

Influence of AlF_3 and hydrothermal conditions on morphologies of $\alpha\text{-Al}_2\text{O}_3$

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Abstract: Homogeneous $\alpha\text{-Al}_2\text{O}_3$ platelets were synthesized by introducing AlF_3 to alumina precursor. The effects of AlF_3 additive on the phase transformation and morphology of the prepared $\alpha\text{-Al}_2\text{O}_3$ platelets were investigated. The results show that a single phase of $\alpha\text{-Al}_2\text{O}_3$ with an average particle size of 8 μm can be obtained at 900 °C with 2% AlF_3 additive. The transformation temperature decreasing is attributed to introduction of Al^{3+} vacancy and to the formation of intermediate compound of AIOF, which is considered to accelerate the mass transportation from transitional Al_2O_3 to $\alpha\text{-Al}_2\text{O}_3$. AlF_3 concentration and hydrothermal temperature can also affect the morphology of $\alpha\text{-Al}_2\text{O}_3$. When hydrothermal temperature is 120 °C, the morphology of $\alpha\text{-Al}_2\text{O}_3$ transforms from irregular to flat hexangular platelet with increasing AlF_3 concentration. As hydrothermal temperature increases, the morphology of $\alpha\text{-Al}_2\text{O}_3$ with 2% AlF_3 additive changes from polyhedron to hexangular platelet and then to vermicular.

Key words: $\alpha\text{-Al}_2\text{O}_3$ platelets; AlF_3 ; hydrothermal treatment; morphology

1 Introduction

Alumina is one of the most important oxides and has been intensively studied over a long period because of its widely potential applications in ceramic, glass, functional materials, adsorbents, catalysts and catalyst supports etc[1–3]. Alumina exists in a number of metastable transition phases as well as the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ or corundum.

As for the wet chemical methods, it is known that almost all those salt-derived aluminum hydroxides dehydrate to form $\gamma\text{-Al}_2\text{O}_3$. The transformation proceeds through the following sequence, $\gamma\text{-}\delta\text{-}\theta\text{-}\alpha$ [4]. The $\gamma\text{-Al}_2\text{O}_3$ is a metastable defect spinel with the oxygen atoms in cubic packing and aluminum in both tetrahedral and octahedral coordinations. The δ and θ forms of alumina are also metastable defect spinels, making the rearrangement process from $\gamma\text{-Al}_2\text{O}_3$ to $\theta\text{-Al}_2\text{O}_3$ of relatively low energy[5–7]. However, the transformation from $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ involves a significant change in the oxygen sublattice from cubic peaking to hexagonal close packing and generally requires temperatures above 1 200 °C for complete conversion to the thermodynamically

stable corundum phase. The gained $\alpha\text{-Al}_2\text{O}_3$ 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 $\alpha\text{-Al}_2\text{O}_3$. Some studies have already been carried out on the phase transformation of alumina. For example, some papers dealt with the mechanisms of phase transformation and the transformation mechanism of $\gamma\text{-}$ to $\alpha\text{-Al}_2\text{O}_3$, involving the conversion of cubic close packing of oxygen ions into stable hexagonal close packing[1,8–9]. While others reported the methods for enhancing the kinetic rate of phase transformation[10]. It is known that the temperatures of $\gamma\text{-}$ to $\alpha\text{-Al}_2\text{O}_3$ transition can be influenced by some cation additives. For example, the addition of transition metals such as Fe^{2+} , Cr^{3+} and Ti^{4+} has been reported to accelerate the $\gamma\text{-}$ to $\alpha\text{-Al}_2\text{O}_3$ phase transformation, whereas Cs^+ , Ba^{2+} , La^{3+} , Si^{4+} additives are well known to retard it[11–14].

In this work, fluoride aluminum was introduced to the alumina precursor synthesized by aluminum alkoxide hydrolysis and hydrothermal treatment methods. The

effects of AlF_3 additive on the phase transformation and the morphologies of the prepared $\alpha\text{-Al}_2\text{O}_3$ particles are investigated.

