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Morphology control of α-Al_2O_3 platelets by molten salt synthesis

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Abstract

It is of great importance to control the morphology of α-Al_2O_3 plate-like powders since α-Al_2O_3 platelets with different shapes are needed in various applications. This paper was focused on how to control the morphology of α-Al_2O_3 platelets by molten salt synthesis. Results show that the morphology of α-Al_2O_3 platelets is affected by the heating temperature, heating time, the molten salts species, the weight ratio of salt to powders, additives and the addition of nano-sized seeds. Especially, it is very effective to control the morphology of α-Al_2O_3 platelets by adjusting the addition of additives such as $Na_3PO_4 \cdot 12H_2O$ and $TiOSO_4$. α-Al_2O_3 flakes with irregular shape are obtained by the addition of $Na_3PO_4 \cdot 12H_2O$, while thick α-Al_2O_3 particles with hexagonal shape are obtained by the addition of $TiOSO_4$. The combination addition of $Na_3PO_4 \cdot 12H_2O$ and $TiOSO_4$ makes it possible to obtain thin α-Al_2O_3 platelets with discal shape. A small amount of nano-sized seeds addition also has a strong effect on the size of α-Al_2O_3 platelets. However, if the seeds are added too much, the overlapping and abnormal crystal growth of α-Al_2O_3 platelets occur, and the size distribution becomes nonuniform. The effect mechanism of additives and seeds on the morphology of α-Al_2O_3 platelets was also discussed in this paper.

Keywords: B. Platelets; D. α-Al_2O_3; Molten salt synthesis; Additives; Seeds

1. Introduction

Plate-like α-Al_2O_3 powders are applied widely because they exhibit excellent properties, which derive from α-Al_2O_3 and the special two-dimensional structure. For example, α-Al_2O_3 platelets can be added into the ceramics as seeds to induce the abnormal grain growth, leading to the improvement of fracture toughness [1]. Textured Al_2O_3 ceramics with anisotropic properties can be prepared by templated grain growth when suitable α-Al_2O_3 platelets are chosen as templates [2]. Due to high aspect ratio and heat conductivity, α-Al_2O_3 platelets can be added into the plastics to improve the thermal conductivity [3–5]. The commercial slurry for the primary polishing of hard disc is superior in good dispersion stability and desirable orientation when α-Al_2O_3 platelets are added [4]. Since α-Al_2O_3 platelets with different shapes are needed in various applications [4,5], it is of great importance to control the morphology.

Molten salt synthesis is one of the most important techniques to prepare plate-like α-Al_2O_3 powders [5–10]. Compared with the conventional solid-state reaction, the preparation temperature and time can be greatly reduced because of high diffusivity of the components in the molten salt. Besides, the morphology of α-Al_2O_3 can be easily changed by many factors, for example, the precursors, the molten salts, heating temperature, heating time and so on. In this paper, α-Al_2O_3 platelets were obtained by molten salt synthesis using $Al_2(SO_4)_3$ as raw materials, which was often chosen during molten salt synthesis in the previous investigations [5–9]. First, the effects of heating temperature, heating time, the molten salts species, and the weight ratio of salt to powders on the morphology of α-Al_2O_3 were studied. Considering that the addition of some additives not only decreases the transformation temperature of α-Al_2O_3 [11–14], but also changes the morphology of α-Al_2O_3 platelets obviously [5,8], it is necessary to investigate to control the morphology of α-Al_2O_3 platelets by additives. As the most often-used additives, PO_4^{3-} (introduced by trisodium phosphate) and Ti^{4+} (introduced by titanyl sulfate) were chosen in this paper to study the influence of additives on the morphology of α-Al_2O_3 platelets synthesized by molten salt synthesis. The

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platelet morphology of α-Al_2O_3 powders was also significantly influenced by the addition of seeds [4,5,9], thus the effect of nano-sized α-Al_2O_3 seeds on the morphology of α-Al_2O_3 platelets was also studied. At the same time, the effect mechanism of $Na_3PO_4{\cdot}12H_2O$, $TiOSO_4$ and seeds on the morphology of α-Al_2O_3 platelets was discussed.

