Journal of Ceramic Processing Research. Vol. 11, No. 2, pp. 254~258 (2010)

JOURNAL OF
Ceramic Processing Research

Influence of additives on the morphology of α-Al_2O_3 platelets synthesized in a molten salt

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Trisodium phosphate ($Na_3PO_4·12H_2O$) and titanyl sulfate ($TiOSO_4$) were chosen to study the influence of additives on the morphology of α-Al_2O_3 platelets synthesized by molten salt synthesis. When $Na_3PO_4·12H_2O$ is added, α-Al_2O_3 platelets become thin and quite irregular. Besides, less overlapped particles can be found. When $TiOSO_4$ is added, regular hexagonal α-Al_2O_3 platelets with a decreased size and increased thickness are obtained. When 0.51 wt% $Na_3PO_4·12H_2O$ and 12 wt% $TiOSO_4$ are added, α-Al_2O_3 platelets with a regular shape and an aspect ratio of 12.5 are developed. The mechanism of $Na_3PO_4·12H_2O$ and $TiOSO_4$ on the morphology of α-Al_2O_3 platelets is also discussed in this paper.

Key words: Platelets, α-Al_2O_3, Molten salt synthesis, Additives.

Introduction

Plate-like α-Al_2O_3 powders are applied widely since they have excellent properties, which derive from α-Al_2O_3 and the special two-dimensional structure. α-Al_2O_3 platelets can be added into ceramics as seeds to induce abnormal grain growth, leading to a significant improvement of fracture toughness[1]. When suitable plate-like α-Al_2O_3 are chosen as templates, textured Al_2O_3 ceramics with anisotropic properties can be prepared by templated grain growth [2]. Owing to their high aspect ratio and heat conductivity, α-Al_2O_3 platelets can also be used as fillers and added into plastics to improve their thermal conductivity [3]. α-Al_2O_3 platelets with different shapes are required in various applications, so it is of great importance to control the morphology.

Molten salt synthesis (MSS) is often used to synthesize α-Al_2O_3 platelets [4-11]. During MSS, the morphology can be easily changed by many factors, such as the molten salts used [4], precursors [8, 9], additives [8, 12-15], crystal seeds [7, 9-10], calcination temperature and time [11] etc. Additives are best to control the morphology of plate-like α-Al_2O_3 during MSS. Plate-like α-Al_2O_3 can be synthesized at a lower temperature when some additives such as LiF, ZnF_2, AlF_3 and TiO_2 are added [12-14]. Besides, Hashimoto and Yamaguchi's experimental results show that the morphology of α-Al_2O_3 platelets can be marked changed when only a small amount of Cu^{2+}, Co^{2+}, Ce^{4+} and F^- are added [15]. Therefore, it is necessary to study the effect of additives on the morphology of α-Al_2O_3 platelets.

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Phosphate is often used as an additive owing to its high ion strength and charge density. α-Al_2O_3 flakes are easily obtained by the addition of a phosphate, and the morphology of α-Al_2O_3 platelets is related to the amount of the phosphate addition[16, 17]. Plate-like α-Al_2O_3 particles can not be obtained when less than 0.1 wt% phosphate (in terms of oxide relative to the weight of the Al_2O_3 [17]) is added, but as the amount increases to 2 wt%, the growth of the thickness of platelets can not be inhibited. Ti^{4+} accelerates the phase transformation obviously and is also one of the most important additives [14]. In the present study, PO_4^{3-} (introduced by trisodium phosphate) and Ti^{4+} (introduced by titanyl sulfate) were chosen to study the influence of additives on the morphology of α-Al_2O_3 platelets synthesized by MSS. The mechanism of trisodium phosphate ($Na_3PO_4·12H_2O$) and titanyl sulfate ($TiOSO_4$) on the morphology of α-Al_2O_3 platelets will also be discussed.

Experimental Procedure

In order to obtain plate-like α-Al_2O_3 powders with smooth surfaces and avoid the tendency toward crystal twinning and aggregation, α-Al_2O_3 platelets were synthesized by MSS with reference to the literature [16]. Table 1 shows the raw materials used in the experiments. NaCl and KCl with a molar ratio of 1 : 1 were used as the molten salt. $Al_2(SO_4)_3·18H_2O$ and the mixed salt with a molar ratio of 1 : 4 were dissolved in de-ionized water by heating to about 70 °C, and the resulting solution is designated as aqueous solution (a). Also Na_2CO_3 was completely dissolved in de-ionized water, and the resulting solution is designated as aqueous solution (b). Aqueous solution (b) was added into aqueous solution (a) where stirring was maintained at 70 °C. Stirring was continued

