

THE INFLUENCES OF FLUORIDES ON THE TRANSFORMATION OF α -ALUMINA CRYSTALS

#QINGBO TIAN***, XIAOJIE YANG***, YUE WANG**, ZHIJIE LV**

*Co-innovation Center for Green Building of Shandong Province., Shandong Jianzhu University, Jinan 250101, P. R. China;

**School of Material Science and Engineering, Shandong Jianzhu University, Jinan 250101, P. R. China;

***Shandong Institute for Product Quality Inspection, Jinan 250100, P. R. China

#E-mail: tqb11@sdjzu.edu.cn

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Influence of addition of aluminum fluoride (AlF_3) and ammonium fluoride (NH_4F) on transformation of α - Al_2O_3 from boehmite was investigated. Transformation of α - Al_2O_3 occurred at about 1050°C and 950°C, when boehmite contained AlF_3 and NH_4F additives respectively, which was 150°C and 300°C lower than that without any additives. The formed α - Al_2O_3 consisted of clear, hexagonal plate-like particles about 2-3 μm in diameter and 200 nm in thickness. However, the formed hexagonal platelet particles gradually became blunt at edges and decreased in sizes at the higher calcinating temperatures. The transfer of α - Al_2O_3 morphology was due to the diminution and disappearance of fluorine. The fluoride coated on the surfaces were firstly decomposed and then fluorine entered the lattices of crystals was volatilized. The fluoride with tiny particles attached on the surface had a same chemical bonding of F-Al-O with that in the lattices of crystals.

INTRODUCTION

The high pure alumina ceramics have attracted more attentions from the researchers and engineers in the ceramic field over the last decades due to their unique combination of properties such as high hardness, high strength, good electrical resistivity and optical performance [1-7]. Over the years a number of methods have been developed for the fabrication of high dense alumina ceramic. However, to produce high-density alumina ceramic, the characteristics of the α -alumina powders used are always a substantial factor, in which, the dispersion of α -alumina powders with relatively finer grains is generally required. In general, the formation of α -alumina from boehmite occurs at temperature as high as 1200°C after a series of polymorphic transformation, including γ -alumina, δ -alumina, θ -alumina and α -alumina [8-11]. A high transformation temperature inevitably results in the coarsening and heavy aggregation of α -alumina particles [9, 12]. Therefore, it is imperative to reduce the α -alumina transformation temperature in order to achieve the uniform α -alumina particles without hard agglomerates.

There were some methods invented to decrease the transformation temperature to overcome the possibility of powder agglomeration problems by adding surfactants [8, 13], the seeds [14-16], or mineralizers [9, 13, 17-23]. Among them, the addition of mineralizer was proved to be an effective method. It was reported that the incorpo-

ration of ammonium nitrate induced the transformation of intermediate phases to the stable α - Al_2O_3 structure at a lower temperature. They concluded that an amount of high energy defects were introduced in the transition alumina matrix by the decomposition of ammonium nitrate and the evolution of oxides of nitrogen and nitric acid, which would promote the reaction of transition alumina to α - Al_2O_3 [9, 13]. The main drawback of this method was that a large number of ammonium nitrate were contained and an amounts of nitride inevitably volatilized during the calcination processes, causing the environmental problem. Chlorides were expected to decrease the converting temperature of α - Al_2O_3 , for the addition of chloride promoted crystallization of MgO. However, the discouraging results were often obtained [11, 17]. Nowadays, fluorides were commonly used as mineral additives to promote α - Al_2O_3 crystal growth [17-20]. It was determined that a small number of fluorides additives could efficiently induced the transformation of transition alumina phases [18, 19, 21]. A decline of the converting temperature between 130°C to 400°C was reported according to the variety of fluorides by the forming bridges between fluoride ions and aluminum ions on alumina surfaces [19]. It seemed that some fluorides, such as AlF_3 , ZnF_2 , CaF_2 , NH_4F and MgF_2 , had a positive effect on decreasing the transformation temperature of α - Al_2O_3 [22]. However, most of them would introduce other metal elements except aluminum, which could apparently not apply to

prepare high purity α - Al_2O_3 . NH_4F and AlF_3 would be decomposed into fluoride or nitride, and volatilized with the rise of transformation temperature, could not introduce metal impurities contamination to the powders.

Meanwhile, the addition of fluorides to a transition alumina or transition alumina precursor enhanced the formation of α - Al_2O_3 crystal with the preferred morphology. A plate-like α - Al_2O_3 crystal was prepared by the addition of aluminum fluoride powder to γ -alumina or η - Al_2O_3 [23, 24]. In another work the hydrofluoric acid was added to boehmite, alumina platelets with an average size of about 25 nm were achieved [25]. The α - Al_2O_3 particles having a very high aspect ratio were used as fillers or pigments in rubbers or plastics to exhibit good dispersibility [26], or as reinforcements in ceramics to improve their mechanical properties, especially the fracture toughness [27, 28].

In this paper, two kinds of fluoride, aluminum fluoride (AlF_3) and ammonium fluoride (NH_4F) were used to reduce the phase transformation temperature of α - Al_2O_3 in calcination process of boehmite precursor. The influences of the fluorides on the phase transformation processes and morphology were characterized. And the mechanism action of them was also analyzed.

