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Synthesis of plate-like α-Al_2O_3 single-crystal particles in NaCl–KCl flux using $Al(OH)_3$ powders as starting materials

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Abstract

Plate-like α-Al_2O_3 single-crystal particles were successfully synthesized in NaCl–KCl flux using $Al(OH)_3$ powders as starting materials, and the influence of pre-calcining of $Al(OH)_3$ powders on the phase formation and morphology of α-Al_2O_3 powders was focused. When $Al(OH)_3$ powders are used as starting materials, the synthesized product at 900 °C is mainly composed of α-Al_2O_3 and κ-Al_2O_3, and most synthesized particles show alveolate morphology. At 1100 °C, single-phase α-Al_2O_3 powders are developed, in which there are many aggregations of intensively bound plate-like particles. In contrast, using porous amorphous Al_2O_3 powders obtained by pre-calcining $Al(OH)_3$ powders at 550 °C for 3 h as the starting material, plate-like α-Al_2O_3 single-crystal particles can be well developed above 900 °C. The reason of the influence of pre-calcining of $Al(OH)_3$ powders on the phase formation and morphology of α-Al_2O_3 powders is also discussed in the paper.

Keywords: B. Platelets; D. Al_2O_3; Single-crystal particles; Molten salt synthesis

1. Introduction

α-Al_2O_3 ceramic is one of the most important materials in ceramic industry because of the unique chemical, electrical and mechanical properties, but its wide use is limited by low fracture toughness owing to its equi-axed grains. The investigations [1–5] show that α-Al_2O_3 ceramics with plate-like grains have high fracture toughness, which opens up a new way to fabricate α-Al_2O_3 ceramics with high fracture strength and toughness. So far, extensive studies have been carried out to obtain plate-like grains, in which seeding is considered to be one of the most effective methods because the amount, size, and distribution of plate-like grains in the fired ceramics can be controlled by the seeds [1,5]. In this technology, plate-like α-Al_2O_3 single-crystal particles with suitable size are considered to be ideal seeds. In addition, plate-like α-Al_2O_3 single-crystal particles are also effective to improve the mechanical strength and toughness of other ceramics [6–9], glass [10], and metals of Al [11].

So far, there have been some reports [12–16] on the preparation of plate-like α-Al_2O_3 powders, in which molten salt synthesis (MSS) [15,16] is considered to be one of the simplest techniques to prepare plate-like α-Al_2O_3 powders. Compared with the conventional solid-state reaction, the preparation temperature and time can be significantly reduced because of high diffusivity of the components in the molten salt. In the previous investigations [15,16], aluminum sulfate ($Al_2(SO_4)_3$) is used as the starting material and Na_2SO_4 is used as molten salt media. In both cases, a high synthesizing temperature is required due to the high melting point of Na_2SO_4. Moreover, it is deleterious to the environment due to the production of poisonous SO_3 (g) and SO_2 (g) during the thermal decomposition of $Al_2(SO_4)_3$. As a starting material, $Al(OH)_3$ may be superior to $Al_2(SO_4)_3$ because it is cheaper and there is no pollution during the process. At the same time, the melting point of NaCl–KCl is lower than that of Na_2SO_4, and is probably beneficial to decrease the forming temperature of α-Al_2O_3. Therefore, it is desirable to develop a process to synthesize plate-like α-Al_2O_3 single-crystal particles from $Al(OH)_3$ powders at relatively low temperature. This work describes our preliminary results on the fabrication of plate-like

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Table 1
The main characteristics of $Al(OH)_3$ powders, porous amorphous Al_2O_3 powders (obtained by calcining $Al(OH)_3$ powders at 500 °C for 3 h in air), and the synthesized products in NaCl–KCl flux at 900 and 1100 °C

	The starting materials		The synthesized products			
	$Al(OH)_3$	Porous amorphous Al_2O_3	$Al(OH)_3$ at 900 °C	$Al(OH)_3$ at 1100 °C	Porous amorphous at 900 °C	Porous amorphous at 1100 °C
Phase assemblage	–	–	κ- and α-Al_2O_3	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3
Average particle diameter (μm)	0.5	1.5	–	–	2.4	2.6
Specific surface area (m^2/g)	5.2	162	62	16	1.7	1.6

α-Al_2O_3 single-crystal particles using $Al(OH)_3$ as starting materials, and the influence of pre-calcining of $Al(OH)_3$ powders on the phase formation and morphology of α-Al_2O_3 powders is focused.

