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# Influences of precursor and additive on the morphology of nanocrystalline α-alumina

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## Abstract

The temperature for complete transformation to α-$Al_2O_3$ changed with precursor and the transformation temperature is lower in the case of using aluminum nitrate precursor as compared to aluminum sulfate precursor. The size of alumina particles obtained using aluminum nitrate precursor was smaller than that obtained using aluminum sulfate precursor, and this may be related to the ability of precursor anion to provide colloid stability. The particles obtained from aluminum nitrate precursor have elongated shape, while those obtained from aluminum sulfate precursor have spherical shape, and it could be attributed to the different characteristics of precipitate formed in the initial stage of reaction. The addition of $AlF_3$ results in decrease of the phase transition temperature to α-alumina. The effect of $AlF_3$ additive on modification of morphology of particles is different depending on the precursor. The change of morphology of α-alumina particles to the plate-like shape was observed in the case of using aluminum nitrate precursor, but not in the case of using aluminum sulfate precursor.

*Keywords:* A. Ceramics; B. Chemical synthesis; C. Electron microscopy; D. Microstructure

## 1. Introduction

Recently much attention has been paid to the synthesis of nanocrystalline ceramics. It is well known that the mechanical properties of ceramics strongly depend on their microstructure, which closely relates with the shape and size of the ceramic particles. It has been shown that the mechanical properties of ceramics can be improved by the formation of nanocrystalline structure [1]. Among various ceramics, alumina, especially nano-sized α-alumina has proven to be one of the most important materials because it has many applications both as structural and functional materials due to its excellent properties [2]. It was reported that nano-sized ball-like alumina could improve some mechanical properties, such as the fracture strength and toughness [1]. In addition, it was demonstrated that the morphology of alumina particles affects the mechanical properties [3]. The nano-sized plate-like grains can increase fracture toughness more significantly than the ball-like grains because the plate-like grains can form crack bridging easily in ceramics matrix [4,5]. Thus, it can be said that the alumina ceramic components required for advanced engineering and structural applications need particles having desired morphology. It was reported that the precursor could affect the morphology and particle size of micro-sized alumina [6]. It was also demonstrated that some additive, especially fluorides, could decrease phase transformation temperature to α-alumina and change the morphology of alumina [4,7].

In the present work, nanocrystalline α-alumina particles were prepared using different precursors and additive. The influences of precursor (aluminum sulfate or aluminum nitrate) and additive (metal fluorides) on the morphology of alumina particles were studied.

## 2. Experimental

The nano-sized α-alumina particles were prepared using a method reported in literature [4]. $NH_4OH$ solution

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($0.2\,\mathrm{mol\,l^{-1}}$) was added slowly into $Al(NO_3)_3 \cdot 9H_2O$ or $Al(SO_4)_3 \cdot 18H_2O$ solution ($4.5\,\mathrm{mol\,l^{-1}}$) under stirring. Polyethylenegylcol (PEG) solution was used as a dispersant. The pH of slurry was adjusted to 9.0 and then the precipitate was aged with constant stirring for 1 h. The slurry was filtered and dried at 70 °C for 24 h. After that the dried gel was milled with alcohol in high purity alumina medium for 24 h. In some cases, $AlF_3$ (2 wt%) was added in this stage. Then gel was dried at 55 °C for 24 h and calcined at different temperatures for 1 h with heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$. The particle phase was identified using an X-ray diffractometer (XRD; PHILIPS, X'Pert-MPD System) with Ni filtered Cu K$\alpha$ radiation. The particle morphology was characterized by scanning electron microscopy (FE-SEM; JEOL, JSM-6700F).