EXPERIMENTAL

A high-purity boehmite powder with a purity of at least 99.995 % was supplied by the Advanced Ceramic Center, Dalian Jiaotong University, China. The chemical agents of AlF_3 and NH_4F (chemical pure grade, > 99.5 %) as additives were purchased from Guoyao Group Chemical Reagent Co. Ltd., China. The fixed amounts of the additives were wet-mixed with boehmite powder in the deionized water and thoroughly dispersed by stirring for 5 h. The amount of additive was 2.8 % (mass ratio of fluorine to boehmite). Then the mixture slurry was dried, calcinated between 850 - 1300°C for 1 - 10 h. As a comparison, boehmite powder without any additives was also prepared by the same processes. The size and morphology of the powders were observed using scanning electron microscope (SEM: Quanta FEG 250, USA). The phases evolvments of boehmite with temperatures were identified by x-ray diffraction (XRD: Rigaku D/Max-2400, Japan). The content of fluorine in the samples was evaluated by X-ray fluorescence analysis (XRF: ZSX Primus II, Japan). The fluorine bonding in the samples was analyzed by X-ray photoelectron spectroscopy (XPS: Escalab 250, UK). The system pressure during analyses was 1.33×10^{-7} Pa. The radiation was a monochromatized Al source (1486.6 eV). All spectra were referenced to C_{1s} located at binding energy (BE) of 284.8 eV. Surveys were recorded at 150 eV pass energy and high resolution F_{1s} spectrum at 20 eV pass energy, then fitted with XPSPEAK 4.1 software.

RESULTS AND DISCUSSION

Phase transformation

Figures 1 and 2 show XRD patterns of boehmite samples without any additives calcinated at various temperatures and times. As shown in Figure 1a, after the powder is calcinated at 1100°C and holding for 1 h, the XRD patterns mainly illustrated are diffraction peaks of the transient alumina phases, such as θ - Al_2O_3 , δ - Al_2O_3 and γ - Al_2O_3 . After calcinated at 1150°C for 1 h, the diffraction peaks of the transient alumina phases and the peaks of α - Al_2O_3 appear (seeing Figure 1b). With the increase of calcinating temperature, the intensity of diffraction peaks of α - Al_2O_3 is evidently strengthened. As the calcinating temperature reaches 1200°C holding for 1 h, all the diffraction peaks have vanished except

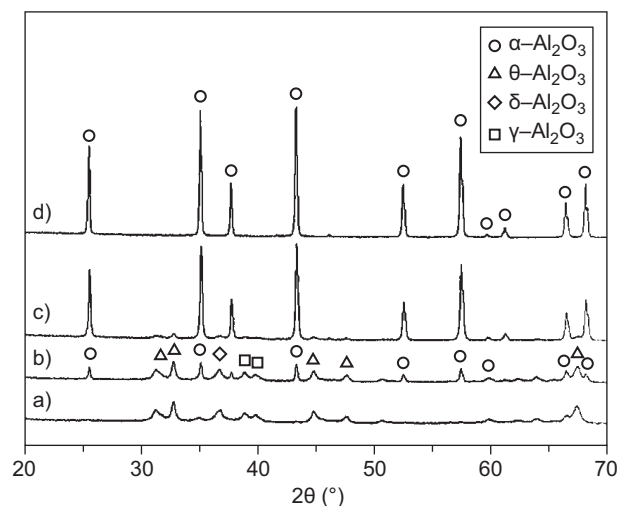


Figure 1. XRD patterns of boehmite powders calcinated at: a) 1100°C for 1 h, b) 1150°C for 1 h, c) 1200°C for 1 h, and d) 1300°C for 0.5 h.

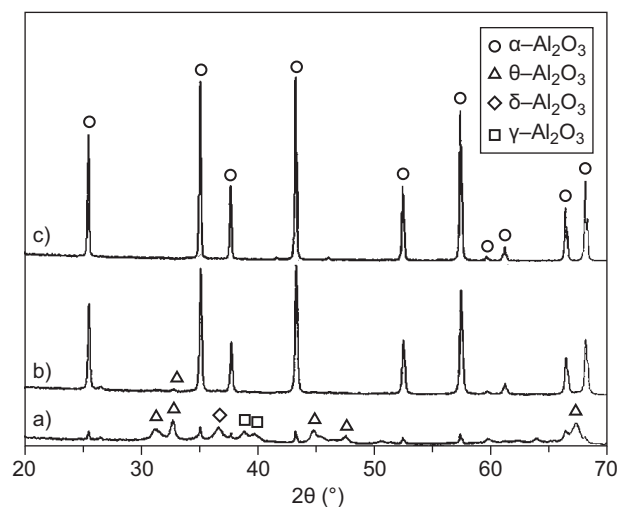


Figure 2. XRD patterns of AlOOH powders calcinated at: a) 1100°C for 600 min, b) 1150°C for 300 min, and c) 1400°C for 20 min.

the peaks of α -Al₂O₃, indicating that α -Al₂O₃ with complete crystallization is synthesized (Figure 1c). Further increasing the calcinating temperature to above 1200°C, no diffraction peaks of new phases are emerged (Figure 1d).

The calcinating times also have significant influences on the transformation of α -Al₂O₃ from the transient phases. Calcinated at 1150°C for 1 h, as it is seen in Figure 1b, most of the diffraction peaks are identified as the transient alumina phases. With the extension of the calcinating time, the transient phases gradually transform into α -Al₂O₃. After holding for 5 h at 1150°C, the XRD patterns show that nearly all diffraction peaks are identified as α -Al₂O₃ phases, indicating that boehmite has almost finished the conversion to α -Al₂O₃, as shown in Figure 2b. As calcinating at 1400°C, the calcinating time of 20 min is enough to complete the crystallization (Figure 2c). Taking into account of the resultant effects of the calcinating temperatures and calcinating times, the relationship between the calcinating processes and the complete formation of α -Al₂O₃ phase is obtained, as shown in Figure 3. It is assumed that boehmite is completely converted into α -Al₂O₃, while there are only diffraction peaks of α -Al₂O₃ phase, not the diffraction peaks of transient alumina phases are identified by XRD. Three features can be clearly seen from the curve. The converting time shows greatly decline with the converting temperature, and there are different slopes also observed in the curve. It is easily understandable considering the forming of α -Al₂O₃ from the transient phases is a reconstructive transformation and proceeds through a nucleation and growth processes [7, 26]. In high temperature range, the transformation is controlled by the rate of structural arrangement; while in low temperature, it is controlled by mass transfer rate. Another feature in the curve is that there is an incubation time of ~20 min, during which, the minimum calcinating temperature to finish the transformation to α -Al₂O₃ is about 1400°C. The third feature is that there is a minimum critical temperature, below which, α -Al₂O₃ phase cannot be completely converted, even after long holding hours (Figure 2a).