2. Experimental procedure

$Al(OH)_3$ powders with purity of 99.99% were provided by Zhongzhou Branch China Aluminum Co. Ltd. The $Al(OH)_3$ powders were calcined at 550 °C for 3 h in air to form Al_2O_3, which is composed of amorphous phase by X-ray diffraction analysis (XRD). The main characteristics of the $Al(OH)_3$ and the synthesized amorphous Al_2O_3 powders are summarized in Table 1. The synthesized amorphous Al_2O_3 powders have larger specific surface area than $Al(OH)_3$ powders because of the remained porosity after the dehydration of $Al(OH)_3$ powders. Because the synthesizing temperature of α-Al_2O_3 can be decreased by the addition of α-Al_2O_3 powders during molten salt synthesis [17], 5 wt% α-Al_2O_3 powders with average particle size of 0.5 μm were also added in the starting materials in this work.

The powder mixtures containing either $Al(OH)_3$ and α-Al_2O_3 powders or the synthesized amorphous Al_2O_3 and α-Al_2O_3 powders were firstly ball-milled in de-ionized water for 24 h using high-purity α-Al_2O_3 balls. Then, the salt mixture with the weight ratio of NaCl (purity: 99.5%) and KCl (purity: 99.5%) of 1:1 was added into each mixture and ball-milled for another 24 h. The weight ratio of starting materials and salt was 1:2. The dried powder mixtures were placed in the covered alumina crucibles, and then heated at 900 and 1100 °C for 4 h in air. The synthesized products were washed repeatedly with hot de-ionized water to remove the remained salt. The phase assembly of the synthesized products was characterized by XRD and the morphology was observed by scanning electron microscope (SEM). The specific surface area and particle size of the powders were examined by the Brunauer–Emmett–Teller method (BET) and the quasi-elastic light scattering method (QELS), separately.

3. Results and discussion

Fig. 1 shows XRD patterns of the synthesized products in NaCl–KCl flux at 900 and 1100 °C for 4 h. Using $Al(OH)_3$ powders as the starting materials, the synthesized product at 900 °C is mainly composed of α-Al_2O_3 and κ-Al_2O_3, see Fig. 1(a). At 1100 °C, κ-Al_2O_3 disappears and single-phase α-Al_2O_3 is developed, see Fig. 1(b). In contrast, using the amorphous Al_2O_3 powders obtained by calcining $Al(OH)_3$ powders at 550 °C for 3 h as the starting materials, only single-phase α-Al_2O_3 can be observed at 900 and 1100 °C.

Fig. 2 shows SEM micrographs of the synthesized powders in NaCl–KCl flux at 900 °C for 4 h using $Al(OH)_3$ powders as the starting materials. The powders are nubby and inhomogeneous. The arrowed area in Fig. 2(a) is further magnified in Fig. 2(b). It can be seen that although there are a few particles with smooth surfaces, most particles have rough surfaces and show alveolate morphology. When the powder mixture is fired in NaCl–KCl flux at 1100 °C for 4 h, some accumulations of intensively bound plate-like α-Al_2O_3 grains are developed, see the arrowed area in Fig. 3. Besides, there are still a few α-Al_2O_3 particles with smooth surfaces. The specific surface area of the synthesized powders at 900 °C is 62 m^2/g and it decreases to 16 m^2/g at 1100 °C.

Fig. 4(a) shows SEM micrographs of the synthesized powders in NaCl–KCl flux at 900 °C for 4 h using the porous amorphous Al_2O_3 obtained by calcining $Al(OH)_3$ powders at 550 °C for 3 h as the starting materials. The synthesized α-Al_2O_3 powders are uniform and the average diameter is 2.4 μm. Further magnification shows that they are dense particles with smooth surfaces. The synthesized product at 1100 °C is also plate-like and the average diameter is 2.6 μm, see Fig. 5. The specific surface area of the synthesized powders at 900 and 1100 °C is 1.7 and 1.6 m^2/g, respectively. These results indicate that the synthesizing temperature plays