2 Experimental

Solution A was prepared by adding aluminum isopropoxide to certain content of analytical grade isopropanol (A.R., Dalian Inorganic Chemical Co., China). Certain amount of AlF_3 (C.P., Shanghai Reagent Co., China) was added to the mixture solution of deionized water and isopropanol to make slurry B. The slurry B was dispersed by ultrasonic for 10 min and then mixed with solution A at $65\text{ }^\circ\text{C}$ under rapid stirring and refluxing for 2 h. The resulting product was transferred into a Teflon-lined stainless autoclave to fill 80% of the total volume. The autoclave was sealed and maintained at certain temperature for 24 h. The autoclave was then allowed to cool naturally to room temperature and a white precipitated powder was obtained. The powder was filtered and washed several times with absolute ethanol and distilled water, and then dried in vacuum at $60\text{ }^\circ\text{C}$ for 12 h. Al_2O_3 particles were obtained by annealing the as-synthesized powders in air at different temperatures for 3 h.

The crystal structure of the product was examined by X-ray diffraction (XRD, Cu K_α radiation, D/max-rB, Japan). An overview of the sample morphology was checked with a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan).

3 Results and discussion

3.1 Phase transformation of Al_2O_3

Fig.1 shows the XRD patterns of the gained powders from the precursor without additive after

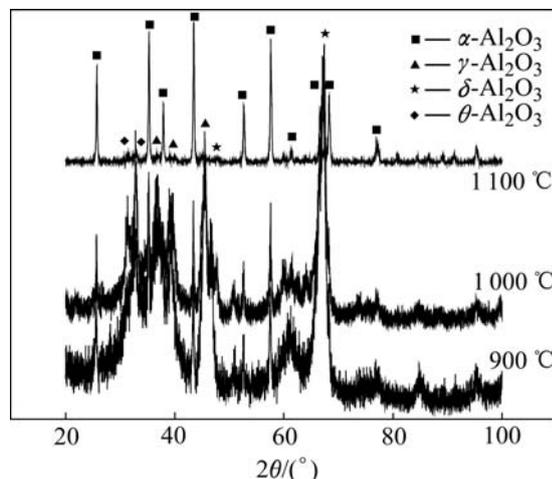


Fig.1 XRD patterns of calcined powders from precursor without additive

hydrothermal treatment at $120\text{ }^\circ\text{C}$ and calcination at different temperatures. Diffraction peaks corresponding to $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ are found for the sample calcined at $900\text{ }^\circ\text{C}$. No significant change in the structure is found after calcination at temperature up to $1\ 000\text{ }^\circ\text{C}$. The amount of $\alpha\text{-Al}_2\text{O}_3$ increases drastically when the calcination temperature increases up to $1\ 100\text{ }^\circ\text{C}$. However, a small amount of $\theta\text{-Al}_2\text{O}_3$ remains.

Fig.2 shows the XRD patterns of the gained powders from precursor with 2% AlF_3 additive after hydrothermal treatment at $120\text{ }^\circ\text{C}$ for 24 h and calcination from 550 to $1\ 200\text{ }^\circ\text{C}$. It can be seen that $\gamma\text{-Al}_2\text{O}_3$ forms for the sample calcined at $550\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$. The phase transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ is completed at $900\text{ }^\circ\text{C}$ and no significant change is found after the calcination at temperature up to $1\ 200\text{ }^\circ\text{C}$.

