystallized  $\alpha$ - $\text{Al}_2\text{O}_3$  platelets. For this reason, there have been some reports on the preparation of plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  powders by the molten salt method [1, 10-12]. For example, Zhu et al. [1] prepared plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  single-crystal particles in a NaCl-KCl flux using porous amorphous  $\text{Al}_2\text{O}_3$  powders as starting materials. Lee et al. [10] obtained plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  in a  $\text{Na}_2\text{SO}_4$  flux using  $\gamma$ - $\text{Al}_2\text{O}_3$  as the starting material.

Adding oxide components in the flux, would aid the formation of low melting point liquids, enhance the volume fraction, change the viscosity of the glassy phase and maybe avail the generation of plate-like alumina during firing. For example, the ternary of  $\text{Na}_2\text{O}$ - $\text{K}_2\text{O}$ - $\text{SiO}_2$  has the lowest melting point of 540 °C.

In the present study, plate-like  $\alpha$ - $\text{Al}_2\text{O}_3$  single-crystal particles were prepared in a NaCl-KCl flux by sintering at 1000 °C for 4 h, using  $\text{Al}(\text{OH})_3$  powder as the starting material. The influence of silica on the alumina phase transition and morphology development were examined. But, the main phase was  $\gamma$ - $\text{Al}_2\text{O}_3$  in the sample by sintering at 1000 °C, and mullite,  $\text{SiO}_2$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  phases were observed in the sample by sintering at 1200 °C, when silica was added. And some abnormal particles were observed in the sample with Si added by sintering at 1000, 1100 and 1200 °C.

### Experimental procedure

The starting materials used were aluminum hydroxide (chemical grade, Xi'an chemical reagent factory, Xi'an,

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China), sodium chloride (chemical grade, Dengfeng chemical reagent factory, Tianjing, China), potassium chloride (chemical grade, Baishi chemical co., Tianjing, China) and sodium silicate (chemical grade, Shanghai chemical reagent factory, Shanghai, China).

Amorphous phase  $\text{Al}_2\text{O}_3$  was obtained by sintering  $\text{Al}(\text{OH})_3$  powder at  $500^\circ\text{C}$  for 3 h. The synthesized amorphous  $\text{Al}_2\text{O}_3$ , nucleant, salt and water were mixed by stirring. The salt was obtained by mixing  $\text{NaCl}$  and  $\text{KCl}$ , with a weight ratio of 1 : 1. The weight ratio of the  $\text{Al}_2\text{O}_3$  and salt was 1 : 2. A 10 wt% nucleant was added because the synthesizing temperature of  $\alpha\text{-Al}_2\text{O}_3$  can be decreased by the addition of a nucleant during molten salt synthesis. Then, the powder mixtures were placed in covered alumina crucibles, dried at  $60^\circ\text{C}$  for 4 h and heated at  $1000^\circ\text{C}$  for 4 h. The synthesized products were washed repeatedly with hot distilled water to remove the remains salt.

The phase assembly of the washed products was characterized by XRD (Dandong Fangyuan, Dandong, China) using  $\text{CuK}\alpha$  radiation, and a step width of 0.1  $^\circ$ s. The morphology of the products washed with water was observed by SEM (JSM-6390LV, JEOL, Japan).

## Results and Discussion

XRD pattern of the specimen sintered at  $1000^\circ\text{C}$  for 4 h is shown in Fig. 1. Only the  $\alpha\text{-Al}_2\text{O}_3$  phase were observed in the without a Si addition sample. The SEM micrographs of the product without a Si addition are shown in Fig. 2, where the product was sintered at  $1000^\circ\text{C}$  for 4 h. A mass of relatively well-developed and interlocked plate-like  $\alpha\text{-Al}_2\text{O}_3$  particles were observed, with a diameter range from  $5\ \mu\text{m}$  to  $10\ \mu\text{m}$  and a thickness range from  $0.6\ \mu\text{m}$  to  $1.5\ \mu\text{m}$ .