As NH₄F or AlF₃ is added to boehmite as an additive respectively, the similar trends are observed (also seen in Figure 3). First, the converting times sharp decrease with rise of the converting temperatures. Second, there all exist an incubation time and a minimum critical converting temperature. However, the differences are also obvious. The critical temperature is different with the fluorides added in the powder. The converting temperature (as the calcinating time is 5 h) of α -Al₂O₃ is 975°C and 875°C in the sample with AlF₃ and NH₄F as additives respectively, which is 175°C and 275°C lower than that of boehmite without any additives. The addition of NH₄F and AlF₃ to boehmite both induces the transformation of α -Al₂O₃ and it seems that addition of NH₄F to boehmite is more efficient than addition of AlF₃. The phase transformation

of α -Al₂O₃ is a kind of reconstruction of crystal lattice and a nucleation growth process requiring large amounts of energy to overcome the barrier energy for nucleation [8, 29], so in the case of no external interference, the phase transformation temperature is usually over 1200°C [30]. Although different mechanisms for addition of fluorides on decreasing the formation temperature of α -Al₂O₃ were presented, the most accepted view was that the deformed crystal lattice of the transient alumina phases decreased the temperature of formation as a result of the addition of fluorides [19, 31, 32]. As AlF₃ is added, the gaseous HF will form by the reaction of water and fluoride, enters the γ -Al₂O₃ lattice and weakens the crystal bond. Therefore, the activation energy of transformation to α -Al₂O₃ decreases [19]. After NH₄F is added, NH₄⁺ ion will be decomposed before the reaction of fluoride during the calcinating processes. The decomposition of NH₄F introduces a considerable amount of high energy defects in the transition alumina, which will destroy the normal arrangement of atom and induce the transformation of the transition alumina to α -Al₂O₃ [9, 14, 21]. Therefore, the converting temperature of α -Al₂O₃ from transition alumina further is decreased due to mutual roles of the decomposition of ammonite and fluoride [22]. Another difference is the minimum calcinating temperature corresponding the incubation time. The lower the critical converting temperature is, the lower the minimum calcinating temperature to finish the transformation to α -Al₂O₃ in the incubation time.

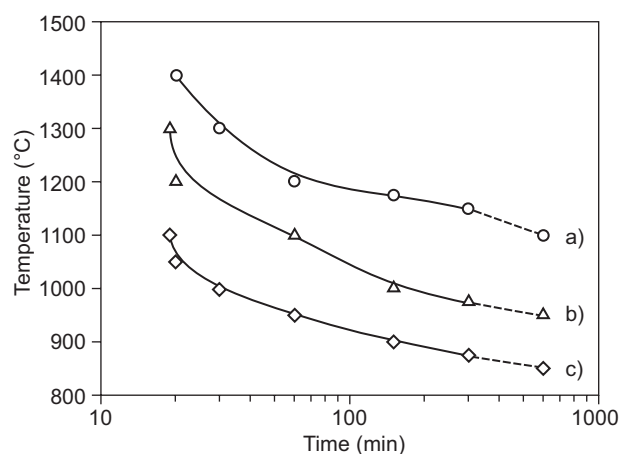


Figure 3. Influences of the calcinating processes on complete crystallization of α -Al₂O₃ phase.

Morphology of calcinated powders

Figure 4 shows SEM images of samples without any additives calcinated at various temperatures. As shown in Figure 4a, after the hold time of 1 h at 1200°C, SEM image of sample indicates that the powder particles show axiolitic or spherical shapes, and have an average size of about 200 nm. The morphology of the sample calcinated at 1400°C, as shown in Figure 4b, the leading

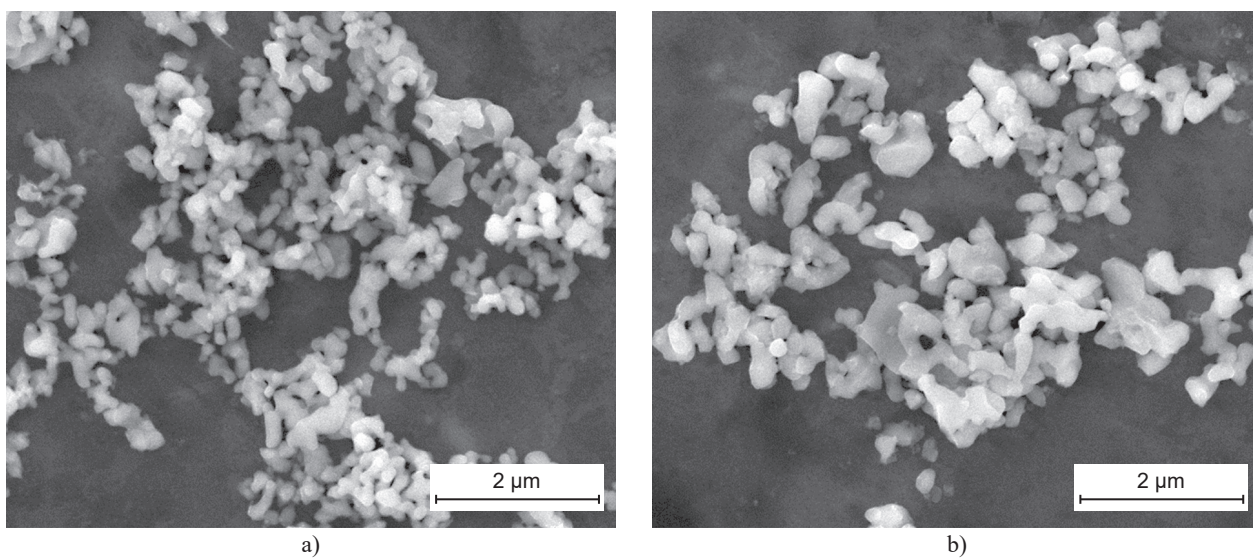


Figure 4. SEM images of boehmite powders without any additives calcinated 1 h at: a) 1200°C, and b) 1400°C.

