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Short communication

Effect of AlF_3 seed concentrations and calcination temperatures on the crystal growth of hexagonally shaped α-alumina powders

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Abstract

To synthesize micro-sized and high crystalline α-alumina particles with uniformly and rapidly at low temperatures, various concentrated AlF_3 seeds were added into an anhydrous ethanol solution saturated by an aluminum hydroxide starting material, gibbsite $Al(OH)_3$. Hexagonal shaped α-alumina powders highly crystallized were observed at lower temperature of 750 °C, in the ranges from 0.01–5.0 mol% seed concentrations, and the α-alumina crystal growth depends on the concentrations of added AlF_3 seed. When 1.0 mol% AlF_3 seeds were added, the largest α-alumina hexagonal crystals (average size about 4.8 m after calcination at 900 °C) were produced. Additionally the crystallinity and size of α-alumina particle increases linearly with the calcination temperature. The size rapidly increased with an increase of calcination temperatures to 800 °C and then gradually increased up to 900 °C. This result shows that crystal growth of α-alumina is affected by seed concentrations and crystallized calcination temperature.

Keywords: Rapid crystal growth; $Al(OH)_3$; AlF_3 seeds; Hexagonal shaped α-alumina

1. Introduction

Alumina (Al_2O_3) undergoes many meta-stable polymorphs to form thermodynamically stable α-Al_2O_3, the corundum hcp packed form [1]. Alpha alumina (α-Al_2O_3) materials are utilized in many areas of modern industry because of its unique mechanical, electrical, and optical properties [2,3]. The properties are governed by its processing techniques, and refining α-Al_2O_3 to obtain superior micro-crystal are great interested in recent years [4,5]. The growths of micro-crystals are mainly determined by the relative growth rates of the various crystal faces, which are dependent on internal structural factors and external conditions, such as, temperature, precursor concentration, pH value, and the added seeds. Accordingly, the growth of metal oxide crystal is arrived by studying growth mechanism of crystals. Normally, α-Al_2O_3 crystals are obtained via a sequence of phase transformations such as non-crystalline/amorphous $Al_2O_3 \rightarrow \gamma\text{-} \rightarrow \delta\text{-} \rightarrow \theta\text{-} \rightarrow$ α-Al_2O_3 [6,7]. A number of papers have described the effect of a small amount of ceramic oxide seed particles on microstructure formation from meta-stable alumina to α-Al_2O_3 [8–10]. In our previous study [11], we reported that 1200 °C was required to achieve full transformation from unseeded boehmite (AlOOH) to α-Al_2O_3. The addition of hexagonal structured AlF_3 seeds, which are iso-structural with α-Al_2O_3, provides low energy sites for heterogeneous nucleation, and thus, reduces the energy barrier required for nucleation. The result can supply a rapid crystallization rate and at low temperature (less than 750 °C) the phase transformation into α-Al_2O_3. In our previous study, we have focused on lowering the calcination temperature and controlling the morphology by AlF_3 seed addition, however the influence of seed concentration and calcination temperature on the crystal growth of α-Al_2O_3 were not examined.

In the present study, the size of hexagonally shaped rhombohedral α-Al_2O_3 particles are controlled by addition of various concentrated AlF_3 seeds into an anhydrous ethanol solution saturated by $Al(OH)_3$ particles during the sol–gel process. Furthermore, this study has also tried to investigate the changes in crystal size and morphology depends on the calcination temperature. Thermally treated Al_2O_3 powders

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were prepared at various AlF_3 seed concentrations in the ranges of 0.01–5.0 mol%, and the prepared powders are characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). In addition, rate of crystal growth to produce perfect α-Al_2O_3 particles were inferred using the relation between the calcination temperature and particle size determined from SEM images.

