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Influence of fluorides on phase transition of α-Al_2O_3 formation

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Abstract

Homogeneous α-Al_2O_3 particles have been synthesized by introducing fluorides in the alumina precursor. The effects of LiF, ZnF_2 and AlF_3 additives on the phase transformation and the micrograph of the prepared α-Al_2O_3 particles are investigated. It is shown that, at a heating rate of 5 °C min^{-1}, addition of 2% fluoride relative to the initial mass of the precursor decreases the transformation temperature by 300 °C for LiF and AlF_3 and well-dispersed α-Al_2O_3 powders with average particle size of ∼2 μm were obtained. The mechanism of the influence can be explained by the formation of intermediate compound (AlOF), which was considered to accelerate the mass transportation from θ- to α-Al_2O_3. The addition of ZnF_2 can slight reduce the θ- to α-Al_2O_3 phase transition temperature. However, the effect on the phase transition of α-Al_2O_3 formation is not obvious.

Keywords: α-Al_2O_3; Fluoride; Phase transformation; Morphology

1. Introduction

Alumina exists in a number of metastable transition phases as well as the thermodynamically stable α-Al_2O_3 or corundum. These metastable polymorphs include γ-Al_2O_3 (cubic spinel), δ-Al_2O_3 (tetragonal), θ-Al_2O_3 (monoclinic) and so on. Moreover, it has been noted that the starting phase of alumina polymorphs may vary, depending on the processing techniques, and the phase transition sequence can take place by various routes. By physical vapor deposition (PVD) techniques, a commonly reported transition route is amorphous $\rightarrow\gamma \rightarrow \theta + \delta \rightarrow \alpha$, in which the transformation products at each stage may be a mixture of several phases [1]. As to wet chemical methods, it is known that almost all those salt-derived aluminum hydroxides or hydrate alumina dehydrate to form γ-Al_2O_3. The transformation proceeds through the following sequence, forming several increasingly ordered transition aluminas before final rearrangement into the corundum structure: $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ [2]. The γ-Al_2O_3 is a metastable defect spinel with the oxygen atoms in cubic packing and aluminum in both tetrahedral and octahedral coordination. The δ and θ forms of alumina are also metastable defect spinels, making the rearrangement process from γ-Al_2O_3 to θ-Al_2O_3 of relatively low energy. However, the transformation from θ-Al_2O_3 to α-Al_2O_3 involves a significant change in the oxygen sublattice from cubic to hexagonal close packing and generally requires temperatures above 1200 °C for complete conversion to the thermodynamically stable corundum phase. The gained α-Al_2O_3 with hard agglomeration or vermicular morphology makes sintering to full density even more difficult due to the formation of large pores that are often entrapped within grains.

Thus, lowering the phase transformation temperatures is the target for preparing agglomeration free and homogeneous α-Al_2O_3. Many methods have already been carried out to lower the phase transition temperature of α-Al_2O_3 formation. A variety of potential nucleation aids such as α-Al_2O_3, α-Fe_2O_3, α-Cr_2O_3 and MgO were introduced in the transition alumina or alumina precursor [3–8]. The effect of these ''seeds'' is primarily dependent on the similarity of the crystal structure to α-Al_2O_3. Additives with a crystal structure very different from α-Al_2O_3 tend to have less or no effects on the transformation to α-Al_2O_3 [9]. Nevertheless, it has been reported [10–14] that the addition of low levels of fluoride decreases the temperature of the polymorphous transformation of α-Al_2O_3 formation

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effectively, which is of practical industrial interest. Živković et al. [10] investigated the influence of AlF_3 on the kinetics and mechanism of $Al(OH)_3$ and AlOOH dehydration and on the α-Al_2O_3 polymorphous transformation temperature. The influences of added fluorides (AlF_3, CaF_2, MgF_2, LiF, NaF and Na_3AlF_6) on the temperature of the polymorphous transformation γ- to α-Al_2O_3 were also presented [11–13].