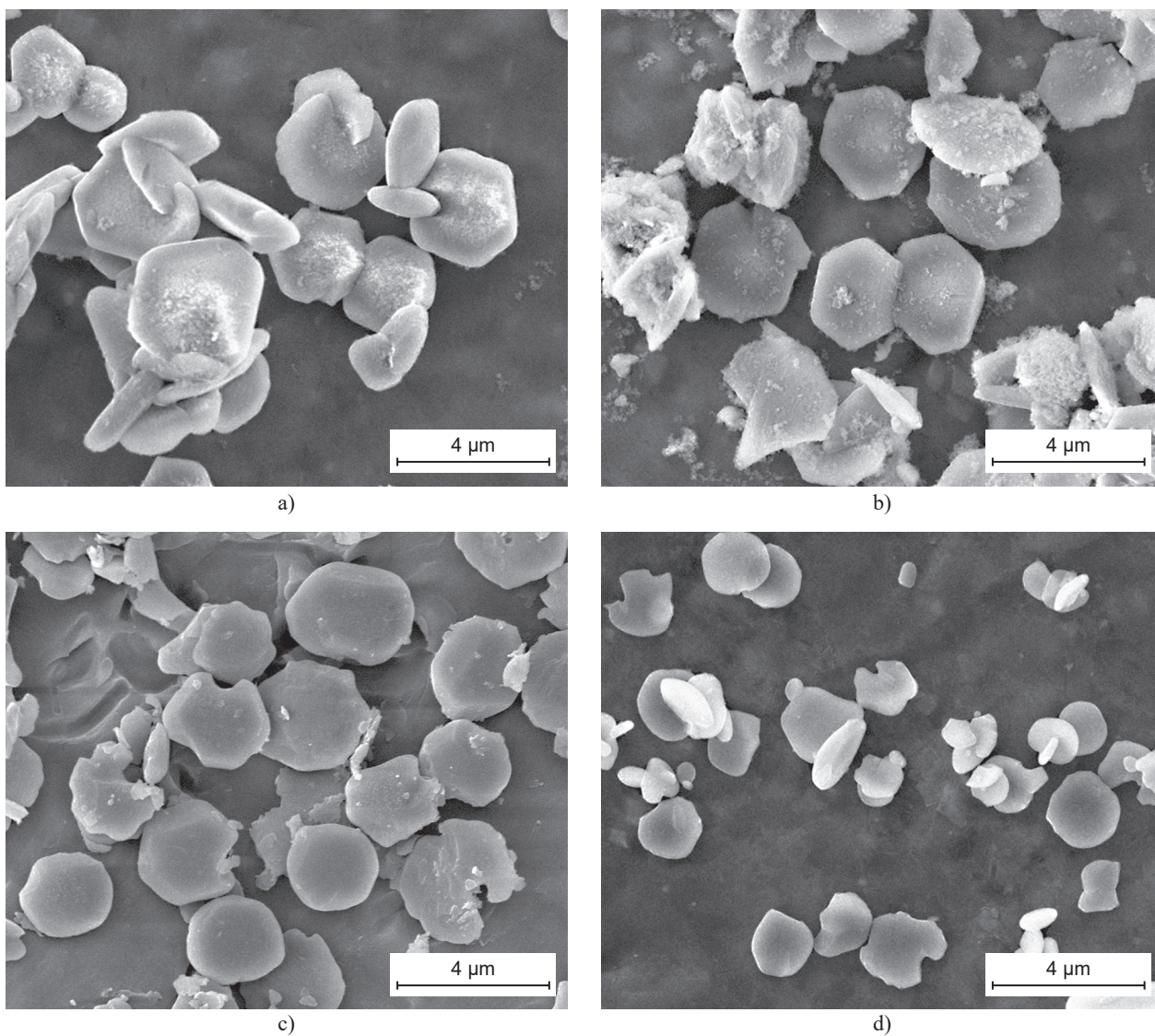


Figure 5. SEM images of boehmite powders with AlF₃ additive calcinated at: a) 1000°C for 2.5 h, b) 1100°C for 1 h, c) 1200°C for 1 h, and d) 1300°C for 1 h.

crystal form with the spindle-like shape is observed, also a slight amount of axiolitic or spherical particles are accompanied. Compared with the sample calcinated at 1200°C, the sample has an average larger particle size of about 500 nm, and vermicular morphology rigid agglomeration is formed due to the extensive necking and reagglomeration of the particles. In the sample with AlF_3 additive calcinated for 2.5 h at 1000°C, SEM image (Figure 5a) indicates that the sample has formed crystalline alumina platelets, in which, the very well-defined hexagonal platelet-shaped crystals with a diameter of $\sim 2 - 3 \mu\text{m}$ and thickness of $\sim 0.5 - 0.7 \mu\text{m}$ are crystallized. An increase the calcinating temperature to 1100°C shows a little increase in powder particle size, where it reaches an average size of about 3-4 μm in diameter, as shown in Figure 5b. Further increasing calcinating temperature to 1200°C induces change of the morphology, where the circular and elliptical platelets-shaped particles are observed, although the particle sizes do not show great changes compared with that of

samples calcinated between 1000 - 1100°C (Figure 5c). Increasing the calcinating temperature to 1300°C, however, results in a moderate decrease in particle size, along with the formation of more round and less irregular platelet-shaped crystals with an average platelet diameter of $\sim 1.5 \mu\text{m}$ (Figure 5d).