Table 1. the raw materials used in the experiment

raw material	Aluminum sulfate	Sodium carbonate	Sodium chloride	Potassium chloride	Sodium sulfate	Potassium sulfate	Trisodium phosphate	Titanyl sulfate
formula	$Al_2(SO_4)_3{\cdot}18H_2O$	Na_2CO_3	NaCl	KCl	Na_2SO_4	K_2SO_4	$Na_3PO_4{\cdot}12H_2O$	$TiOSO_4$
source	Meixing Chemical Company, Shanghai	Hongguang Chemical Company, Shanghai	Chemical Agent Company, Shanghai	Lingfeng Chemical Company, Shanghai	ShihuiHewei Chemical Company, Shanghai	Medical Combine of China, Shanghai	Medical Combine of China, Chemical Agent Company	The Fifth Company of Reagent, Shenyang
purity	99.5%	99.5%	99.5%	99.5%	99.5%	99.0%	99.5%	99.5%

for 15 minutes. At the same time, either $Na_3PO_4{\cdot}12H_2O$ (0.17 wt%, 0.34 wt%, 0.51 wt%, 0.68 wt%) or $TiOSO_4$ (1 wt%, 3 wt%, 6 wt%, 9 wt%, 12 wt%) was added to control the morphology of the powders. In particular, 0.51 wt% $Na_3PO_4{\cdot}12H_2O$ and 12 wt% $TiOSO_4$ were added to study their combined effect on the morphology of α-Al_2O_3 platelets. The resulting mixture of the two solutions was a gel. This gel was evaporated at 120 °C for 24 h to dryness, and the dried product was calcined at 1200 °C for 4 h. After being ultrasonic cleaned with de-ionized water repeatedly to remove the remaining salt and then dried, α-Al_2O_3 platelets were obtained. Meanwhile, α-Al_2O_3 powders without additives were also synthesized for comparison. The phase assembly of the powders was examined by X-ray diffraction analysis (XRD, RIGAKU, D/MAX-RB) with $Cu_{K\alpha}$ radiation (λ = 1.5418 Å). The morphology of α-Al_2O_3 platelets was observed by a scanning electron microscope (SEM, S-570).

Results and Discussion

Phase analysis

Fig. 1 shows XRD pattern of the synthesized powders. Only the peaks of α-Al_2O_3 are detected, indicating that single phase α-Al_2O_3 is synthesized by MSS.

Effect of $Na_3PO_4{\cdot}12H_2O$ addition on the morphology of α-Al_2O_3 platelets

Fig. 2(a) shows α-Al_2O_3 powders synthesized by MSS with no additive. Most of α-Al_2O_3 platelets are hexagonal, and there are a few overlapped particles. The size and shape of α-Al_2O_3 platelets are scarcely affected by 0.17 wt% $Na_3PO_4{\cdot}12H_2O$, and some of them still agglomerate and overlap with each other. When 0.34~0.68 wt% $Na_3PO_4{\cdot}12H_2O$ is added, there is a significant change in the morphology of the plate-like α-Al_2O_3. Fig. 2(b) shows the morphology of α-Al_2O_3 platelets with 0.51 wt% $Na_3PO_4{\cdot}12H_2O$ added. The platelets become thin and quite irregular. However, less overlapped particles can be found, which shows that the agglomeration of α-Al_2O_3 platelets is inhibited by a certain amount of PO_4^{3-} effectively.

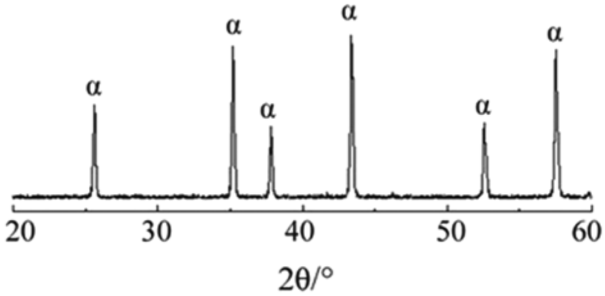

Fig. 1. XRD pattern of the synthesized α-Al_2O_3 powders.