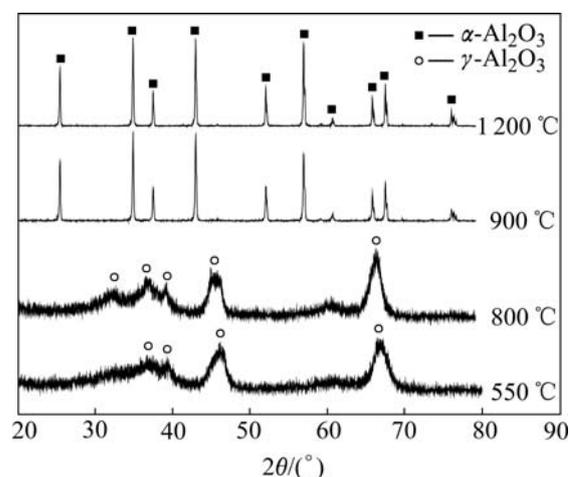
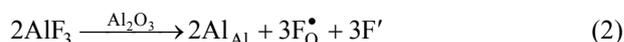
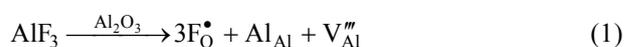


Fig.2 XRD patterns of Al_2O_3 precursor with AlF_3 calcined at different temperatures

Generally, the transformation from metastable transition phases to $\alpha\text{-Al}_2\text{O}_3$ involves a significant change in the oxygen sublattice and usually a temperature above $1\ 200\text{ }^\circ\text{C}$ is required for complete conversion to the thermodynamically stable corundum phase. It can be seen from Fig.2 that the addition of AlF_3 can enhance the kinetic rate of the phase transformation from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ and reduce the transformation temperature of $\alpha\text{-Al}_2\text{O}_3$ phase. During the heat treatment, the existence of AlF_3 destroys the well-regulated atomic packing configuration and introduces Al^{3+} vacancy. When AlF_3 is introduced to alumina precursor, two defect reactions may take place as follows:



The vacancies and interstitial atoms can be formed

through these reactions. There are no significant distinctions between F^- radius and O^{2-} radius, so F^- can not take interstitial sites. Comparatively, the formation energy of vacancy is lower than that of interstitial atoms. Thus, the defect can give priority to Al^{3+} vacancies. Al^{3+} vacancies accelerate Al^{3+} diffusion and reduce the transformation temperature of $\gamma-Al_2O_3$ to $\alpha-Al_2O_3$.

In addition, some intermediate compounds can be formed in the case of the phase transformation. They can also accelerate the mass transportation from transitional phase to $\alpha-Al_2O_3$. It is known that $\gamma-Al_2O_3$ is highly active and has large surface area. Thus, it is strongly hygroscopic to adsorb H_2O in the air. During the heat treatment, AlF_3 can take the following reversible reaction with H_2O adsorbed[15]:



And the positive reaction may be performed through the secondary reactions as follows.

1) The gaseous intermediate compound, $AlOF$, can be synthesized by the following reaction.

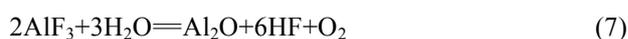


The gaseous intermediate compound, $AlOF$, can play the role of gas transmission and accelerate atomic transference velocity to enhance the phase

transformation. In this work, although it is quite difficult to define the composition of the intermediate compound, it can ultimately transform into alumina:



2) The intermediate compound, Al_2O , can be synthesized as:



Finally, Al_2O takes part in the following reactions and transforms into alumina:



Similarly, the intermediate compound, Al_2O , can enhance the phase transformation by accelerating atomic transference velocity.

3.2 Morphology of $\alpha-Al_2O_3$

The morphologies of the gained powders from precursor with 2% AlF_3 additive after hydrothermal treatment at 120 °C for 24 h and calcination from 800 to 1 200 °C were examined by SEM. Fig.3 shows the SEM micrographs of the obtained products. The microstructure of the sample calcined at 800 °C is floccule and the