In this paper, fluorides were introduced in the alumina precursor synthesized by coprecipitation method from $NH_4Al(SO_4)_2{\cdot}12H_2O$ with NH_4HCO_3. The effects of LiF, ZnF_2 and AlF_3 additives on the phase transformation and the micrograph of the prepared α-Al_2O_3 particles are investigated.

2. Experimental

Analytical grade $NH_4Al(SO_4)_2{\cdot}12H_2O$ (A.R., Jinshan Chemical Co., Shanghai, China) and NH_4HCO_3 (A.R., Shanghai Chemical Co., Shanghai, China) were used as raw materials. The alumina precursor was prepared by adding a NH_4HCO_3 solution (2.0 mol l^{-1}) slowly into a rapidly stirred $NH_4Al(SO_4)_2$ solution (0.3 mol l^{-1}). Polyethylene glycol (PEG, molecular weight 1000) was used as dispersant to prevent the precursor from agglomerating. When the slurry pH was adjusted to 8.0 by a pH meter (pHS-25, REX, China), the slurry was constantly stirred for 1 h, after which the precipitate was aged in the beaker for 10 h. The precipitate was washed with de-ionized water and alcohol. The precursor mixed with alcohol by adding LiF, CaF_2 and AlF_3, respectively, and then dried at 90 °C for 12 h. The alumina precursors were calcined at different temperatures for 2 h with a heating rate of 5 °C min^{-1}.

TG-DSC analysis was recorded on a Netzsch STA 449C instrument. Measurements were taken under a continuous flow of air (20 ml min^{-1}). Samples were heated at 10 °C min^{-1} to 1300 °C and then cooled to room temperature. Phase identification was performed by a Rigaku D/max2200PC X-ray diffractometer (XRD) using nickel filtered Cu Kα radiation in the range of $2\theta = 10^\circ$ to 80°with a scanning speed of 4° min^{-1}. The morphology and the size of the prepared alumina powders were investigated by a JEOL JEM-200CX transmission electron microscopy (TEM).

3. Results and discussion

Previous work [15] on precipitation of aluminum compounds using NH_4HCO_3 as the precipitant revealed that Al^{3+} may precipitate as pseudo-boehmite (AlOOH) or ammonium dawsonite [$NH_4Al(OH)_2CO_3$], mainly depending upon the concentration of the precipitant solution and the reaction temperature. In the present work, both AlOOH and $NH_4AlO(OH)HCO_3$ were contained in the gained precursor, as confirmed by TG-DSC analysis below. Fig. 1 shows the TG-DSC curves of the precursor heated at the rate of 10 °C min^{-1}. The total mass-loss determined for the alumina from the synthesized precursor was 43.76%. Calculations of the theoretical mass-loss based on the stiochiometries of AlOOH and $NH_4Al(OH)_2CO_3$ yield a value of 15.02 and 63.34%, respectively. So the gained compound precursor can be

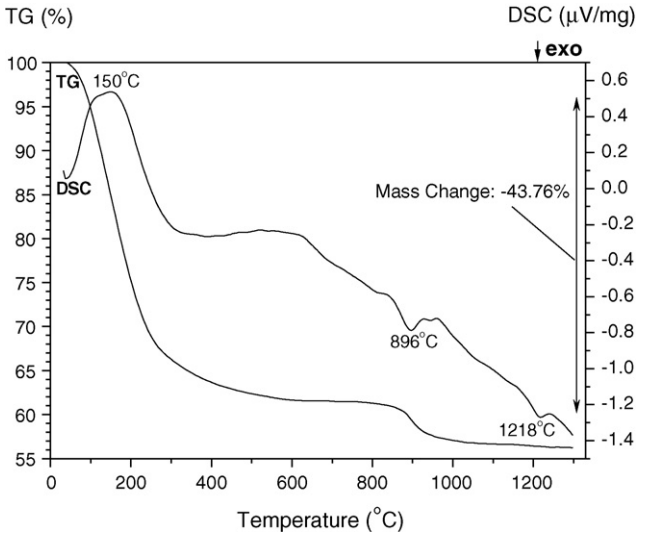

Fig. 1. TG-DSC curves of the precursor heated at the rate of 10 °C min^{-1}.