2. Experimental procedure

α-Al_2O_3 platelets were prepared according to the flow chart shown in Fig. 1. $Al_2(SO_4)_3{\cdot}18H_2O$ (purity: 99.5%, Meixing Chemical Company, Shanghai) and Na_2CO_3 (purity: 99.5%, Hongguang Chemical Company, Shanghai) were used as raw materials. Either mixture sulfate salts (Na_2SO_4:K_2SO_4 = 1:1, molar ratio) or mixture chloride salts (NaCl:KCl = 1:1, molar ratio) were used as molten salts when considering that the mixture salts are more beneficial to the development of α-Al_2O_3 platelets than pure salt. During the preparation of saturated solution A, $Al_2(SO_4)_3{\cdot}18H_2O$ and the salts were mixed according to the ratio of 1:2, 1:4 and 1:6 respectively, and then were dissolved in de-ionized water at 70 °C. The saturated solution B was obtained by dissolving Na_2CO_3 in de-ionized water. Solution B was added slowly into solution A at 70 °C and kept stirring rapidly for 15 min. The obtained gel was dried at 120 °C for 24 h and then the product was heated at 1100–1300 °C for 0.5–8 h. The final powders were ultrasonic cleaned with de-ionized water repeatedly to remove the remained salt and then dried.

Either 0.17–0.68% $Na_3PO_4{\cdot}12H_2O$ or 1–12% $TiOSO_4$ was added during the formation of sol–gel to control the morphology of α-Al_2O_3 powders. The addition amount of $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$ is presented by weight, respectively in terms of P_2O_5 and $TiOSO_4$, relative to the weight of α-Al_2O_3 particles. In order to study the effect of nano-sized α-Al_2O_3 seeds on the morphology of α-Al_2O_3 platelets, 0.1–1 wt.% globular α-Al_2O_3 powders with the average diameter of 60 nm were added during the formation of sol–gel. Mixture chloride salts which were composed of NaCl and KCl according to molar ratio of 1:1 were used as molten salts.

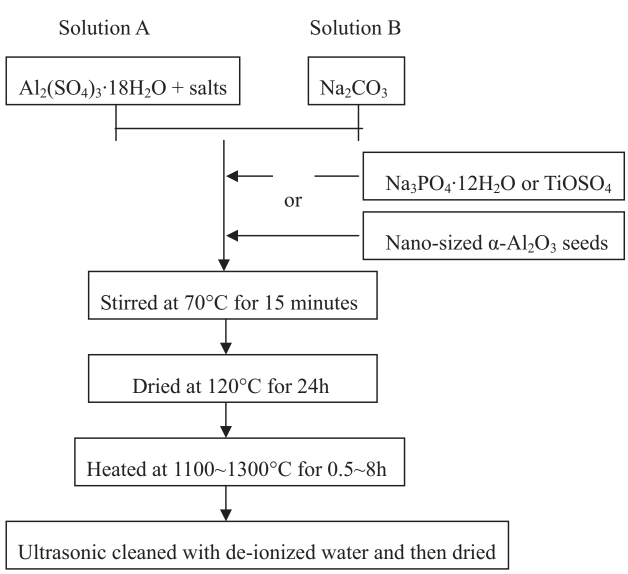

Fig. 1. Flow chart of α-Al_2O_3 platelets.

The phase assembly of the final powders was examined by X-ray diffraction analysis (RIGAKU, D/MAX-RB) with CuKα radiation (λ = 1.5418 Å). The morphology of α-Al_2O_3 particles was observed by scanning electron microscope (SEM, S-570).

3. Results and discussion

3.1. Effect of processing parameters on the morphology of α-Al_2O_3 platelets

X-ray diffraction analysis indicates single phase α-Al_2O_3 is synthesized by molten salt synthesis when heated above 1100 °C. The increase of heating temperature and time helps to the development of α-Al_2O_3 and it is easy to obtain well-developed α-Al_2O_3 platelets with big size. However, there is no obvious change in the shape and size of α-Al_2O_3 platelets when the heating temperature increases above 1200 °C or the time exceeds 4 h. Therefore, from the viewpoint of economy, the heating temperature should not be higher than 1200 °C and the heating time should not be longer than 4 h in order to obtain well-developed hexagonal α-Al_2O_3 platelets. In subsequent experiments, α-Al_2O_3 powders were synthesized at 1200 °C for 4 h.

In addition to the heating temperature and time, the morphology of α-Al_2O_3 platelets is affected by the ratio of salt to powders. Fig. 2(a) shows the morphology of α-Al_2O_3 platelets heated at 1200 °C for 4 h in NaCl–KCl flux when the ratio of salt to powders is 2:1. Most of α-Al_2O_3 platelets are hexagonal, but there are some overlapped particles. The more the molten salts are used, the more the crystal growth space is provided and the higher diffusivity of the components in the molten salts is. Therefore, when the ratio of salt to powders increases to 4:1, the overlapping of powders improves, and the diameter of α-Al_2O_3 platelets becomes bigger, see Fig. 2(b). But if the ratio of salt to powders is higher than 6:1, the diffusion distance of the components in the molten salts increases. On the contrary, it is not easy to obtain well-developed hexagonal α-Al_2O_3 platelets, and the size is nonuniform, see Fig. 2(c). High ratio of salt to powders also means that much more water will be spent to remove the salts, so the ratio of salt to powders is fixed to be 4:1 in subsequent experiments.