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the particles obtained from the aluminum nitrate or aluminum sulfate precursor without $AlF_3$ additive and calcined at different temperatures. In the case of using aluminum nitrate precursor (Fig. 1(a)), small diffraction peaks corresponding $\theta$-$Al_2O_3$ have been found for the sample calcined at 1000 °C and the phase transformation of $\theta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ completed at 1100 °C. On the contrary, in the case of using aluminum sulfate precursor (Fig. 1(b)), $\theta$-$Al_2O_3$ and $\alpha$-$Al_2O_3$ coexisted for the sample calcined at 1100 °C and high intensities of $\alpha$-$Al_2O_3$ peaks were observed after increasing calcination temperature up to 1200 °C. Normally, the phase transformation temperature of $\theta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ is as high as 1200 °C [8]. It can be seen that the temperature for complete transformation to $\alpha$-$Al_2O_3$ changed with precursor and the transformation temperature is lower in the case of aluminum nitrate precursor as compared to aluminum sulfate precursor. It was reported that $NH_4NO_3$ is formed during the preparation of alumina from aluminum nitrate and ammonia solution [8]. The $NH_4NO_3$ decomposes to release a large amount of energy during calcination, leading to the decrease of temperature for the complete transformation of $\theta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ [4]. In the present work, it seems that the presence of $NH_4NO_3$ results in decrease of the complete transformation temperature for the sample obtained from aluminum nitrate since the $NH_4NO_3$ can be formed only in the case of using aluminum nitrate precursor.

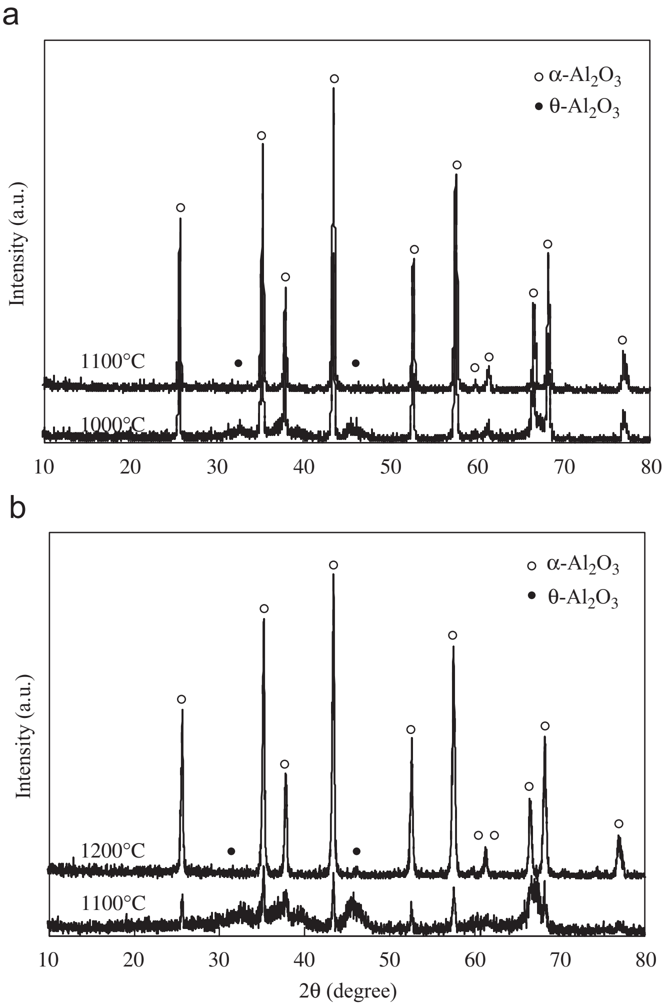

Fig. 1. XRD patterns of the particles obtained without $AlF_3$ additive (a) aluminum nitrate precursor and (b) aluminum sulfate precursor.

Fig. 2 shows SEM micrographs of the $\alpha$-alumina particles obtained without $AlF_3$ additive. The particles shown in Fig. 2(a) were obtained using aluminum nitrate as a precursor and calcined at 1100 °C and those in Fig. 1(b) were obtained aluminum sulfate as a precursor and calcined at 1200 °C. It can be seen in Fig. 2 that the particles obtained from aluminum nitrate precursor are smaller and have a wider size distribution as compared with those obtained from aluminum sulfate precursor. The average particle sizes of $\alpha$-alumina obtained using aluminum and nitrate aluminum sulfate precursor were found to be 118 and 200 nm, respectively. This could be attributed to the poorer ability of sulfate, compared with nitrate, to provide colloid stability that results in termination of agglomeration of the primary particles formed at a larger size [6]. It can be also observed that the particles obtained from aluminum nitrate precursor have elongated shape, while those obtained from aluminum sulfate precursor have spherical shape. It was observed in the initial stage of reaction that aluminum nitrate precursor formed voluminous gelatinous precipitate, whereas aluminum sulfate precursor produced compact granular powders. Similar phenomena were observed by Ramanathan et al. [6] who synthesized alumina powder by the reaction of aluminum nitrate or aluminum sulfate with urea. They claimed that $Al(OH)_3$ gel and amorphous powder of $Al_4(OH)_{10}SO_4$ were formed in the initial stage of reaction from aluminum nitrate and aluminum sulfate precursor, respectively. Thus the change of shape of resultant $\alpha$-alumina particles with precursor could be attributed to the different characteristics of precipitate formed in the initial stage of reaction. The open structure of gelatinous precipitate formed from aluminum nitrate precursor allowed compact crystallites of