expressed as $0.61AlOOH{\cdot}0.39\ NH_4Al(OH)_2CO_3$. The following chemical reactions were expected in the precipitant solution:

$$3NH_4HCO_3 + NH_4Al(SO_4)_2{\cdot}12H_2O = \gamma\text{-}AlOOH + 3CO_2 + 2(NH_4)_2SO_4 + 13H_2O \quad (1)$$

$$4NH_4HCO_3 + NH_4Al(SO_4)_2{\cdot}12H_2O = NH_4Al(OH)_2CO_3 + 3CO_2 + 2(NH_4)_2SO_4 + 13H_2O \quad (2)$$

A broad endothermic peak existing at around 150 °C is attributed to the vaporization of physically absorbed water and the decomposition reaction of the precursor. The decomposition and phase transformation proceeds for γ-AlOOH and $NH_4Al(OH)_2CO_3$ are as follows:

$$\gamma\text{-}AlOOH \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (3)$$

$$NH_4Al(OH)_2CO_3 \rightarrow Amor.\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (4)$$

Close observation has shown that two exothermic peaks appear at 896 and 1218 °C, the former result from the crystallization of amorphous alumina and the later is caused by the θ- to α-Al_2O_3 phase transformation, as can be confirmed by XRD patterns in Fig. 2.

Fig. 2 shows the XRD patterns of the gained powders from the precursor without additive calcined at different temperatures. Diffraction peaks corresponding to θ-Al_2O_3 have been found for the sample calcined at 900 °C. No significant change in the structure has been found after calcination temperature up to 1000 °C. A small amount of α-Al_2O_3 has been detected after calcining at 1100 °C, coexisting with the major phase θ-Al_2O_3. The amount of α-Al_2O_3 increased drastically when the calcination temperature increased up to 1200 °C, however, a small amount of θ-Al_2O_3 was remained.

Fig. 3 shows the TEM micrographs the gained α-Al_2O_3 powders from precursor without additive calcined at 1100 and

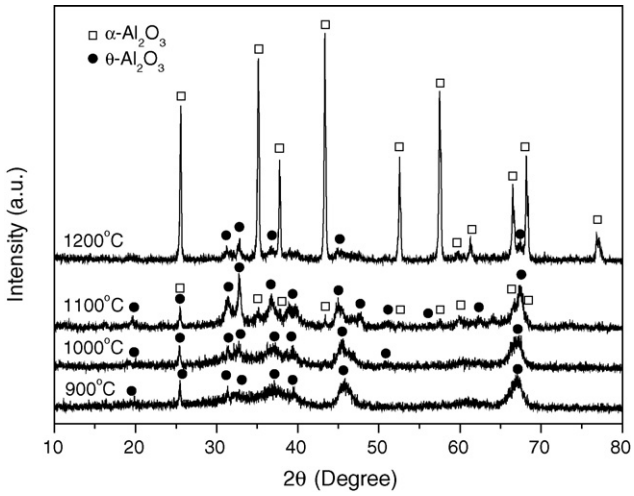

Fig. 2. XRD patterns of the calcined powders from the precursor without additive.