When different fluxes are chosen, there is obvious difference in the morphology of α-Al_2O_3 platelets even though the heating temperature, heating time and the ratio of salt to powders are fixed. As shown in Fig. 2(d), the shape of α-Al_2O_3 particles becomes irregular and the size is nonuniform when Na_2SO_4–K_2SO_4 is used.

3.2. Effect of additives on the morphology of α-Al_2O_3 platelets

The morphology of α-Al_2O_3 platelets is changed easily by the additives rather than processing parameters. The addition of 0.17 wt.% $Na_3PO_4{\cdot}12H_2O$ only leads to a little decrease in the diameter of α-Al_2O_3 platelets. When 0.34–0.68 wt.% $Na_3PO_4{\cdot}12H_2O$ are added, the thickness of α-Al_2O_3 is reduced

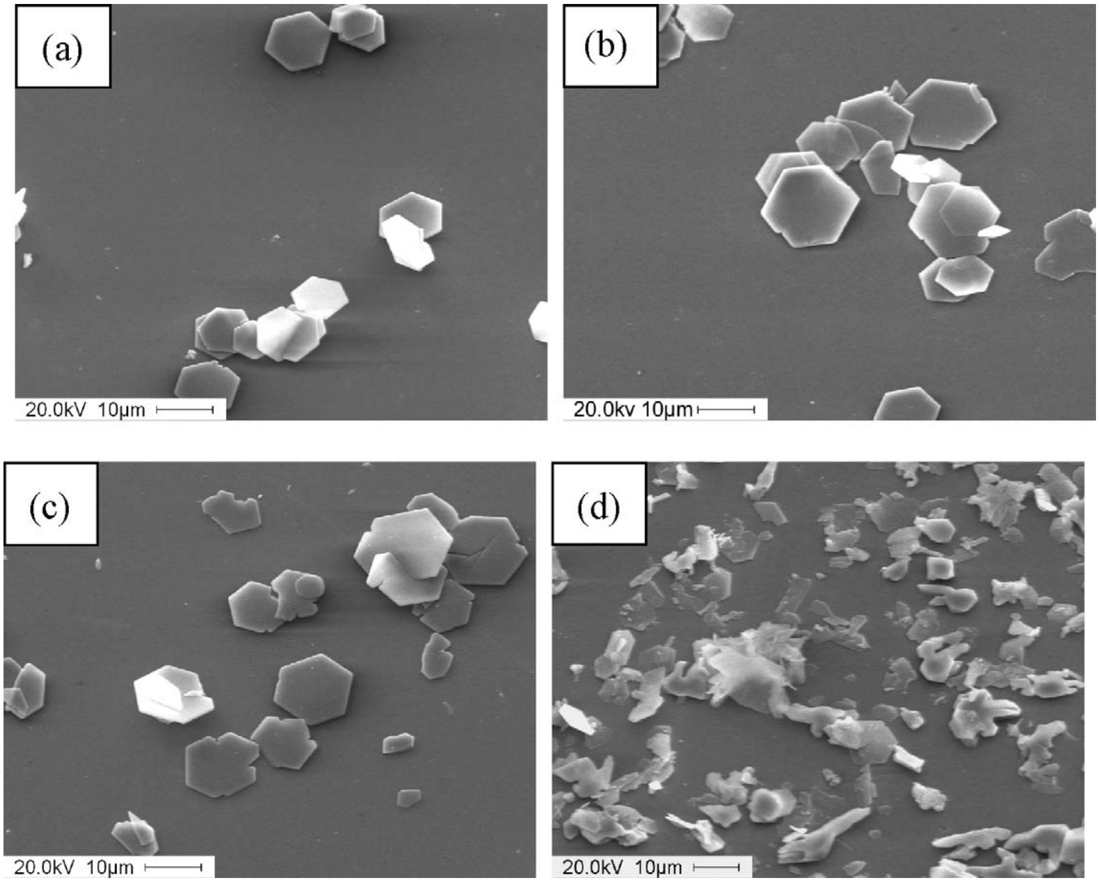

Fig. 2. The morphology of α-Al_2O_3 platelets heated at 1200 °C for 4 h using different molten salts and different ratio of salt to powders. (a) NaCl–KCl, ratio of salt to powders 2:1; (b) NaCl–KCl, ratio of salt to powders 4:1; (c) NaCl–KCl, ratio of salt to powders 6:1; and (d) Na_2SO_4–K_2SO_4, ratio of salt to powders 4:1.

greatly. At the same time, the agglomeration of α-Al_2O_3 powders is inhibited effectively and the particles are overlapped no longer. However, the shape of α-Al_2O_3 flakes becomes quite irregular and the size distribution becomes very broad. SEM micrograph of α-Al_2O_3 flakes added by 0.51 wt.% $Na_3PO_4 \cdot 12H_2O$ in NaCl–KCl flux is shown in Fig. 3(a). α-Al_2O_3 flakes synthesized in Na_2SO_4–K_2SO_4 flux show similar morphology, see Fig. 3(b).