2. Experimental

$Al(OH)_3$ (commonly named gibbsite, monoclinic crystals, 99.95%, Sigma-Aldrich), is one of the mineral form of aluminum hydroxide, and was used as an aluminum precursor in this study. AlF_3 (aluminum fluoride, 99.99%, Sigma-Aldrich) was used as a seed to control the crystal morphology and the formation temperature required to produce α-Al_2O_3 crystals. The procedure was done using a commercial sol–gel method. Briefly, 1.0 mol of $Al(OH)_3$ was added to anhydrous ethanol, and well-stirred for 1 h until completely dispersed. Then 0.01, 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, or 5.0 mol% of AlF_3 seeds were added into the anhydrous ethanol solution saturated by $Al(OH)_3$, and the pH was raised to 9 by adding dilute NH_4OH to induce the rapid hydrolysis of $Al(OH)_3$. Here note that AlF_3 seeds are almost insoluble in ethanol. The final mixture was stirred homogeneously for 5 h to surround AlF_3 particles by $Al(OH)_3$ particles uniformly. The mixture was heated at 60 °C for 6 h to remove solvent, and dried at 50 °C for 24 h. As-prepared alumina powders were then heated under air condition with a heating rate of 10 °C min^{-1} at a temperature range of 200–750 °C, and then maintained at each temperature for at least 10 h to obtain the α-Al_2O_3 powder. Here For comparison, Al_2O_3 powder obtained from $Al(OH)_3$ ethanol solution without AlF_3 seeds was also prepared, and heat-treated at 1100 °C to obtain the α-Al_2O_3 structure.

Thermally treated alumina powders were identified by powder XRD (model MPD from PANalytical) using nickel-filtered CuKα radiation (30 kV, 30 mA) at 2θ angles of 10–80 °. The scan speed used was 10° min^{-1} and the time constant was 1 s. The size and shape of the alumina powders obtained at different calcination temperatures were measured by field emission scanning electron microscopy (FESEM, S-4100, Hitachi).

3. Results and discussion

Fig. 1 shows the XRD pattern of the thermally treated alumina phases prepared with and without 1.0 mol% of AlF_3 seed in $Al(OH)_3$ saturated ethanol solution. The used AlF_3 seeds are same as that of our previous study [11]. AlF_3 seed has a hexagonal crystal structure (P63/mmc) with spherical particles of 100 nm. Al_2O_3 is a structurally complex oxide that forms several metastable phases, which transform in the order of gibbsite → γ- → κ- → α-Al_2O_3. In this study, α-Al_2O_3 exhibit peaks at 2θ angles of 25.57, 35.14, 37.76, 43.39, 46.16, 52.53, 57.47, 61.27, 66.49, 68.18, and 76.84, corresponding to (012), (104), (110), (113), (202), (024), (116), (018), (214), (300) and (1010) planes, respectively [12]. α-Al_2O_3 belongs to rhombohedral crystal system and the space group of *R*3*c*. The rhombohedral system can be thought of cubic system stretched along a body diagonal, $a=b=c$; $\alpha=\beta=\gamma\neq 90^\circ$. In some classification schemes, the rhombohedral lattice system is combined with the hexagonal lattice system. Unlikely that observed in our previous study, κ-type was obtained in this study and θ-type was not obtained when gibbsite was used as an aluminum precursor, indicating that the alumina phases formed during heat treatment depend on the aluminum starting material. Most significantly, α-crystallization is formed perfectly at 750 °C throughout the κ-Al_2O_3 phase because of AlF_3 seeds. These result shows that AlF_3 seeds significantly affect the crystallinity of α-Al_2O_3. The mechanism of phase transformation was provided in our previous study [11]. Briefly AlF_3 seeds in anhydrous ethanol solvent are surrounded by negatively charged $Al(OH)_3$. These complexes then further react to form metal–oxygen polymeric networks -[–Al–O–Al–O–Al–]-, due to the eliminations of H_2O or ROH between the aggregated particles. Here the transformation from meta-stable intermediates to α-Al_2O_3 involves a significant change in the oxygen sub-lattice and usually temperatures above 1200 °C are required for complete conversion into the thermodynamically stable corundum phase. However, the addition of AlF_3 can enhance the rate of phase transformation from metastable Al_2O_3 to α-Al_2O_3 with reduced temperature. Generally during heat treatment, AlF_3 can participate into the following reversible reaction [13]:

$$2AlF_3 + 3H_2O \rightarrow Al_2O_3 + 6HF$$

However, the more positive reaction maybe performed through the next reactions in this study.