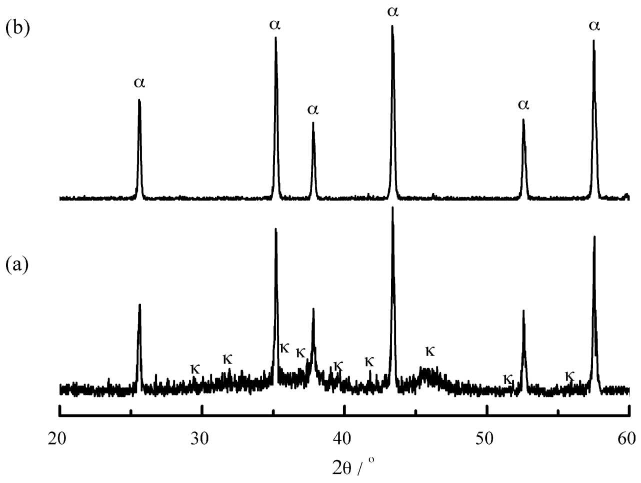

Fig. 1. XRD patterns of the powders synthesized at (a) 900 °C and (b) 1100 °C for 4 h using $Al(OH)_3$ powders as the starting materials.

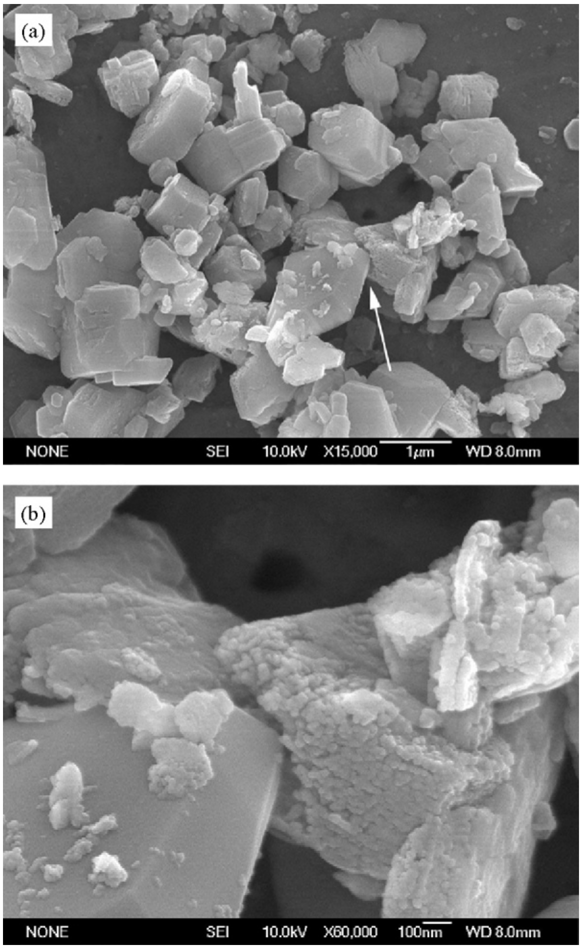

Fig. 2. SEM micrographs of the product synthesized at 900 °C for 4 h using $Al(OH)_3$ powders as the starting materials. (a) Low magnification; (b) high magnification.