The addition of $TiOSO_4$ is helpful in the formation of hexagonal α-Al_2O_3 platelets synthesized in NaCl–KCl flux. Meanwhile, α-Al_2O_3 particles tend to become small and thick, see Fig. 4. When the addition amount of $TiOSO_4$ increases from 1 wt.% to 6 wt.%, the average diameter of plate-like particles decreases from about 12.2 μm to 8.6 μm, and the average thickness increases quickly from 0.7 μm to 2.1 μm. There is a slight change in the diameter and thickness of α-Al_2O_3 platelets when more than 6 wt.% $TiOSO_4$ are added.

As indicated above, α-Al_2O_3 flakes with irregular shape are obtained by the addition of $Na_3PO_4 \cdot 12H_2O$, while thick α-Al_2O_3 particles with hexagonal shape are obtained by the

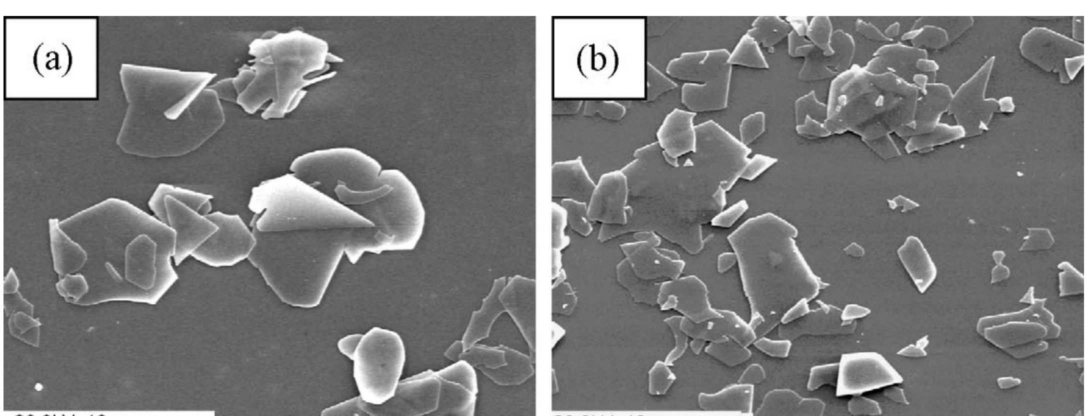

Fig. 3. The morphology of α-Al_2O_3 platelets added by 0.51 wt.% $Na_3PO_4 \cdot 12H_2O$ in different fluxes: (a) NaCl–KCl and (b) Na_2SO_4–K_2SO_4.