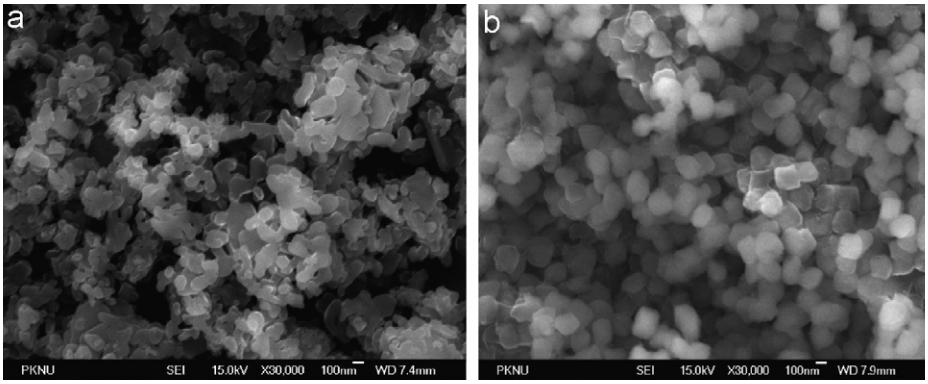

Fig. 2. SEM micrographs of the α-alumina particles obtained without $AlF_3$ additive (a) aluminum nitrate precursor calcined at 1100 °C and (b) aluminum sulfate precursor calcined at 1200 °C.

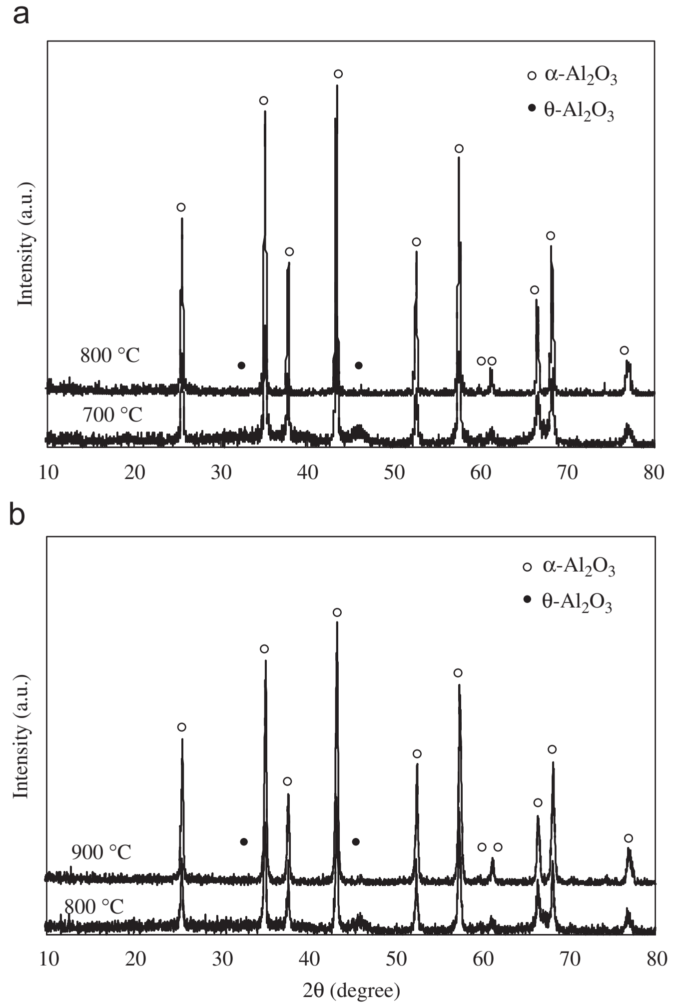

Fig. 3. XRD patterns of the particles obtained with $AlF_3$ additive (a) aluminum nitrate precursor and (b) aluminum sulfate precursor.

boehmite formed to undergo rearrangement and agglomeration freely, resulting in the evolution of the typical morphology characteristics of boehmite, namely elongated structure [6]. On the other hand, the compact and strongly bonded agglomerates formed initially from aluminum sulfate precursor retained their structure during crystallization into boehmite, resulting in spherical structure of final α-alumina particles [6].