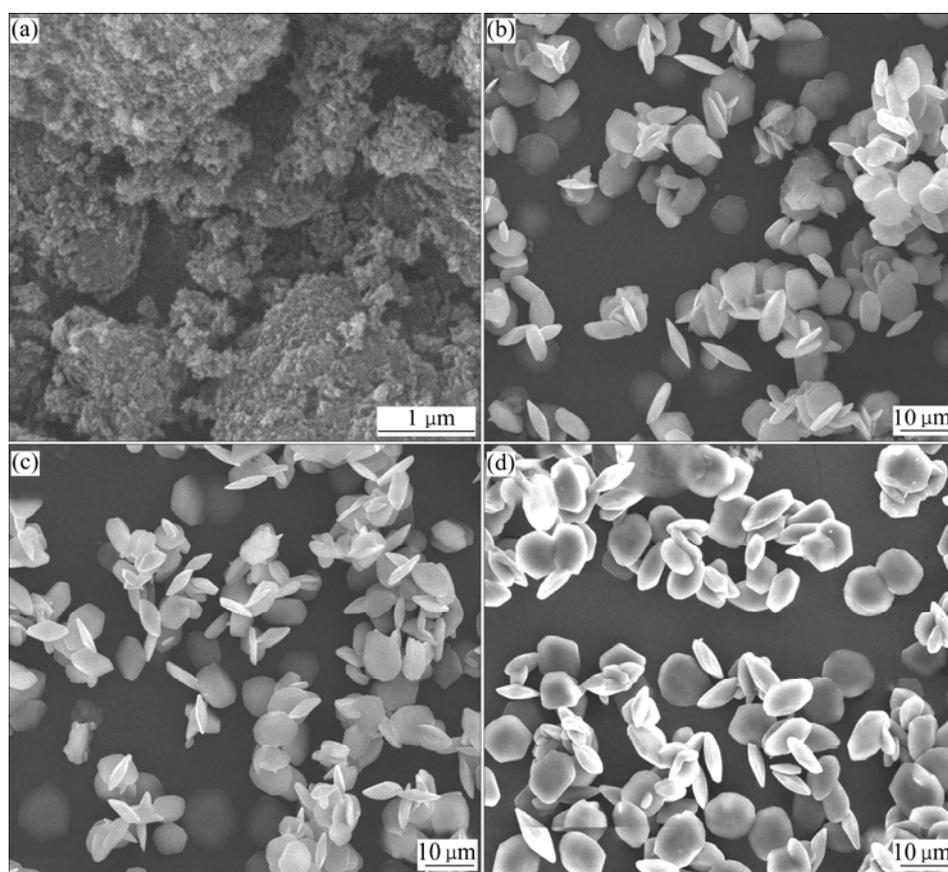


Fig.3 SEM micrographs of samples treated at different temperatures: (a) 800 °C; (b) 900 °C; (c) 1 000 °C; (d) 1 200 °C

full-grown crystal is not seen. The alpha phase does not appear, which is convinced by XRD pattern at 800 °C as shown in Fig.2. When the calcinating temperature is raised to 900, 1 000 and 1 200 °C, respectively, the morphologies of those particles are plate-like and there is no remarkable change in particle size. It is shown that once alpha phase is obtained, the effects of temperature on morphology and size are rather feeble.

Fig.4 shows the SEM micrographs of the gained α -Al₂O₃ powders from precursors with different AlF₃ concentration calcined at 1 200 °C. It can be seen that