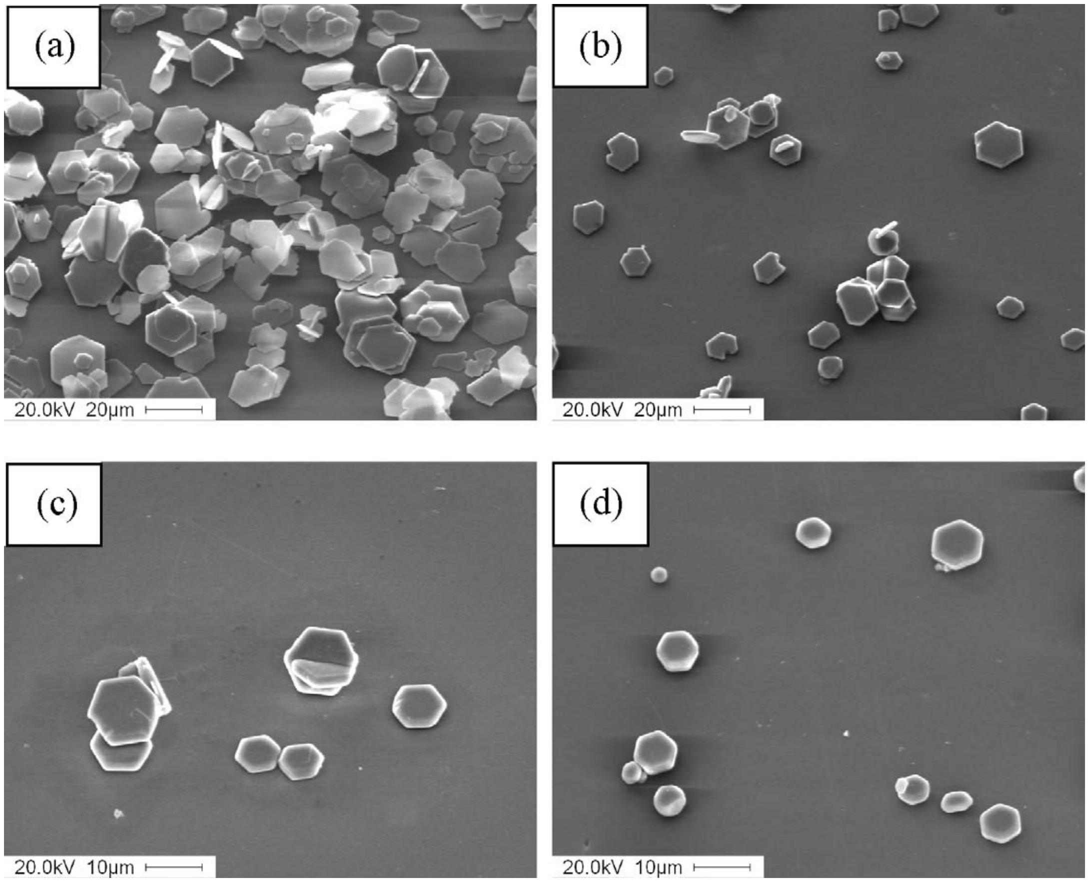

Fig. 4. The effect of $TiOSO_4$ addition on the morphology of α-Al_2O_3 platelets synthesized in NaCl–KCl flux: (a) 1 wt.% $TiOSO_4$; (b) 3 wt.% $TiOSO_4$; (c) 6 wt.% $TiOSO_4$; (d) 11 wt.% $TiOSO_4$.

addition of $TiOSO_4$. The combination addition of $Na_3PO_4 \cdot 12H_2O$ and $TiOSO_4$ probably leads to the further change in the morphology of α-Al_2O_3 platelets. Fig. 5(a) and (b) shows α-Al_2O_3 platelets synthesized in NaCl–KCl flux when 0.51 wt.% $Na_3PO_4 \cdot 12H_2O$ + 3 wt.% $TiOSO_4$ and 0.51 wt.% $Na_3PO_4 \cdot 12H_2O$ + 12 wt.% $TiOSO_4$ are added, separately. The addition of $Na_3PO_4 \cdot 12H_2O$ helps the formation of thin α-Al_2O_3 platelets, but their shape is still irregular if only 3 wt.% $TiOSO_4$ is added, see Fig. 5(a). Thin α-Al_2O_3 platelets with discal shape are obtained by the addition of 0.51 wt.% $Na_3PO_4 \cdot 12H_2O$ + 12 wt.% $TiOSO_4$, see Fig. 5(b). A similar phenomenon is also found in α-Al_2O_3 platelets synthesized in Na_2SO_4–K_2SO_4 flux, as shown in Fig. 5(c) and (d). Especially, when 0.51 wt.% $Na_3PO_4 \cdot 12H_2O$ + 12 wt.% $TiOSO_4$ are added, not only thin α-Al_2O_3 platelets with discal shape are obtained in Na_2SO_4–K_2SO_4 flux, but also the overlapping and agglomeration of α-Al_2O_3 platelets are restrained, see Fig. 5(d). It is very effective to control the morphology of α-Al_2O_3 platelets by adjusting the addition of $Na_3PO_4 \cdot 12H_2O$ and $TiOSO_4$.

3.3. Effect of nano-sized seeds on the morphology of α-Al_2O_3 platelets

The size of α-Al_2O_3 platelets is affected significantly by the addition of a small amount of nano-sized seeds. Fig. 6 shows SEM micrographs of α-Al_2O_3 synthesized in NaCl–KCl flux when added by 0.1 wt.%, 0.5 wt.% and 1 wt.% seeds. For convenience to compare, the micrograph of α-Al_2O_3 platelets without seed addition is also given. The average diameter of α-Al_2O_3 platelets decreases from about 12.2 μm to 1.8 μm quickly even though added by 0.1 wt.% seeds. With the increase of seed amount, the diameter and aspect ratio of α-Al_2O_3 platelets tends to decrease, and the size becomes nonuniform. When 0.5 wt.% seeds are added, there are some overlapped particles and a few α-Al_2O_3 crystals with abnormal growth. The addition of 1 wt.% seeds leads to more crystals with abnormal growth and agglomeration of powders, and the size distribution of α-Al_2O_3 platelets becomes very broad. It seems that the seeds are added too much to obtain a narrow size distribution of α-Al_2O_3 platelets.