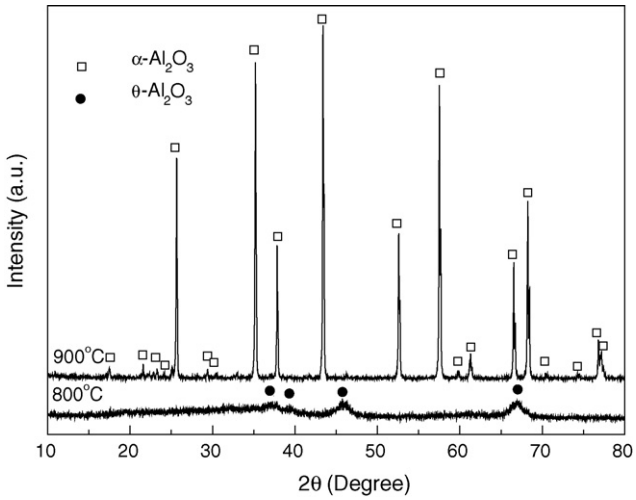

Fig. 4. XRD patterns of the calcined powders from precursor with LiF additive.

1200 °C for 2 h. It was found that rod-like and spherical particles of θ-Al_2O_3 coexisted, as shown in Fig. 4a. With increase of calcination temperature up to 1200 °C, the resultant vermicular microstructure of α-Al_2O_3 particles formed and a small amount of θ-Al_2O_3 was remained.

Fig. 4 shows the XRD patterns of the gained powders from precursor with LiF additive calcined at 800 and 900 °C. It can be seen that θ-Al_2O_3 formed for the sample calcined at 800 °C. The phase transformation of θ-Al_2O_3 to α-Al_2O_3 completed at 900 °C. At this temperature, high intensities of α-Al_2O_3 peaks observed indicate crystallite growth of the grains, which can be observed from Fig. 5. Homogeneous and well-dispersed α-Al_2O_3 powders with particle size of ∼2 μm were gained with LiF as additive. The interesting result obtained is original compared to prior work by Živković et al. They added LiF up to 2% relative to the initial mass of $Al(OH)_3$ and found that the addition of LiF did not influence the temperature of γ- to α-Al_2O_3 phase transformation [11]. It is considered that the differences in the gained precursors and phase transformation proceeds result in the great difference in the phase transformation temperature between our work and their.

The gained powders from precursor with ZnF_2 additive calcined at different temperatures were identified by XRD, as shown in Fig. 6. By 800 °C, the XRD pattern only gives

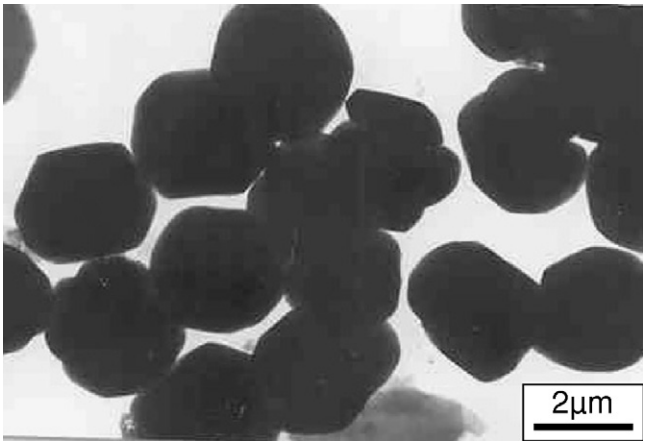

Fig. 5. TEM micrograph of the gained α-Al_2O_3 powders from precursor with LiF calcined at 900 °C.

diffraction peaks of θ-Al_2O_3 and amorphous background. The θ-Al_2O_3 XRD pattern is very broad indicating the existence of fine crystallite, which can be observed from Fig. 7.