For comparison purposes, samples with NH_4F as an additive are prepared exactly the same fluorine content as the samples with AlF_3 . After undergoing the same powder preparation and heat treatment, the crystalline alumina with platelet-shaped particle is also formed, as shown in Figure 6. The hexagonal-shape crystals with thickness of $\sim 0.4 - 0.5 \mu\text{m}$ and with diameter of $\sim 4 - 5 \mu\text{m}$ are observed in the sample calcinated at 1000°C for 1 h, as shown in Figure 6a. Increasing the calcinating temperature to 1100°C and 1200°C leads to a little change of the hexagonal-shape crystals, in which, the edges of the crystals become round and irregular (Figures 6b and 6c). We also have observed a decrease in particle size as the calcinating temperature increased to 1200°C.

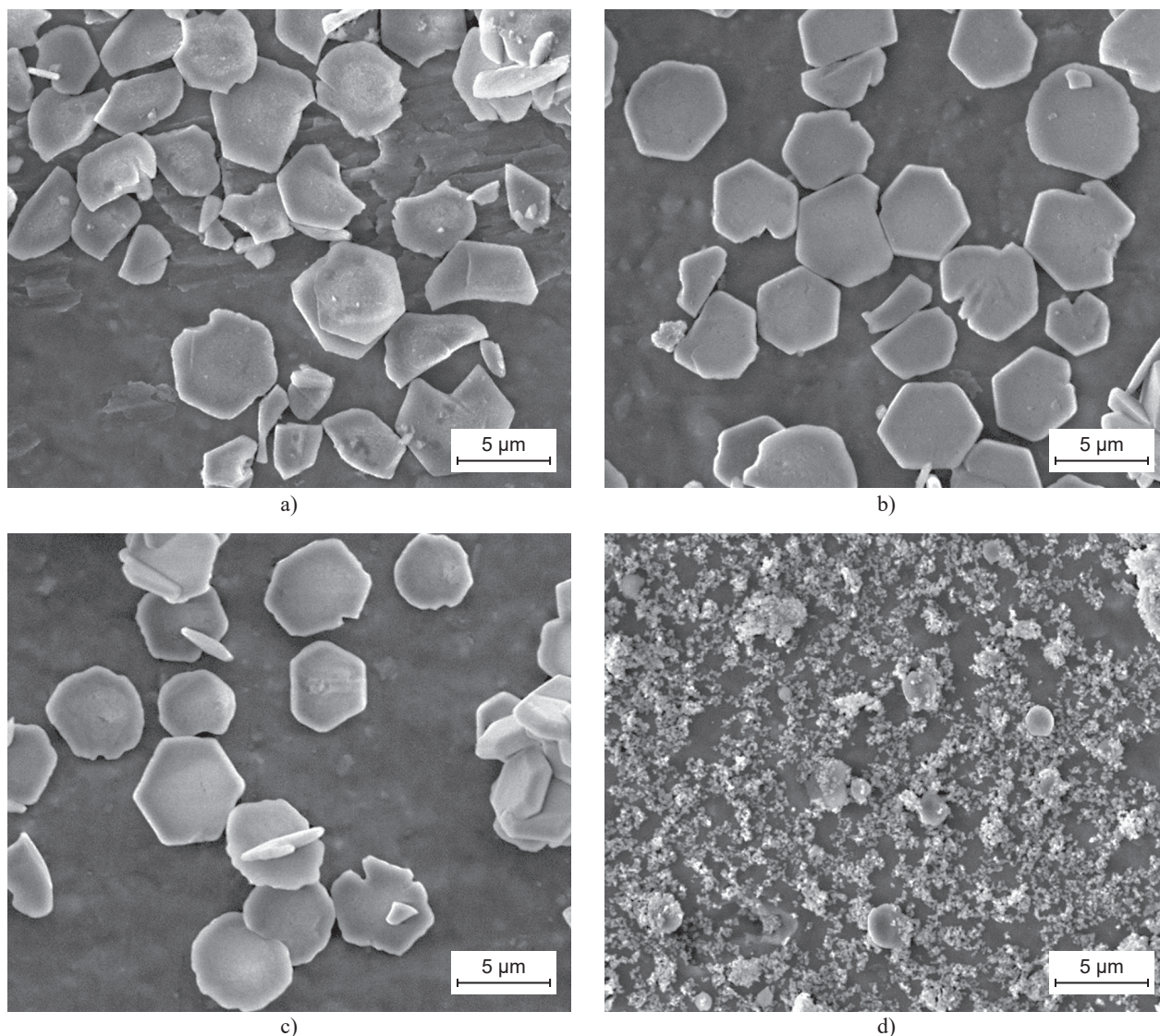
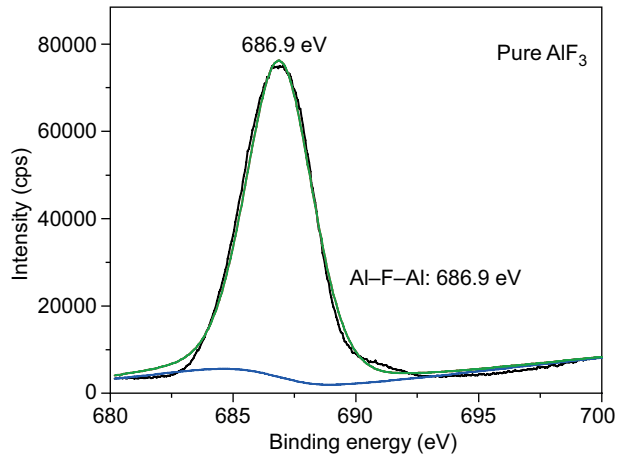


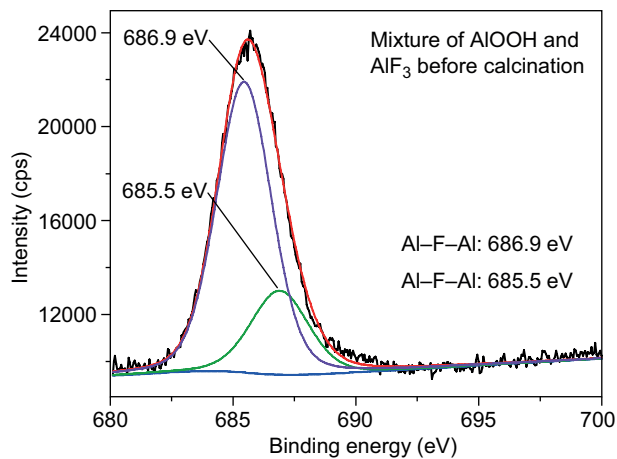
Figure 6. SEM images of boehmite powders with NH_4F additive calcinated 1 h at: a) 1000°C, b) 1100°C, c) 1200°C, d) and 1300°C.