4. Discussion

4.1. The effect mechanism of $Na_3PO_4 \cdot 12H_2O$ and $TiOSO_4$ on the morphology of α-Al_2O_3 platelets

The crystal structure of α-Al_2O_3 is composed of a hexagonal close-packed oxygen layer with Al^{3+} occupying the interstitial sites. α-Al_2O_3 belongs to trigonal system in which the lattice points occupy (0, 0, 0), (2/3, 1/3, 1/3) and (1/3, 2/3, 2/3) for hexagonal coordinate, so the {0 0 0 1} faces are hexagon.

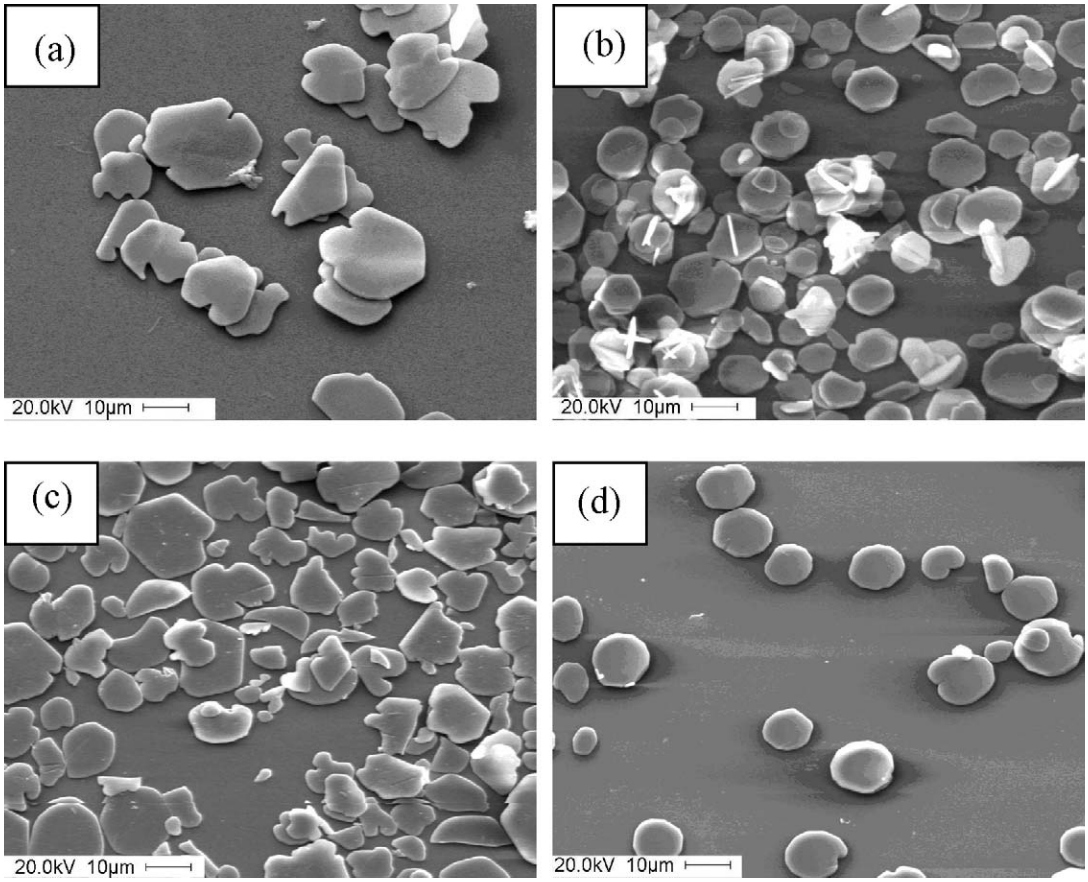

Fig. 5. The effect of combination addition of $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$ on the morphology of α-Al_2O_3 platelets in different fluxes: (a) NaCl–KCl, 0.51 wt.% $Na_3PO_4{\cdot}12H_2O$ + 3 wt.% $TiOSO_4$; (b) NaCl–KCl, 0.51 wt.% $Na_3PO_4{\cdot}12H_2O$ + 12 wt.% $TiOSO_4$; (c) Na_2SO_4–K_2SO_4, 0.51 wt.% $Na_3PO_4{\cdot}12H_2O$ + 3 wt.% $TiOSO_4$; (d) Na_2SO_4–K_2SO_4, 0.51 wt.% $Na_3PO_4{\cdot}12H_2O$ + 12 wt.% $TiOSO_4$.