Fig. 3 shows the XRD patterns of the particles obtained from the aluminum salt precursors with addition of $AlF_3$ and calcined at different temperatures. It is clear that the addition of $AlF_3$ reduces the transformation temperature significantly. The phase transformation to α-$Al_2O_3$ completed at 800 and 900 °C in the case of using aluminum nitrate and aluminum sulfate precursor, respectively. It was claimed that an intermediate compound, AlOF, can be formed by addition of metal fluoride in the case of phase transformation and AlOF accelerates the mass transportation from transition alumina to α-alumina [9].

Furthermore, it was also reported that the addition of $AlF_3$ could modify the morphology of α-alumina particles into plate-like shape [7]. Fig. 4 shows SEM micrographs of the α-alumina particles obtained with addition of $AlF_3$. As can be seen Fig. 4, some particles with plate-like shape were found in the case of using aluminum nitrate precursor (Fig. 4(a)), while spherical particles were formed in the case of using aluminum sulfate precursor (Fig. 4(b)). It could be said that the effect of $AlF_3$ additive on modification of morphology of particles is different depending on the precursor. It may be attributed to the different characteristics of precipitate formed in the initial stage of reaction. As mentioned above, the rearrangement of crystallites of boehmite formed from aluminum nitrate precursor can take place easily, whereas the compact and strongly bonded agglomerates formed from aluminum sulfate precursor retained their structure during crystallization.

## 4. Conclusions

The temperature for complete transformation to α-$Al_2O_3$ is lower in the case of using aluminum nitrate precursor as compared to aluminum sulfate precursor. The size of alumina particles obtained using aluminum nitrate precursor was smaller than that obtained using aluminum

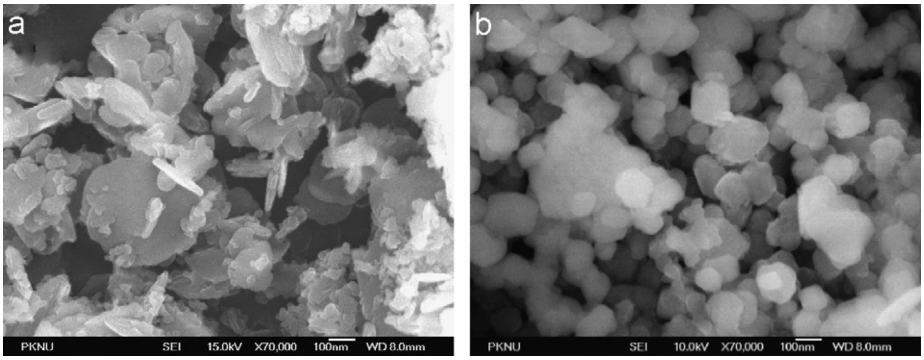

Fig. 4. SEM micrographs of the $\alpha$-alumina particles obtained with $AlF_3$ additive (a) aluminum nitrate precursor calcined at 800 °C and (b) aluminum sulfate precursor calcined at 900 °C.

sulfate precursor, and it may be due to the poorer ability of sulfate to provide colloid stability. It was also observed that the particles obtained from aluminum nitrate precursor have elongated shape, while those obtained from aluminum sulfate precursor have spherical shape, and it could be attributed to the different characteristics of precipitate formed in the initial stage of reaction. The $AlF_3$ additive decreased the phase transition temperature to $\alpha$-alumina. The effect of $AlF_3$ additive on modification of morphology of particles is different depending on the precursor. It was observed that, only in the case of using aluminum nitrate precursor, the addition of $AlF_3$ changed the morphology of $\alpha$-alumina particles to the plate-like shape.

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