XPS spectrum analysis

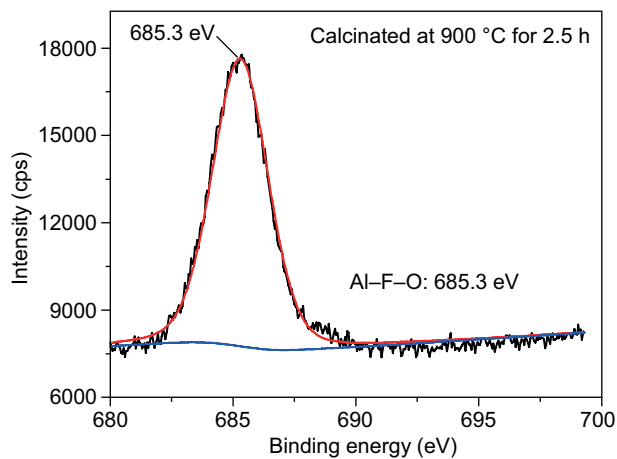
Especially as the calcinating temperature attains up to 1300°C, a drastic decrease in powder particle size occurs, along with the formation of particle-shaped crystals with an average diameter of ~ 500 nm. The morphology of most crystals consists of a wide particle size distribution of angular particles, accompanied with a slight amount of small platelet-shaped crystals (Figure 6d).



a)



b)

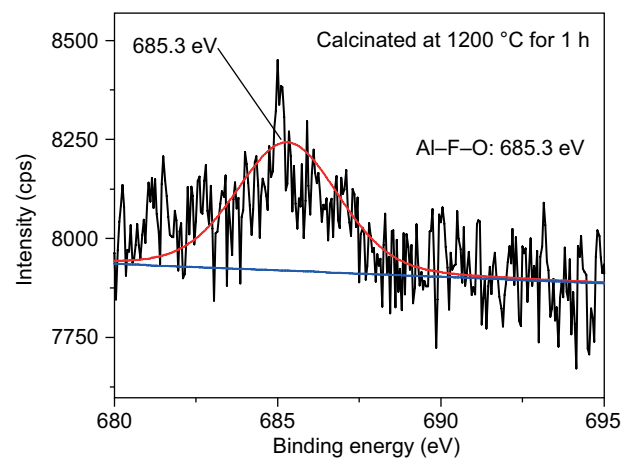


c)

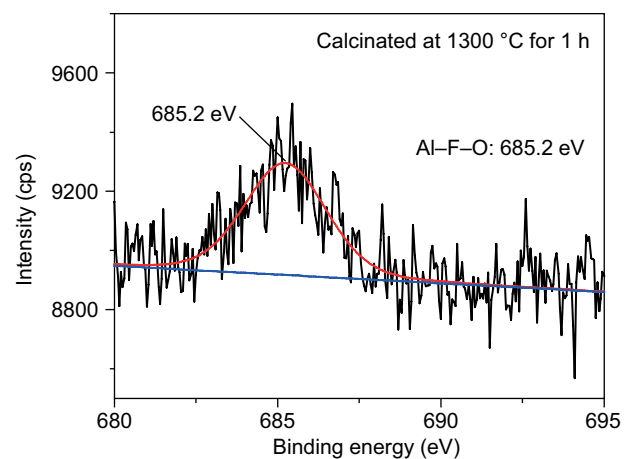
Figure 7 and 8 show the F^{1s} spectrum for samples with AlF_3 or NH_4F additives before and after calcination, in which the pure AlF_3 and NH_4F agents are also investigated for comparison. The peak at ~ 686.9 eV in pure AlF_3 agent is attributed to Al-F-Al bonding [33, 34], whereas the contribution at the peak of ~ 686.2 eV in pure NH_4F agent might be due to H-F bond (Figure 7a and 8a).

The Al-F-Al peak shifts towards lower binding energy are observed in boehmite powder mixed with AlF_3 , as shown in Figure 7b. From the F^{1s} spectrum of powder, two peaks are observed: one is a main peak at 685.5 eV; the other is a minor peak at 686.9 eV. In the powder with NH_4F as an additive, however, three peaks are observed: One peak is at ~ 686.2 eV, which is attributed to H-F bond observed in pure NH_4F ; the other two peaks are at ~ 685.3 and 686.9 eV, which are very close those observed in the AlF_3 -added sample (Seeing Figure 8b).

As mentioned in the experimental section, AlF_3 or NH_4F were thoroughly wet-mixed with boehmite



d)



e)

Figure 7. XPS spectrum of F^{1s} core levels in the pure AlF_3 and AlF_3 -added powders with different preparation conditions.

powder in the deionized water and dried. As AlF_3 or NH_4F is introduced into boehmite, chemically bonds between the Al^{3+} central ion in boehmite particles and the F^- ions in AlF_3 or NH_4F are produced $[\text{Al-F-Al}(\text{OH})_x]_y$ during the mixing by substituting oxygen with fluorine [31]. Therefore, the main peak at $685.3 \sim 685.5$ eV is due to mostly F-Al-O bonding, whereas the minor con-

tributions at 686.9 eV and 686.2 eV are due to Al-F-Al and H-F bond respectively. This means that the new bondings have formed during the preparation of dried samples before calcination [25].