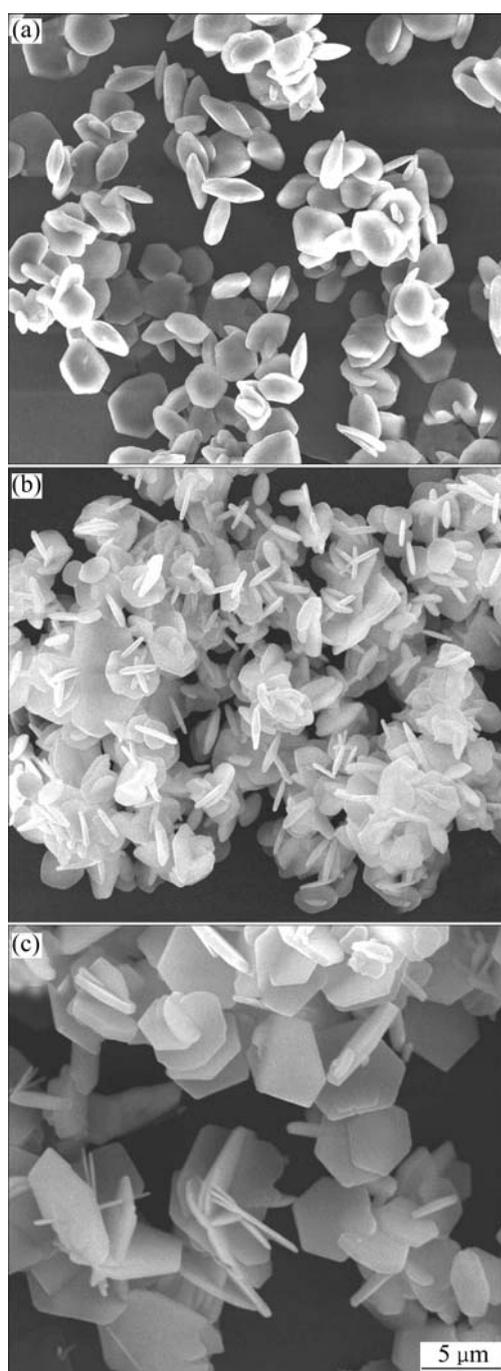


Fig.4 Effect of AlF₃ concentration on morphology of α -Al₂O₃: (a) 2%AlF₃; (b) 10%AlF₃; (c) 20%AlF₃

α -Al₂O₃ passes through the morphology transformation of irregular platelet to flat hexangular platelet as AlF₃ concentration is increased.

α -Al₂O₃ belongs to rhombohedral crystal system and the space group is $R\bar{3}c$. The existence of AlF₃ additive causes different growth rate along the respective crystal axis and finally has effects on the morphology of α -Al₂O₃. In view of crystal growth, the microstructure is determined by crystal growth rate. The crystal plane with larger growth rate will gradually disappear and while the crystal plane with smaller growth rate will be maintained. The shape of the crystal plane is relevant to the crystal plane with larger growth rate. The unsaturated surface tension existed on the surface of solid can adsorb AlF₃ around. And the adsorption capacity varies with the anisotropic surface tension. Usually, the surface tension of crystal plane with close-packed atom is smaller. In α -Al₂O₃ unit cell, (0001) and its symmetrical crystal plane takes with close-packed atom. They have weaker capacity to adsorb gaseous molecule and accordingly there are less atoms transferred by gas transmission, thus (0001) and its symmetrical crystal plane are maintained because of the lower growth rate along the crystal axis. Generally, the crystal planes with lower growth rate have more perfect crystal structure, so (0001) and its symmetrical crystal plane are much more smooth than others with excessive crystal defects caused by rapid growth. Then the crystal planes with larger growth rate will gradually disappear and transform to final platelet morphology.

SEM micrographs of α -Al₂O₃ synthesized at different hydrothermal temperatures for 24 h and calcined at 1 200 °C for 3 h are shown in Fig.5. The sample via 120 °C hydrothermal treatment shows the polyhedron morphology, and plate-like morphology can be obtained when the hydrothermal temperature is increased up to 160 °C. Nevertheless, α -Al₂O₃ passes through the morphology transformation of platelet to vermiform morphology with increasing the hydrothermal temperature to 180 °C. And with increasing the hydrothermal temperature up to 240 °C, the α -Al₂O₃ powder obtained is more seriously aggregated and the powders connects with each other.