The characteristic peaks of α-Al_2O_3 appear at 1000 °C with a rather weak intensity, which indicates θ-Al_2O_3 to α-Al_2O_3 transition. The phase transition temperature of α-Al_2O_3

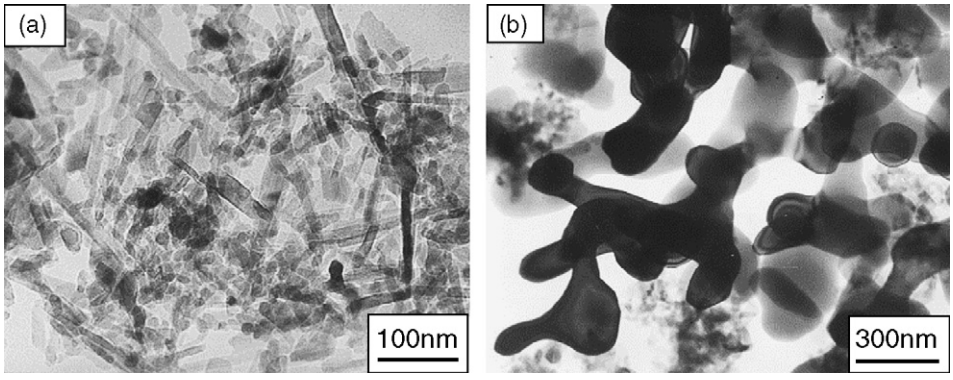

Fig. 3. TEM micrographs of the gained α-Al_2O_3 powders from precursor without additive calcined at (a) 1100 °C; (b) 1200 °C for 2 h.

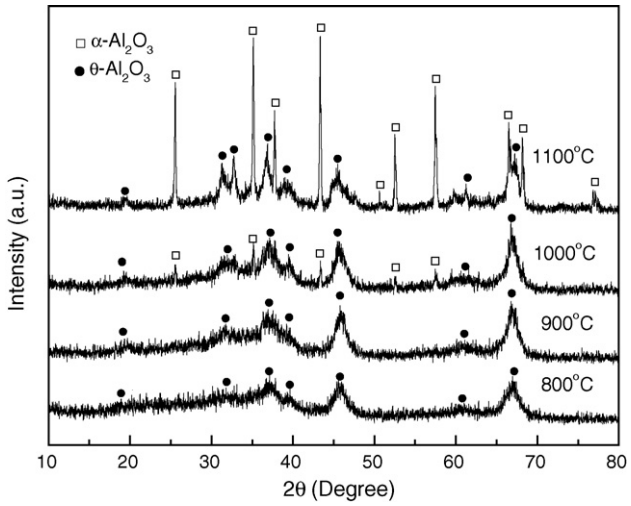

Fig. 6. XRD patterns of the Al_2O_3 precursor with ZnF_2 calcined at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C.

formation in this case is lower than of the gained powders from precursor without additive. With the increase of calcination temperature up to 1100 °C the crystallinity of α-Al_2O_3 improved and more θ-Al_2O_3 converted to α-Al_2O_3. The completion of θ- to α-Al_2O_3 transition occurred till ∼1200 °C. It can be considered that the addition of ZnF_2 can slight enhance the kinetic rate of the θ- to α-Al_2O_3 transition and reduce the phase transition temperature. However, the effect of ZnF_2 additive on the phase transition of α-Al_2O_3 formation in our work is less obvious compared with the result observed by Wu et al. [12,13].

The XRD patterns of the powders from the precursor with AlF_3 calcined at 800 and 900 °C are shown in Fig. 8. It can be seen that the phase transformation of θ- to α-Al_2O_3 occurred at 800 °C and completed at 900 °C. The addition of AlF_3 in the precursor can greatly low the phase transformation of α-Al_2O_3 formation. Homogeneous and well-dispersed α-Al_2O_3 powders with particle size ∼2 μm were gained with AlF_3 additive, as shown in Fig. 9.