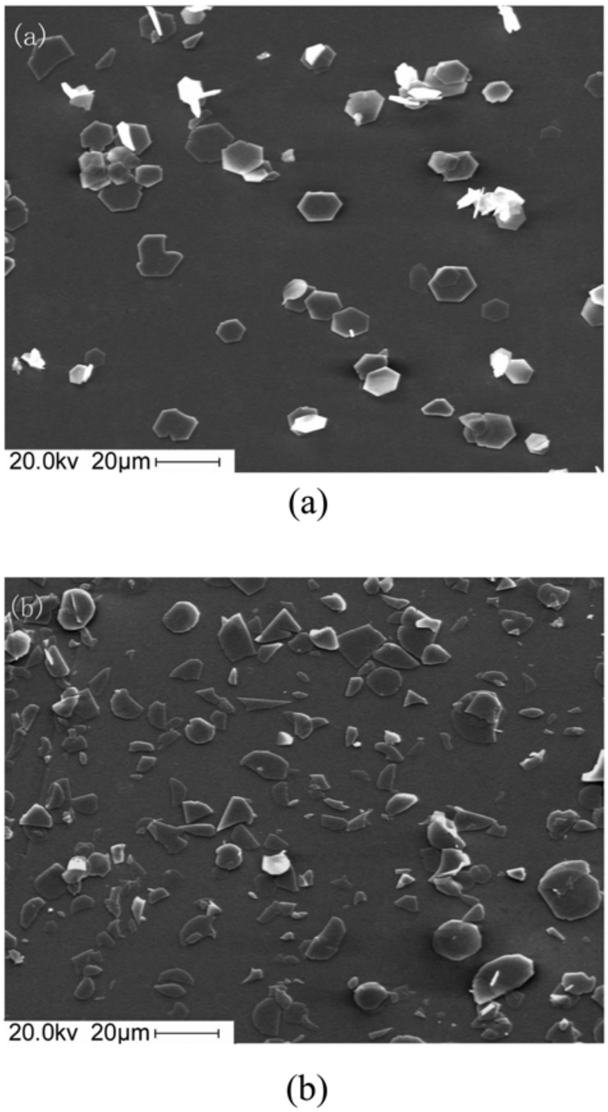

Fig. 2. The influence of a $Na_3PO_4{\cdot}12H_2O$ addition on the morphology of α-Al_2O_3 platelets. (a) 0 wt% $Na_3PO_4{\cdot}12H_2O$; (b) 0.51 wt% $Na_3PO_4{\cdot}12H_2O$.

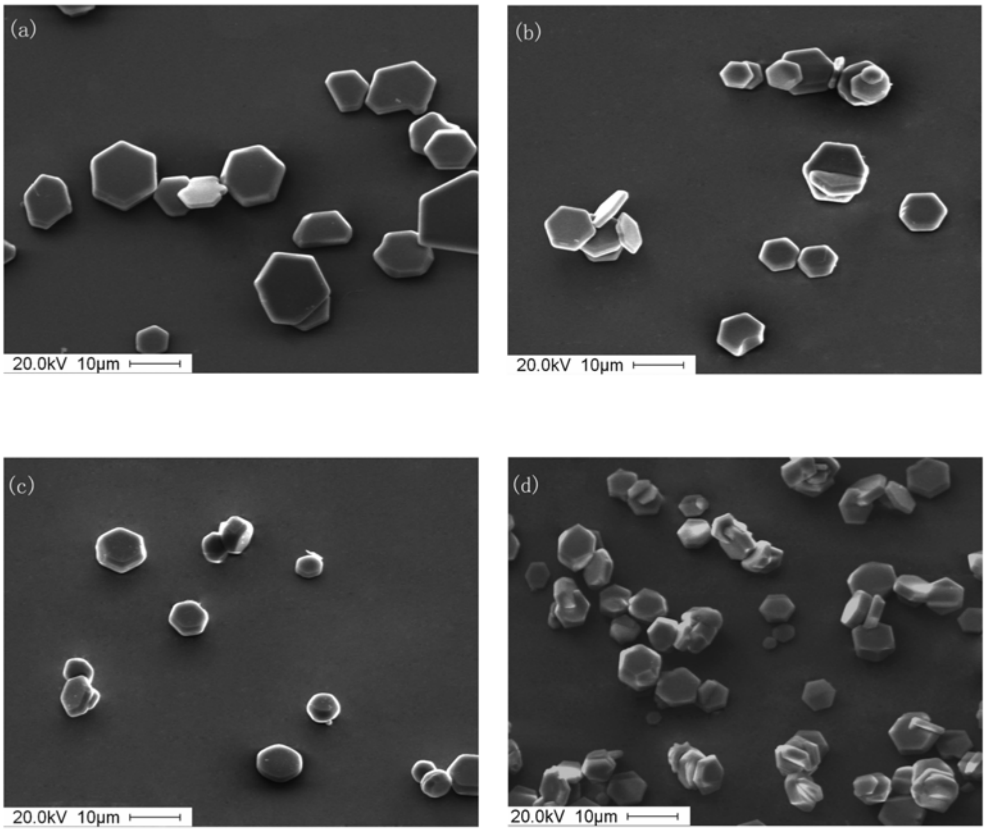

Fig. 3. The influence of $TiOSO_4$ additions on the morphology of α-Al_2O_3 platelets. (a) 3 wt% $TiOSO_4$; (b) 6 wt% $TiOSO_4$; (c) 9 wt% $TiOSO_4$; (d) 12 wt% $TiOSO_4$.