The microscopic mechanism of the crystal growth is essentially the dynamic balance between adsorption and desorption of the growth unit from the microscopic kinetics. When the adsorption rate of the growth unit is larger than the desorption rate, the crystal represents to grow in favor of the formation of α -Al₂O₃ platelets. However, the adsorption rate will be lower than the desorption rate with increasing hydrothermal temperature

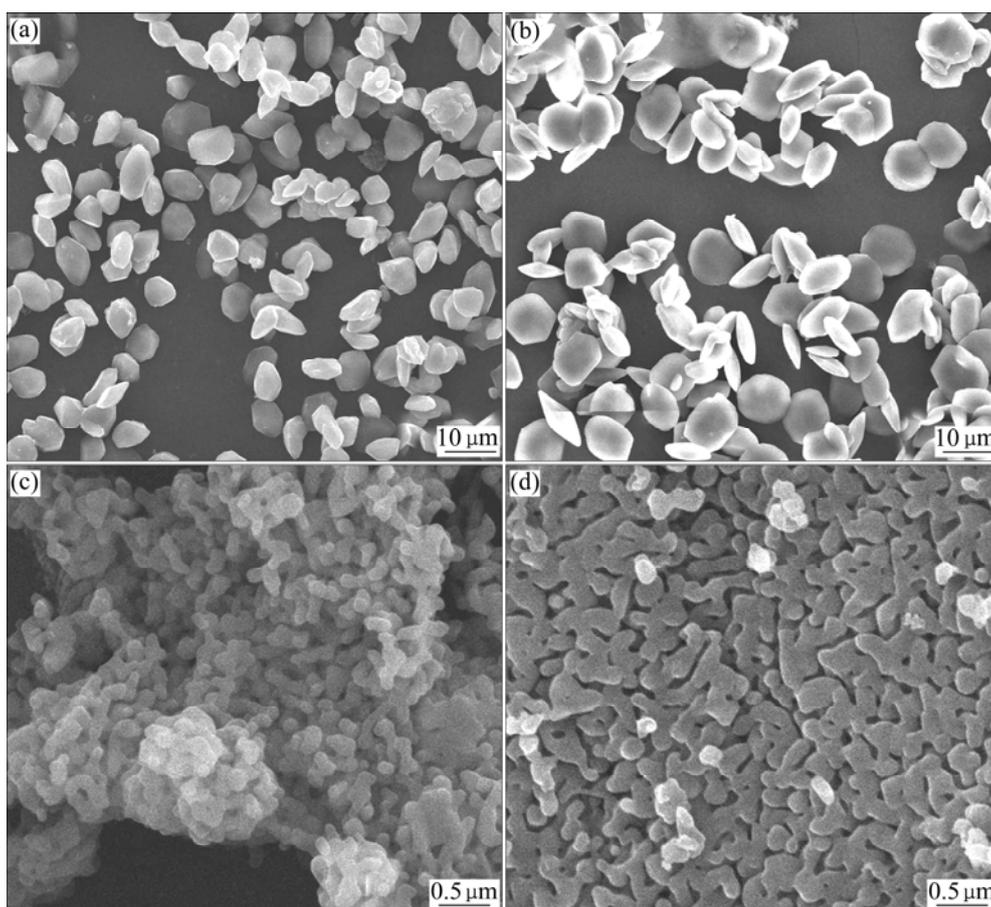


Fig.5 SEM micrographs of samples heat treated at different hydrothermal temperatures: (a) 120 °C; (b) 160 °C; (c) 180 °C; (d) 240 °C

up to the critical value, in which the formation of α - Al_2O_3 platelets is restrained. When the alumina precursor with AlF_3 additive is treated at 240 °C under high pressure, the existence of AlF_3 can make the growth units irregularly syncretize and superpose mutually on the same crystal plane and finally the seriously aggregated microstructure can be formed with the crystal growth. It is well known that AlF_3 presents in a supersaturated mother phase and it can significantly change the nucleation of crystals, the growth and aggregation of nuclei and so on. But the effect of AlF_3 additive varying with the different hydrothermal temperature can result in distinct crystal growth habit during calcinations and then influence the formation of α - Al_2O_3 platelets.

4 Conclusions

1) In hydrothermal process, the transformation temperature of γ - Al_2O_3 to α - Al_2O_3 can be lowered by 300 °C through the addition of 2% AlF_3 and the well-dispersed α - Al_2O_3 powders with an average particle size of 8 μm can be obtained.