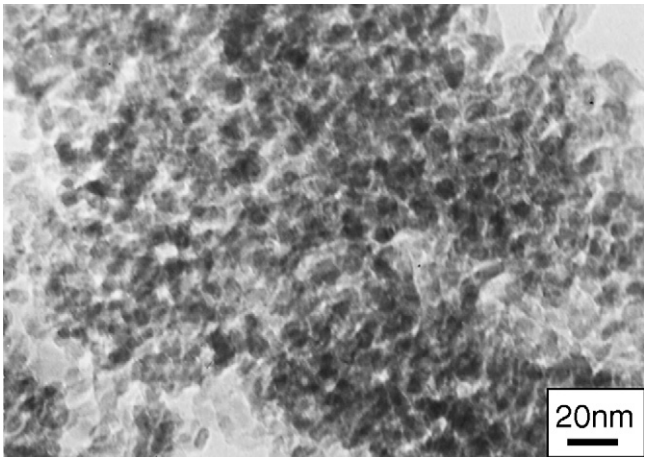

Fig. 7. TEM micrograph of the powders from precursor with ZnF_2 calcined at 900 °C.

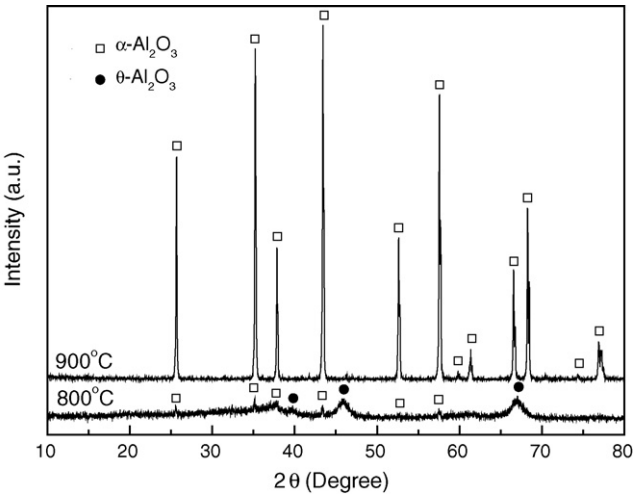

Fig. 8. XRD patterns of the Al_2O_3 precursor with AlF_3 calcined at (a) 800 °C, (b) 900 °C.

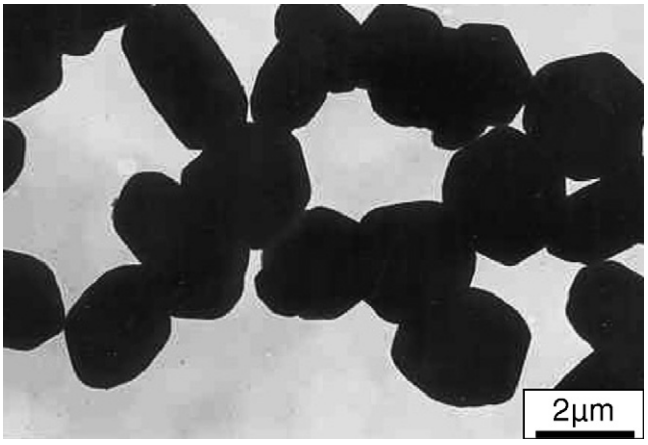

Fig. 9. TEM micrograph of the gained α-Al_2O_3 powders from precursor with AlF_3 calcined at 900 °C.

It is interesting that the morphology of some particles is plate-like with an aspect ration of ∼2. It can be inferred that AlF_3 can enhance the growth rate of grains and modify the shape of α-Al_2O_3 particles. The AlF_3 additive proved to be effective in enhancing the phase transition of α-Al_2O_3 formation because an intermediate compound, AlOF, can be formed in the case of the phase transformation and AlOF can accelerate the mass transportation from transition phase to α-Al_2O_3 [14].

4. Conclusions

Fluorides (LiF, ZnF_2 and AlF_3) were introduced in the alumina precursor synthesized by coprecipitation method. The addition of 2% LiF and AlF_3 decreases the transformation temperature by 300 °C and well-dispersed α-Al_2O_3 powders with average particle size of ∼2 μm were gained. The addition of 2% ZnF_2 can slight enhance the kinetic rate of the θ- to α-Al_2O_3 transition and reduce the phase transition temperature. However, the effect on the phase transition of α-Al_2O_3 formation is not obvious.

Acknowledgements

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