$\alpha\text{-Al}_2\text{O}_3$  nucleation occur when  $\text{Al}_2\text{O}_3$  species dissolve in the flux system until a critical  $\text{Al}_2\text{O}_3$  concentration is reached. Then, the dissolving  $\text{Al}_2\text{O}_3$  quickly precipitate on the surface of  $\alpha\text{-Al}_2\text{O}_3$  nuclei and grow preferentially

along the (0001) crystal planes of  $\alpha\text{-Al}_2\text{O}_3$  due to the relatively lower interface energy, leading to the formation of dense plate-like  $\alpha\text{-Al}_2\text{O}_3$  particles [1].

In this study, it was concluded that the  $\alpha\text{-Al}_2\text{O}_3$  developed into a plate-like form in the presence of a considerable amount of liquid phase because the melting points of sodium chloride and potassium chloride are  $800^\circ\text{C}$  and  $770^\circ\text{C}$ , respectively, and the lowest melting point of the  $\text{NaCl-KCl}$  system is lower than the melting point of potassium chloride. The weight ratio of the  $\text{Al}_2\text{O}_3$  and salt was 1 : 2, as a result there was more liquid when sintered at  $1000^\circ\text{C}$ . Thus it was considered the growth of plates was due to the conditions pertaining in the liquid phase at the firing temperature.

XRD patterns of the specimens with Si added are shown in Fig. 3. When silica was added, the main phase was  $\gamma\text{-Al}_2\text{O}_3$  in the sample by sintering at  $1000^\circ\text{C}$ . And mutinaite,  $\text{SiO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  phase were observed in the sample by sintering at  $1200^\circ\text{C}$ . But the  $\alpha\text{-Al}_2\text{O}_3$  phase was not observed in the samples by sintering at  $1000$ ,  $1100$  and  $1200^\circ\text{C}$ .

The SEM micrographs of the product with Si added are shown in Fig. 4. Some abnormal particles were observed in the samples by sintering at  $1000$ ,  $1100$  and  $1200^\circ\text{C}$ .

The plate-like  $\alpha\text{-Al}_2\text{O}_3$  was not obtained maybe since the dissolution of alumina was hindered and the amorphous alumina phase transition and morphology development were affected by adding silica in the  $\text{NaCl-KCl}$  flux.

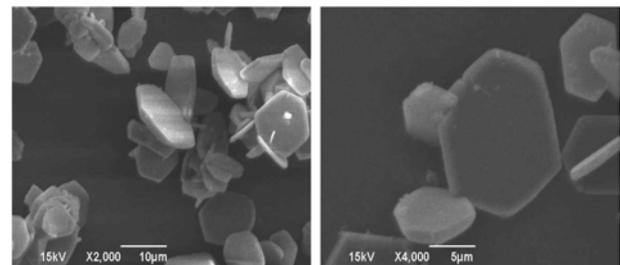


Fig. 2. SEM micrographs of the specimen without a Si addition by sintering at  $1000^\circ\text{C}$  for 4 h, washed repeatedly with hot distilled water.

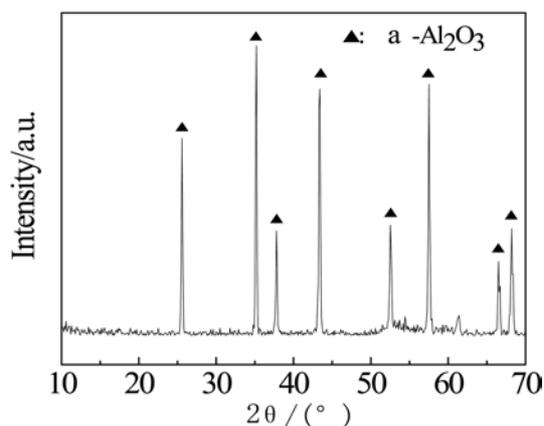


Fig. 1. XRD pattern of the specimen without a Si addition by sintering at  $1000^\circ\text{C}$  for 4 h, washed repeatedly with hot distilled water.