However, the locations of F^{1s} spectrum have obvious changes with the rise of calcinating temperature, as shown in Figures 7c-7e. After calcination at 900°C for 2.5 h, the intensity of the peak at 686.9 eV has disappeared in the AlF_3 -added powder, indicating the fluorine in AlF_3 is volatilized below 900°C . Another peak at 685.5 eV shifts to 685.3 eV and the intensity of it decreases. As the calcinating temperature reaches 1200°C , the intensity of peak at 685.3 eV further decreases. At 1300°C , the left peak shifts towards lower binding energy of 685.2 eV are observed and a lower intensity is also obtained. It is suggested that the new formed fluorinated alumina species with F-Al-O bonding gradually decreases and the peak shifts towards lower binding energy with the rise of calcinating temperatures, which may be due to a diminution of the number of fluorine ligands around Al in (Al-O-Al-F) powders.

In the NH_4F -added powder calcinated at 900°C for 2.5 h, as it is seen in Figure 8c, the peaks at 686.9 eV

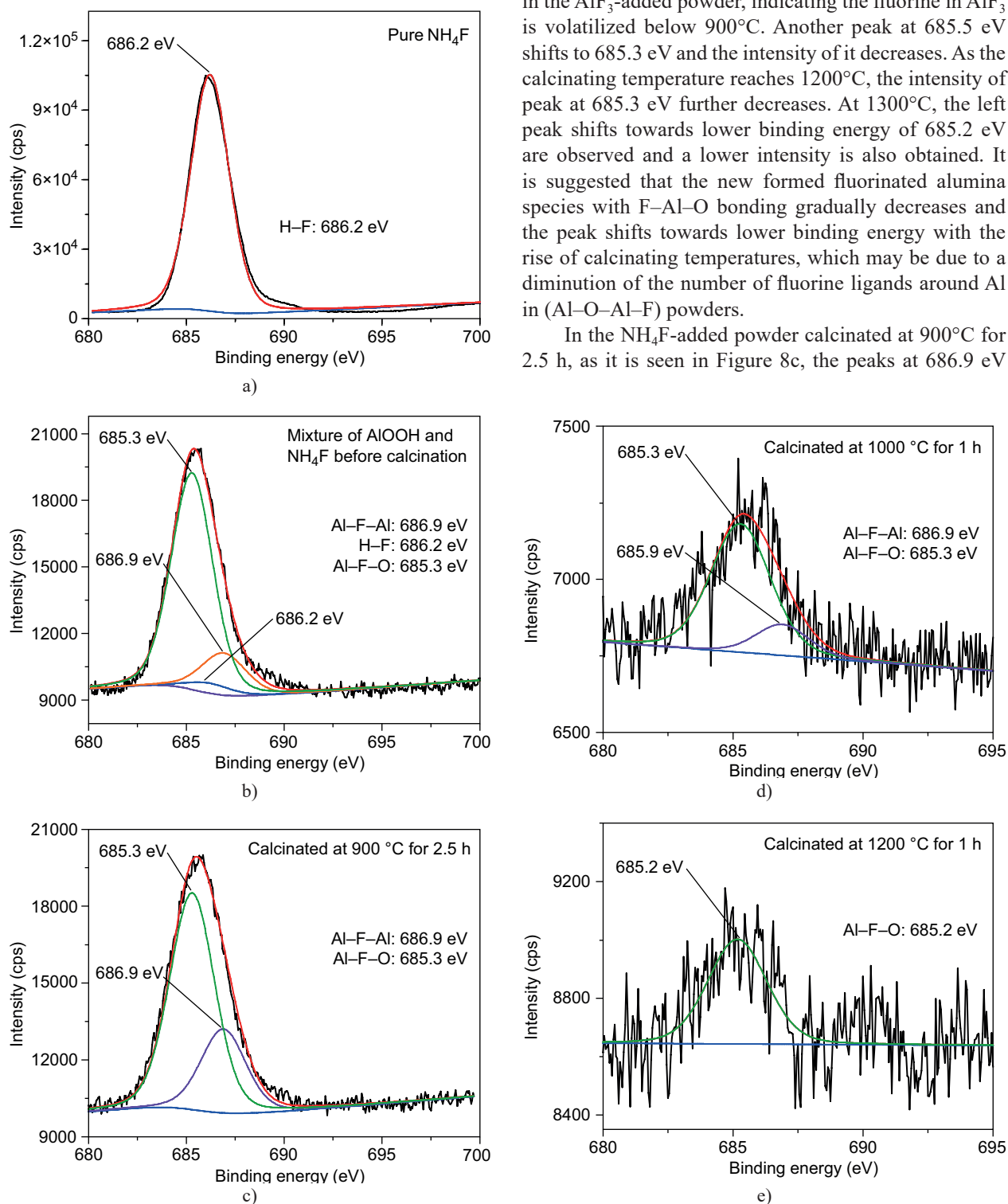


Figure 8. XPS spectrum of F^{1s} core levels in the pure NH_4F and NH_4F -added powders with different preparation conditions.

and 685.3 eV are still observed, but the peak at 686.2 eV is vanished. The intensity of the peak at 686.9 eV decreases; while the peak at 685.3 eV is strengthened. The peak at 685.3 eV cannot be transformed from F–Al–O bonding (at 686.9 eV), since it is not observed in the AlF_3 -added powder (Figures 7b and 7c). Therefore, it can be assumed that the reaction of H–F in the NH_4F with Al^{3+} from boehmite is occurred, producing Al–F–Al bonding (685.3 eV). Calcinated at 1000°C for 1 h, the peaks at 686.9 eV is also vanished and only the peak at 685.3 eV is observed, as shown in Figure 8d. Further increasing the calcination temperature, the change of the peaks has a similar tendency compared with that of AlF_3 -added powder (Figure 8e). The intensity of the peak at 685.3 eV gradually decreases and the peak shifts towards lower binding energy with the rise of calcinating temperature. The difference is that the intensity and the binding energy of the peak at 685.3 eV in the NH_4F -added powders are both lower than that in the AlF_3 -added ones at the same calcinating temperature.