2) Once alpha phase appears, the effects of

temperature on particle morphology and size are quite weak. As AlF_3 concentration is increased, the morphology of α - Al_2O_3 powders could be transformed from irregular platelet to flat hexangular platelet.

3) The plate-like morphology can be transformed into vermiform morphology when the hydrothermal temperature is increased to above 180 °C and the α - Al_2O_3 particles synthesized after 240 °C hydrothermal treatment are seriously aggregated.

References

- [1] TARTAJ P, TARTAJ J. Preparation, characterization and sintering behavior of spherical iron oxide doped alumina particles [J]. *Acta Materialia*, 2002, 50: 5–12.
- [2] DONG Yan, JIANG Jian-qing, LIU Gang, LIANG Chao, SUN Ming-tao. Preparation of alumina as a raw material of phosphor and controlling of its particle size and shape [J]. *Journal of the Chinese Ceramic Society*, 2004, 32(4): 393–397. (in Chinese)
- [3] ZHOU Zhen-jun, YANG Zheng-fang, YUAN Qi-ming. Preparation of small sized α -alumina platelet by sol-gel method [J]. *Bulletin of the Chinese Ceramic Society*, 2003(4): 11–15. (in Chinese)
- [4] SHEPPARD L M. Enhancing performance of ceramic composites [J]. *J Am Ceram Soc*, 1992, 71: 617–631.
- [5] BOWEN P, SHENG J, JONGEN N. Particle size distribution measurement of anisotropic-particles cylinders and platelets-practical

- examples [J]. Powder Technology, 2002, 128: 256–261.
- [6] LI Jiang, PAN Yu-bai, XIANG Chang-shu. Low temperature synthesis of ultrafine α -Al₂O₃ powder by a simple aqueous sol-gel process [J]. Ceramic International, 2006, 32(5): 587–591.
- [7] ZHU H Y, GAO X P, SONG D Y, RINGER SIMON P, XI Y X, FROST RAY L. Manipulating the size and morphology of aluminum hydroxide nanoparticles by soft-chemistry approaches [J]. Microporous and Mesoporous Materials, 2005, 85: 226–233.
- [8] QU Li-hong, HE Chang-qing, YANG Yue, HE Yan-li, LIU Zhong-min. Hydrothermal synthesis of alumina nanotubes templated by anionic surfactant [J]. Materials Letters, 2005, 59: 4034–4037.
- [9] XIE Zhi-peng, LU Ji-wei, GAO Li-chun, XU Li-hua, WANG Xi-dong. Influence of different seeds on transformation of aluminum hydroxides and morphology of alumina grains by hot pressing [J]. Materials & Design, 2003, 24: 209–214.
- [10] WU Yi-quan, ZHANG Yu-feng, HUANG Xiao-xian, GUO Jing-kun. Preparation of platelike nano alpha alumina particles [J]. Ceramics International, 2001, 27: 265–268.
- [11] WU Yi-quan, ZHANG Yu-feng, PEZZOTTI G. Influence of AlF and ZnF on the phase transformation of gamma to alpha alumina [J]. Materials Letters, 2002, 52: 366–369.
- [12] MACEDO M I F, BERTRAN C A, OSAWA C C. Kinetics of the γ - α -alumina phase transformation by quantitative X-ray diffraction [J]. Journal of Materials Science, 2007, 42(8): 2830–2836.
- [13] LOPEZ V A, REYES B J L, SONG S, HERRERA U R. Temperature effect on the zeta potential and fluoride adsorption at the α -Al₂O₃/aqueous solution interface [J]. Journal of Colloid and Interface Science, 2006, 298(1): 1–5.
- [14] LI Jiang, WU Yu-song, PAN Yu-bai, LIU Wen-bing, GUO Jing-kun. Influence of fluorides on phase transition of α -Al₂O₃ formation [J]. Ceramics International, 2007, 33(6): 919–923.
- [15] YAMAI I, SAITO H. Vapor phase growth of alumina whiskers by hydrolysis of alumina fluoride [J]. Journal of Crystal Growth, 1978, 45: 511–516.

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