Effect of $TiOSO_4$ addition on the morphology of α-Al_2O_3 platelets

The addition of $TiOSO_4$ is helpful to obtain regular hexagonal α-Al_2O_3 platelets, as shown in Fig. 3. The more $TiOSO_4$ is added, the smaller and thicker are the particles obtained. The mean diameter and thickness of α-Al_2O_3 platelets as a function of the amount of $TiOSO_4$ addition are shown in Fig. 4. When 3 wt% $TiOSO_4$ is added, the mean diameter and thickness of plate-like particles are about 11 μm and 1.1 μm, respectively. When 12 wt% $TiOSO_4$ is added, the mean diameter and thickness change to about 7 μm and 2.5 μm, and the aspect ratio is only 2.8.

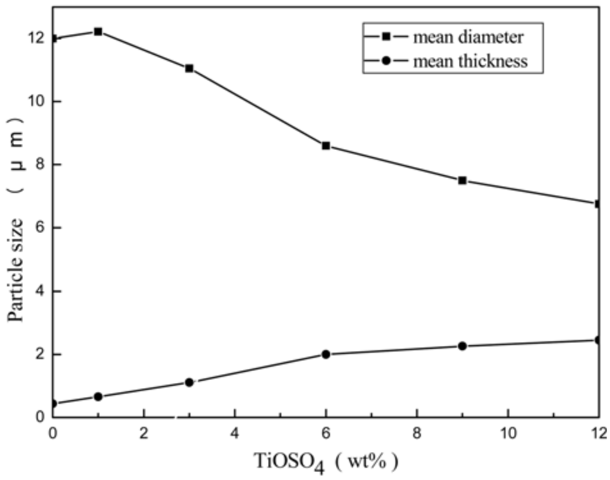

Fig. 4. The mean diameter and thickness of α-Al_2O_3 platelets as a function of $TiOSO_4$ addition amount.

Effect of $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$ addition on the morphology of α-Al_2O_3 platelets

As indicated above, when only $Na_3PO_4{\cdot}12H_2O$ is added, α-Al_2O_3 flakes can be obtained, but they are quite irregular; while when only $TiOSO_4$ is added, α-Al_2O_3 particles with a regular hexagonal shape can be obtained, but they are too thick. Fig. 5 shows α-Al_2O_3 platelets synthesized in the NaCl-KCl salt mixture with the addition of 0.51 wt% $Na_3PO_4{\cdot}12H_2O$ and 12 wt% $TiOSO_4$. In comparison with Fig.2 (b), the extra addition of $TiOSO_4$ makes the shape of α-Al_2O_3 platelets more regular. Compared with Fig. 3(d), thinner α-Al_2O_3 platelets with an aspect ratio of 12.5 are obtained due to the extra addition of $Na_3PO_4{\cdot}12H_2O$. This indicates that effective control of the morphology of plate-like α-Al_2O_3 particles may be achieved by adjusting the additions of $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$.

Discussion

The crystal structure of alumina consists of a hexagonal close-packed oxygen layer with Al^{3+} occupying the

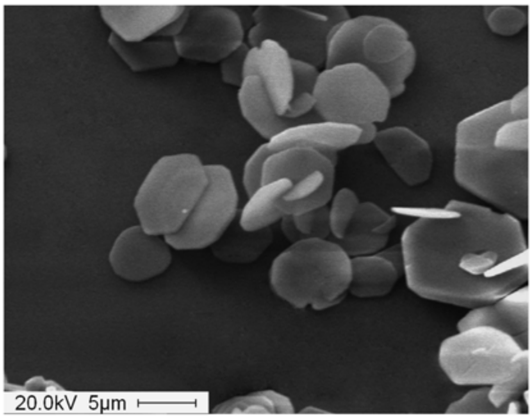

Fig. 5. The morphology of α-Al_2O_3 platelets with 0.51 wt% $Na_3PO_4·12H_2O$ and 12 wt% $TiOSO_4$ added.

interstitial sites. α-Al_2O_3 belongs to the trigonal system in which the lattice points occupy (0, 0, 0), (2/3, 1/3, 1/3) and (1/3, 2/3, 2/3) in the hexagonal coordinate system, so the {0001} faces are hexagons.