DISCUSSION

Although influences of fluorides on reducing $\alpha\text{-Al}_2\text{O}_3$ transformation temperature are different, the incorporation of NH_4F or AlF_3 has changed the morphology of alumina formed, as shown in Figures 5 and 6. The formed $\alpha\text{-Al}_2\text{O}_3$ consists of clear, hexagonal plate-like particles instead of equiaxial or approximately equiaxial grains. However, for the powders prepared under the different temperatures, it appears that a critical temperature of process conditions is somewhere between about 1100°C and 1200°C. Above the critical temperature, a change of the powder morphology will occur. According to Hill and Danzer [25], alumina crystallization takes place by an evaporation-condensation process, in which the platelet shape of the powder is evident as the powders have undergone significant densification. However, the fully dense platelets firstly formed were coated by tiny particles on the surface, which looked like “dust” and was assumed to be AlF_3 by the authors. We also find “the dust” in the powders added with whether AlF_3 or NH_4F (Figures 5a, 5b and 6a). Following reports by some researchers [18, 23, 31, 32], several possible reactions were hypothesized in boehmite powders with fluorides as additives, in which the gaseous intermediate compounds, such as AlF_3 , HF and AlOF , were likely to be formed during the calcinating processes. The formed intermediate compounds might be possible to be attached on the surfaces of crystals as before they were evaporated. Therefore, the “dust” referred above may be one or more than one of them.

However, in observing SEM images of AlF_3 - or NH_4F - added samples the “dust” has disappeared after the high temperature treatment (Figures 5c and 6b). It is also found that the disappearance of the “dust” is corresponded

well with the initiation of decreasing in crystals sizes. With the rises of the calcinating temperature, “the dust” on the surface of powder is firstly disappearing and the surface becomes “smooth”. Then the hexagonal structure cannot retain and the decomposition of platelet crystals at edges occurs. This may be explained by the hypothesis that since the platelet-shaped crystals is formed by evaporation-condensation mechanism due to the fluoride volatile; increasing temperature will promote evaporation and the sublimation of fluorine [25]. In fact, too high temperate may initiate the rapid mass evaporation and the disappearance of fluoride’s effects, eventually resulting in the bluntness of the crystals with hexagonal shapes and diminution in size at higher calcinating temperature. This is also confirmed by comparing the XPS-spectrum.

From the F^{1s} spectrum, the peaks at 686.9 eV, 685.5 eV and 686.2 eV, which are contributed to Al–F–Al, Al–F–O and F–H bonding respectively, are observed in the powders. However, the peaks at 686.9 eV and 685.2 eV have disappeared at 900°C and 1000°C in the AlF_3 - and NH_4F -added powders respectively. There is only the peak at 686.9 eV exits above 1000°C in the powders. Return to SEM images, the “dust” on the surfaces of crystals does not disappear in the sample until 1200°C and 1100°C in the AlF_3 - and NH_4F -added powders respectively. This suggests that Al–F–Al and F–H bonding have disappeared before the “dust” vanishes. Therefore, the “dust” observed in the SEM images must not be a crystal with Al–F–Al or F–H bond, but be a fluorinated alumina species with F–Al–O bonding.

However, after the “dust” has vanished, the fluorine contents are still 0.218 % and 0.185 % left in the AlF_3 - and NH_4F - added samples calcinated at 1200°C for 1 h respectively, which are detected by XRF. That means that there is some fluorine may enter the lattices of alumina except for those coated on the surface of crystals. Kim et al. [31] also reported that F^- ions were centrally located in the lattice center of a $[\text{Al–F–Al–O}]_x$ crystal formed as a transient phase during the preparation of alumina crystal. It is the remained fluorine at lattice centers that keeps the hexagonal structure of $\alpha\text{-Al}_2\text{O}_3$ crystals retained at the high temperature. With the decrease of fluorine at lattices, the hexagonal structure begins to change at crystal edges, resulting in the bluntness of the crystals and the diminution in sizes. This is also confirmed by the XPS-spectrum. In the powders calcinated at 1200°C, the intensity of peak at 686.9 eV contributing to F–Al–O bonding still remains, although the “dust” has vanished, proving the assumption described above that some fluorine atoms have entered the lattices of $\alpha\text{-Al}_2\text{O}_3$. Thus, the fluorine being coated on the surface or entering the lattices of crystals have a structure with same F–Al–O bonding, which is not in agreement with results reported by some papers [25, 35]. With the rise of the calcinating temperature, the intensity of the peak contributing

to the F–Al–O bonding gradually decreases. As the calcinating temperature reaches 1200 - 1300°C (Figures 7d, 7e and 8e), the intensities of the peak become very weak, indicating the fluorine contents are very low in the powders. During this temperature ranges, the platelet-like α -Al₂O₃ cannot retain, decrease in sizes and even turn into particle-shaped crystals with the decrease and disappearance of fluorine.

CONCLUSIONS

The addition of AlF₃ or NH₄F to boehmite decreased α -Al₂O₃ transformation temperature to 1050°C and 950°C respectively, which was 150°C and 300°C lower than that without any additives. The formed α -Al₂O₃ powders consisted of clear, hexagonal platelet-like particles with a diameter of about 2 - 3 μ m and thickness of 200 nm. Fluorine ions in AlF₃ or NH₄F partly entered the lattices of α -alumina, the rest attached on the surface of alumina crystals, which had same F–Al–O chemical bonding. The results also indicated that F–Al–O bonding had formed during mixing process under the condition of water in the powder before calcination, which provided the possibility to achieve and keep the hexagonal structure of α -alumina. After the fluorides coated on the surfaces and entered the lattices of crystals were volatilized, the hexagonal structure cannot retain and the platelet-shaped crystals began to decompose.

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