The crystal development can be regarded as a ‘‘growth unit’’ course. It includes the formation of growth unit, the interfacial adsorption of growth unit, the movement of growth unit and the desorption of growth unit. According to the theoretical model of anionic coordination polyhedron growth units, the crystal growth and the final morphology are dependent on the crystallographic orientation and the combination manner of the growth units [15]. In molten salts, [Al–O_6] octahedron is considered as the growth unit for α-Al_2O_3. $\{1\,0\,\bar{1}\,0\}$ faces often disappear, $\{0\,0\,0\,1\}$ faces appear predominantly and $\{1\,1\,\bar{2}\,0\}$ faces sometimes appear. Therefore, α-Al_2O_3 tends to be hexagonal platelets.

During crystal growth, the morphology of particles may be changed when some ions in the molten salt are adsorbed on the crystal surfaces. When $Na_3PO_4{\cdot}12H_2O$ is added, PO_4^{3-} is inclined to adsorb on $\{0\,0\,0\,1\}$ faces where the apex angles of [Al–O_6] octahedron is the least owing to the Coulomb force. Because PO_4^{3-} has large ionic strength, the superimposition of growth units on $\{0\,0\,0\,1\}$ faces is effectively prohibited by PO_4^{3-}, and the growth of α-Al_2O_3 in the thickness is restricted. The growth units tend to superimpose on the other two faces $\{1\,0\,\bar{1}\,0\}$ and $\{1\,1\,\bar{2}\,0\}$ when they combine with each other. As a result, thin and irregular platelets are finally obtained. Besides, the agglomeration and overlapping of platelets are effectively restrained owing to the electrostatic resistance and stereo-hindrance when enough PO_4^{3-} is adsorbed on the α-Al_2O_3 crystal surfaces.

When $TiOSO_4$ is added, Ti^{4+} ions can diffuse into Al_2O_3 to substitute Al^{3+} ions at high temperatures [5]. In order to keep the electrostatic balance, three Ti^{4+} ions diffuse into the crystal lattice to substitute four Al^{3+} ions. As a result, the development of growth units and crystals may be affected by the lattice deformation due to the existence of extra Al^{3+} vacancies. The growth velocity of $\{1\,0\,\bar{1}\,0\}$ and $\{1\,1\,\bar{2}\,0\}$ crystal faces is reduced and there is a minor difference in the growth velocity of various crystal faces. Thus the addition of $TiOSO_4$ is helpful in the formation of well-developed hexagonal α-Al_2O_3 particles with decreased size and increased thickness.

The morphology of α-Al_2O_3 platelets can be adjusted under the combined action of PO_4^{3-} and Ti^{4+}. On the one hand, the superimposition of growth units on $\{0\,0\,0\,1\}$ faces is effectively inhibited by PO_4^{3-}. On the other hand, the difference in the growth velocity of various crystal faces is reduced by Ti^{4+}. The combination addition of $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$ makes it possible to obtain thin α-Al_2O_3 platelets with discal shape.