The crystal development can be regarded as a series of "growth unit" which includes the formation of growth units, the interfacial adsorption of growth units, the movement of growth units and the desorption of growth units. According to the theoretical model of anionic coordination polyhedron growth units [18], the [Al-O_6] octahedron is considered as the growth unit for α-Al_2O_3. The crystal growth and the final morphology are determined by the crystallographic orientation and the manner of combination of the growth units. The crystal faces, to which the vertexes of an anionic coordination polyhedron point, grow rapidly and they seldom appear or even disappear. The crystal faces, to which the faces of the anionic coordination polyhedron point, grow slowly and they appear predominantly. The faces, to which the edges point, grow at a middle rate and they appear at times. For α-Al_2O_3 crystals, $\{10\bar{1}10\}$ faces often disappear, {0001} faces appear predominantly and $\{11\bar{2}0\}$ faces appear at times. Therefore, α-Al_2O_3 tends to be hexagonal platelets.

However, the development of growth units and the crystal structure are greatly affected by the physical and chemical growth conditions. According to the Pauling Rule, the growth units of α-Al_2O_3 are inclined to combine together with a sharing of corners to form regular hexagonal platelets in the unforced environment. Since an entirely unforced environment can not be provided by the molten salt, it is difficult to obtain perfect particles with very regular shapes and a uniform distribution.

During crystal growth, the morphology of particles may change when some elements in the molten salt are adsorbed on the crystal surfaces owing to Van der Waals force, Coulomb force, chemical bond force etc. The effect of $Na_3PO_4·12H_2O$ might be attributed to the adsorption of PO_4^{3-} on the crystal surfaces. In the [Al-O_6] octahedron, O^{2-} is located on the six apex angles. When the growth units combine in the form of faces, PO_4^{3-} is inclined to adsorb on {0001} faces where the apex angles of the [Al-O_6] octahedron is the least owing to the Coulomb force. Because PO_4^{3-} has a large ionic strength, the superimposition of growth units on {0001} faces is effectively inhibited by PO_4^{3-}, and the growth of particles in the thickness direction [0001] is limited. The growth units tend to superimpose on the other two faces $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ when they combine with each other. As a result, thin and irregular platelets are finally developed. Also, the agglomerating and overlapping phenomena of platelets can be effectively improved due to the electrostatic resistance and steric-hindrance when enough PO_4^{3-} is adsorbed on the α-Al_2O_3 crystal surfaces.

The way $TiOSO_4$ affects the growth of α-Al_2O_3 platelets is different from $Na_3PO_4·12H_2O$ because Ti^{4+} can form a solid solution with Al_2O_3. Nitta *et al* showed the existence of a small amount of hydrated titania in alumina powders by means of chemical analysis [16], which proved the substitution of Ti^{4+} for Al^{3+}. Generally, in order to keep an electrostatic balance, three Ti^{4+} ions will diffuse into the crystal lattice to substitute four Al^{3+} ions at high temperatures, leading to extra Al^{3+} vacancies. This substitution process affects the structural style of the "growth unit" and development of crystals significantly. The growth velocity of $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ crystal faces is reduced and there is a minor difference in the growth velocity of various crystal faces with the increasing amounts of $TiOSO_4$. At last, well-developed hexagon-like α-Al_2O_3 particles with a decreased size and increased thickness are formed.

As indicated above, the growth of particles in the thickness direction [0001] is inhibited owing to the addition of PO_4^{3-}. Besides, the addition of Ti^{4+} promotes the formation of regular hexagonal α-Al_2O_3 particles with a decreased size and increased thickness. When a correct amount of $Na_3PO_4·12H_2O$ and $TiOSO_4$ are added, the shape and aspect ratio of α-Al_2O_3 platelets can be controlled effectively owing to the combined action of PO_4^{3-} and Ti^{4+}.

Conclusions

The influence of additives on the morphology of α-Al_2O_3 platelets by molten salt synthesis was investigated. When $Na_3PO_4·12H_2O$ is added, α-Al_2O_3 platelets become thin and quite irregular owing to the adsorption of PO_4^{3-} on {0001} faces. Also, less overlapped particles can be found. When $TiOSO_4$ is added, regular hexagonal α-Al_2O_3 platelets with a decreased size and increased thickness are formed because of the substitution of Ti^{4+} for Al^{3+}. When 0.51 wt% $Na_3PO_4·12H_2O$ and 12 wt% $TiOSO_4$ are added, α-Al_2O_3 platelets with a regular shape and an aspect ratio of 12.5 are obtained.

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