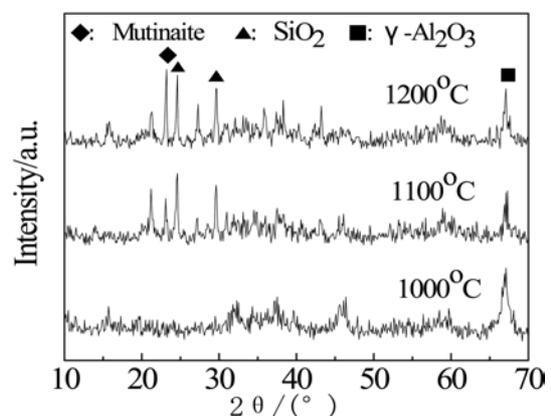
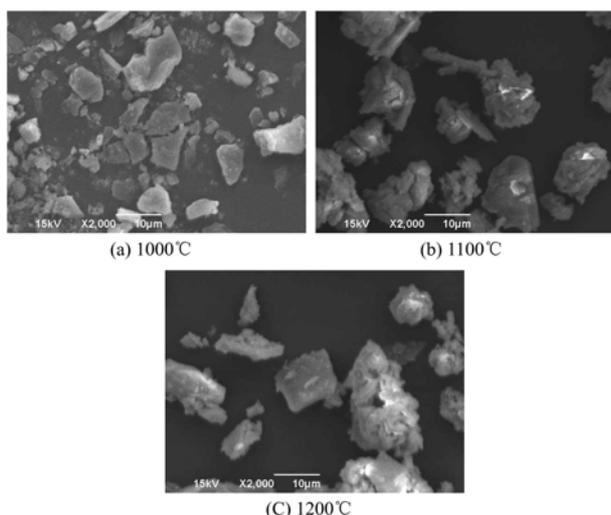


Fig. 3. XRD patterns of the specimens with Si added by sintering at  $1000$ ,  $1100$  and  $1200^\circ\text{C}$  for 4 h, washed repeatedly with hot distilled water.



**Fig. 4.** SEM micrographs of the specimens with Si added by sintering at (a) 1000, (b) 1100 and (c) 1200 °C for 4 h, washed repeatedly with hot distilled water.

### Conclusions

Only the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase was observed in the samples without a Si addition by sintering at 1000 °C for 4 h in a NaCl-KCl flux using  $\text{Al}(\text{OH})_3$  powder as the starting material. Plate-like particles were observed, with a diameter range from 5  $\mu\text{m}$  to 10  $\mu\text{m}$  and a thickness

range from 0.6  $\mu\text{m}$  to 1.5  $\mu\text{m}$ .

When silica was added, the main phase was  $\gamma$ - $\text{Al}_2\text{O}_3$  in the sample by sintering at 1000 °C. Also mutinaite,  $\text{SiO}_2$  and the  $\gamma$ - $\text{Al}_2\text{O}_3$  phases were observed in the sample by sintering at 1200 °C.

### References

1. L. Zhu, Q. Huang and W. Liu, *Ceram. Inter.* 34 [7] (2008) 1729-1733.
2. S. Hashimoto and A. Yamaguchi, *J. Eur. Ceram. Soc.* 19 [3] (1999) 335-339.
3. H. Lu, H. Sun, A. Mao, H. Yang, H. Wang and X. Hu, *Mater. Sci. Eng. A* 406 [1-2] (2005) 19-23.
4. H.J. Kim, T.G. Kim, J.J. Kim, S.S. Park, S.S. Hong and G.D. Lee, *J Phys. Chem. Solids* 69 [5-6] (2008) 1521-1524.
5. G. Pezzotti, H. Okuda, N. Muraki and T. Nishida, *J. Eur. Ceram. Soc.* 19 [5] (1999)601-608.
6. E. Bernardo, G. Scarinci and S. Hreglich, *J. Eur. Ceram. Soc.* 25 [9] (2005) 1541-1550.
7. E. Bernardo and G. Scarinci, *Ceram. Inter.*, 30 [5] (2004) 785-791.
8. D.K. Shukla, S.V. Kasisomayajula and V. Parameswaran, *Compos. Sci. Technol.* 68 [14] (2008) 3055-3063.
9. M. Wei, D. Zhi and D.G. Brandon, *Scr. Mater.* 53 [12] (2005) 1327-1332.
10. S.G. Lee, H.C. Park, B.S. Kang, G.S. Seo, S.S. Hong and S.S. Park, *Mater. Sci. Eng. A* 466 [1-2] (2007)79-83.
11. S. Hashimoto and A. Yamaguchi, *J. Mater. Res.* 14 [12] (1999) 4667-4672.
12. X. Jin and L. Gao, *J. Am. Ceram. Soc.* 87 [4] (2004) 533-540.