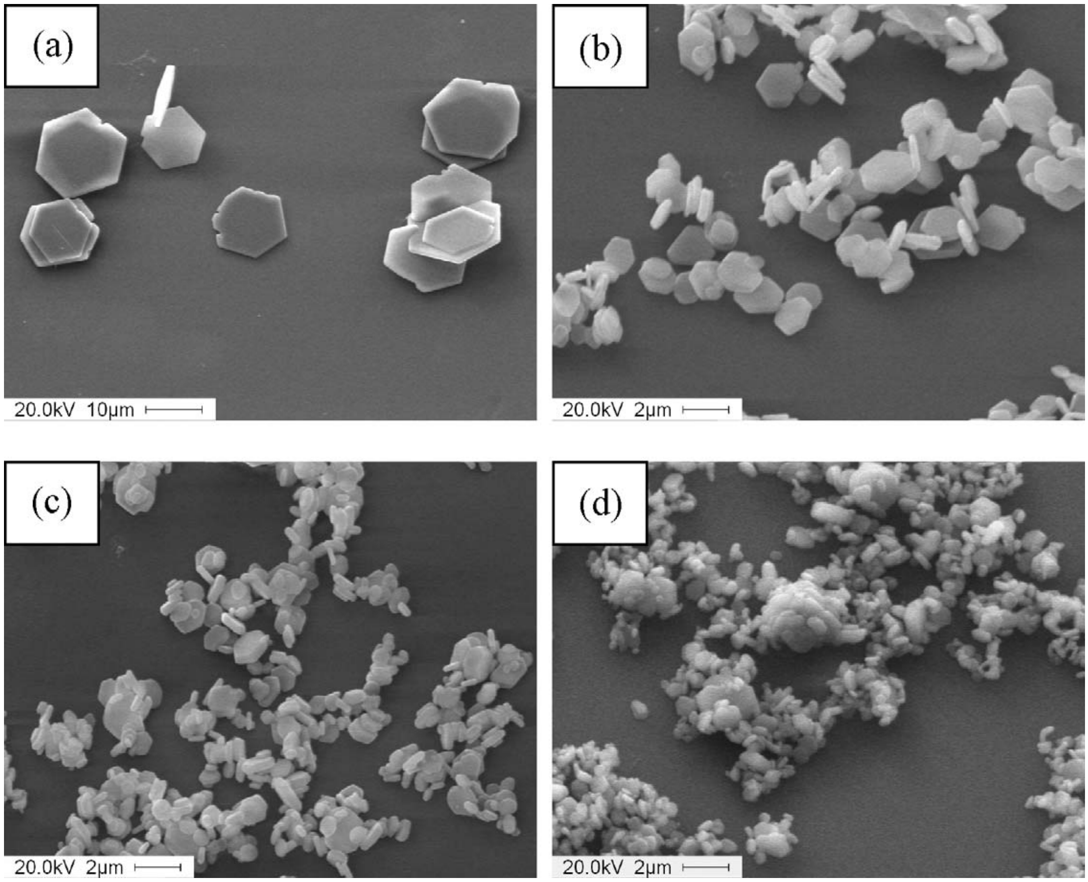

Fig. 6. The effect of nano-sized seeds on the morphology of α-Al_2O_3 platelets: (a) 0 wt.% seeds; (b) 0.1 wt.% seeds; (c) 0.5 wt.% seeds; (d) 1 wt.% seeds.

4.2. The effect mechanism of nano-sized seeds on the morphology of α-Al_2O_3 platelets

The formation of α-Al_2O_3 platelets in molten salt should be a nucleation-growth process. When solution B is added slowly into solution A, the following reaction will happen.

$$3Na_2CO_3 + Al_2(SO_4)_3 + 3H_2O = 3Na_2SO_4 + 2Al(OH)_3 + 3CO_2\uparrow$$

During heating, the thermal decomposition of $Al(OH)_3$ results in the formation of α-Al_2O_3, which can act as the nuclei of α-Al_2O_3 platelets. When nano-sized α-Al_2O_3 seeds are added, extra nucleation sites can be provided by the seeds since they have small size and the same crystal structure as α-Al_2O_3 nuclei. In the later stage, α-Al_2O_3 particles grow large from the nuclei provided by either the nano-sized seeds or α-Al_2O_3 formed by the decomposition of $Al(OH)_3$. Therefore, fine α-Al_2O_3 platelets are obtained accompanied by the increase in the nuclei of α-Al_2O_3. However, α-Al_2O_3 platelets directly developed from nano-sized α-Al_2O_3 seeds have small aspect ratio because it is limited by globular shape of α-Al_2O_3 seeds. As a result, the diameter and aspect ratio of α-Al_2O_3 platelets tends to decrease when more nano-sized α-Al_2O_3 seeds are added. If too much seeds are added, some seeds which close up to each other are probably integrated by α-Al_2O_3 crystals precipitated during molten salt synthesis. The phenomena of overlapping and abnormal crystal growth maybe take place. The size distribution of α-Al_2O_3 platelets becomes very broad.

5. Conclusions

α-Al_2O_3 platelets are synthesized by molten salt synthesis using $Al_2(SO_4)_3$ as raw materials, and their morphology can be changed by the heating temperature, heating time, the molten salts species, the weight ratio of salt to powders, additives and the addition of nano-sized seeds. Especially, it is very effective to control the morphology of α-Al_2O_3 platelets by adjusting the addition of additives such as $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$. α-Al_2O_3 flakes with irregular shape are obtained by the addition of $Na_3PO_4{\cdot}12H_2O$, while thick α-Al_2O_3 particles with hexagonal shape are obtained by the addition of $TiOSO_4$. The combination addition of $Na_3PO_4{\cdot}12H_2O$ and $TiOSO_4$ makes it possible to obtain thin α-Al_2O_3 platelets with discal shape. A small amount of nano-sized seeds addition also has a strong effect on the size of α-Al_2O_3 platelets. However, if the seeds are added too much, the overlapping and abnormal crystal growth of α-Al_2O_3 platelets occur, and the size distribution becomes nonuniform.

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