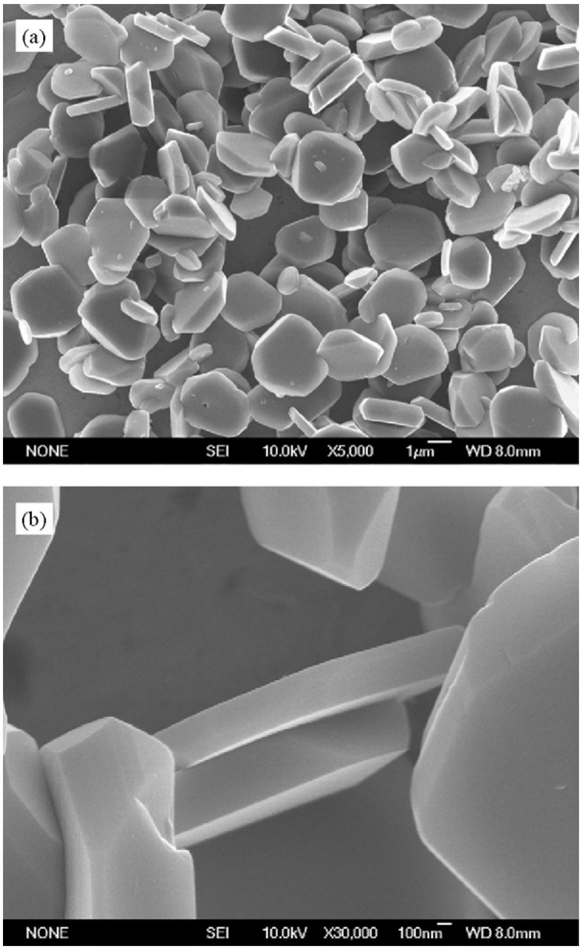

Fig. 4. SEM micrographs of α-Al_2O_3 synthesized at 900 °C using porous amorphous Al_2O_3 powders as the starting materials. (a) Low magnification; (b) high magnification.

a minor role in the size and morphology of plate-like α-Al_2O_3 single-crystal particles when porous amorphous Al_2O_3 powders are used as the starting materials. These well-developed plate-like α-Al_2O_3 single-crystal particles are considered to be the ideal toughening phase in ceramics or other composites.

During molten salt synthesis, the liquid molten-salt environment provides the space and the possibility that the

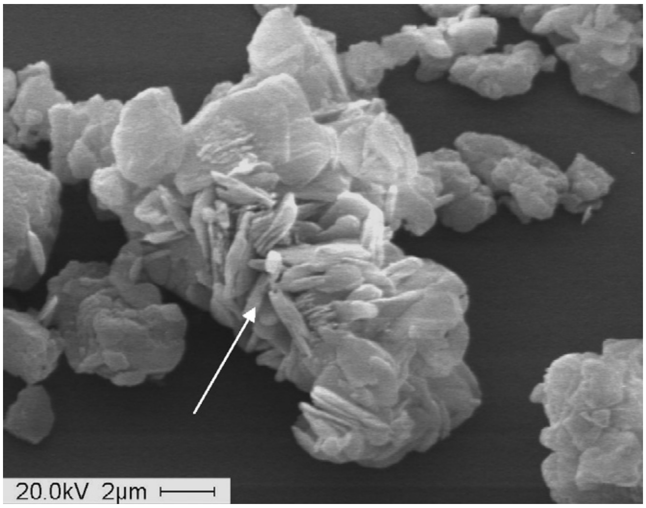

Fig. 3. SEM micrographs of the product synthesized at 1100 °C for 4 h using $Al(OH)_3$ powders as the starting materials.

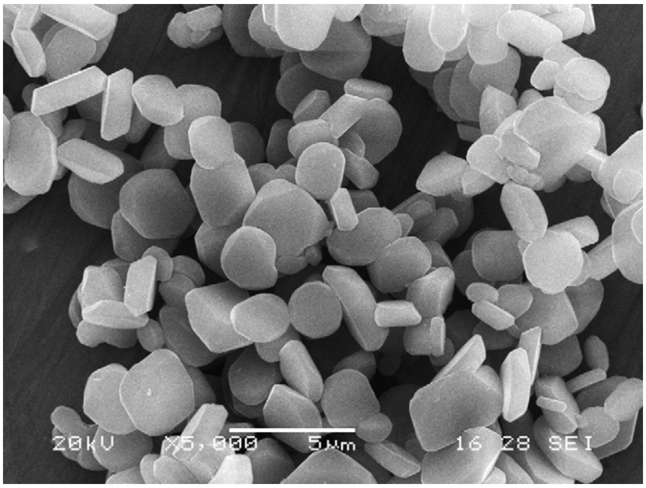

Fig. 5. SEM micrographs of α-Al_2O_3 synthesized at 1100 °C using porous amorphous Al_2O_3 powders as the starting materials.

synthesized powders grow according to crystal characteristic. Besides, the diffusivity of components is increased and the diffusion distance is shortened with the help of salt fluxes. The addition of seeds, which have the same crystal structure and composition as the final products, also provides low energy sites for nucleation due to the reduction of energy barrier required for nucleation. The cooperation of molten salt and α-Al_2O_3 seed makes it possible that the particles with anisotropic morphology can be synthesized at lower temperature and shorter time than the conventional solid-state synthesis [16,17].

In this work, α-Al_2O_3 is more stable than amorphous Al_2O_3 in molten salt and thus it is the amorphous Al_2O_3 that should dissolve in molten salt and precipitate on the surface of α-Al_2O_3 particles. Under the same synthesizing conditions, dissolution rate, diffusion rate, and precipitation rate of the components in molten salt are fixed. The formation rate of the synthesized products is mainly determined by both the interface area of starting materials/molten salt and the interface area of molten salt/growth sites. Owing to the same seed addition, the interface area between the molten salt and growth sites is considered to be the same for different starting materials. Therefore, the interface area of starting materials and the molten salt plays an important role in the formation rate of the synthesized products.

When the porous amorphous Al_2O_3 powders obtained by calcining $Al(OH)_3$ powders at 550 °C for 3 h are used as the starting materials, the water solution of NaCl–KCl can enter into the pores of the amorphous Al_2O_3 powders during milling. After drying, the NaCl–KCl salt is remained inside the porous amorphous Al_2O_3 particles. At the same synthesizing temperature, the formation rate of α-Al_2O_3 is higher since the remained salt in the pores provides extra interface area. The dissolving amorphous Al_2O_3 quickly precipitate on the surface of α-Al_2O_3 seeds and grow preferentially along the (0 0 0 1) crystal plane of α-Al_2O_3 due to relatively lower interface energy, leading to the formation of dense plate-like α-Al_2O_3 powders. It is worth noticing that the formation temperature of single-phase α-Al_2O_3 can be decreased to 900 °C in this work, which is lower than Refs. [15,16].

In contrast, dense $Al(OH)_3$ powders used as the starting materials cannot make the water solution of NaCl–KCl enter inside the powders during milling and the salt are present just outside the $Al(OH)_3$ powders after drying, which is also indicated by the experimental phenomenon that the volume of the mixture of salt and $Al(OH)_3$ is larger than that of salt and amorphous Al_2O_3. Although $Al(OH)_3$ powders also decompose to the porous microstructure at high temperature, it is difficult for the NaCl–KCl salt to enter into the pores due to high viscosity of molten salt. The interface area of starting materials and the molten salt is still small at 900 °C. This results in low formation rate of α-Al_2O_3 and the synthesized powder is composed of α- and κ-Al_2O_3 phase. In Fig. 2, the particles with smooth surfaces are considered to be mainly α-Al_2O_3, which result from the growth of α-Al_2O_3 seeds. In contrast, the particles with alveolate morphology are thought to be mainly the remained κ-Al_2O_3, which result from the decomposition of $Al(OH)_3$ at high temperature.

The viscosity of NaCl–KCl flux decreases with increasing temperature, which makes it easy for the NaCl–KCl flux to enter into the pores of the decomposed $Al(OH)_3$ powders and correspondingly increases the interface area between starting materials and the molten salt. In addition, in situ nucleation of α-Al_2O_3 can also occur at the interface of the decomposed $Al(OH)_3$ powders and molten salt. Therefore, the formation rate of α-Al_2O_3 can be accelerated at high temperature. The precipitation of dissolving component tends to take place on the newly formed α-Al_2O_3 nuclei rather than seeds due to relatively short diffusion distance. The multi-nucleation and growth of α-Al_2O_3 crystals at the surface of these newly formed α-Al_2O_3 nuclei finally result in some accumulations of intensively bound plate-like α-Al_2O_3 particles at 1100 °C. Besides, there is still some α-Al_2O_3 single-crystal particles developed from the growth of α-Al_2O_3 seeds, and they show smooth surface.

4. Conclusions

Well-developed plate-like α-Al_2O_3 single-crystal particles can be successfully synthesized in molten NaCl–KCl at 900 and 1100 °C when the mixture of porous amorphous Al_2O_3 powders (obtained by calcining $Al(OH)_3$ powders at 550 °C for 3 h) and α-Al_2O_3 seeds is used. In contrast, using $Al(OH)_3$ powders and α-Al_2O_3 seeds as starting materials, the synthesized product at 900 °C is mainly composed of α-Al_2O_3 and κ-Al_2O_3, and most synthesized particles show alveolate morphology. At 1100 °C, single-phase α-Al_2O_3 powders are developed, in which there are many aggregations of intensively bound plate-like particles. The remained NaCl–KCl salt inside the porous amorphous Al_2O_3 powders after milling and subsequent drying increases the interface area of salt and starting materials, which is considered to favor the formation and development of plate-like α-Al_2O_3 single-crystal particles during molten salt synthesis.

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