$$AlF_3 + H_2O \rightarrow AlOF + 2HF \quad (1)$$

The gaseous intermediate AlOF plays a vital role for accelerating the atomic transference velocity to enhance the phase transformation. Although it is difficult to define the composition of the intermediate compound, it could ultimately transform into alumina as follows:

$$3AlOF \rightarrow Al_2O_3 + AlF_3 \quad (2)$$

$$2AlOF + H_2O \rightarrow Al_2O_3 + 2HF \quad (3)$$

Consequently, the placement of a seed crystal into solution allows the recrystallization process to expedite by accelerating random molecular collision/interaction. Often, this phase transition is referred to as nucleation. Seeding is therefore said to decrease the amount of time needed for nucleation through a recrystallization process. Using the Scherrer equation [14], crystallite sizes were determined. Calculated α-crystallite sizes based on a special peak of 43.44° were 2553.89 and 3235.30 nm for α-Al_2O_3 powders obtained by thermal treatment at 1100 °C (without seed) and 750 °C (with 1.0 mol% AlF_3 seed), respectively.

Many compounds have the ability to crystallize into different crystal structures – α phenomenon called polymorphism. Each polymorph is in fact a different thermodynamic solid state and the crystal polymorphs are even though same compounds exhibit different physical properties based on dissolution rates, shapes, and

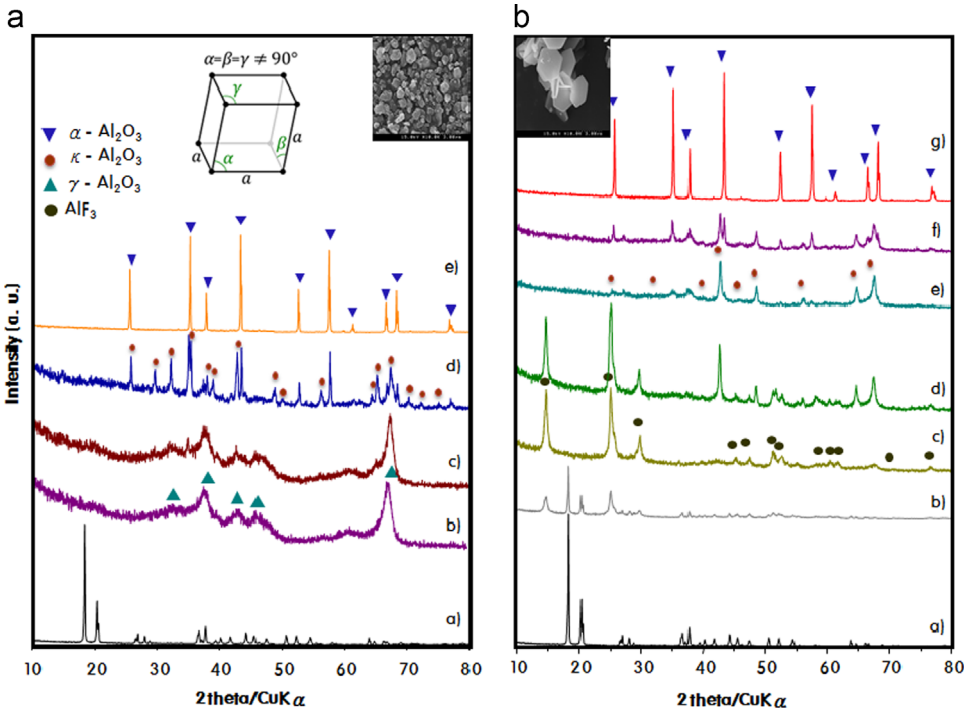


Fig. 1. The XRD patterns of thermally treated alumina phases prepared with or without 1.0 mol% of AlF_3 seed in saturated $Al(OH)_3$ ethanol solutions. (a) Without seeds and (b) with 1.0 mol% AlF_3 seeds: A-(a) AlF_3, -(b) 800, -(c) 900, -(d) 1000, and -(e) 1100 °C; B-(a) AlF_3, -(b) 200, -(c) 400, -(d) 500, -(e) 600, -(f) 700, and -(g) 750 °C.

melting points. Due to this reason, for industrial manufactures the polymorphism has a major importance to produce crystalline products. In the present study, we used eight concentrations of AlF_3 seeds, 0.01, 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mol% to ensure the effect of seed concentrations on morphology and crystal growth. Fig. 2 shows the FESEM photos of nine α-Al_2O_3 powders produced from different seed concentrations after thermal treatment at 900 °C. The SEM images of AlF_3, $Al(OH)_3$, and un-calcinated sample prepared using 1.0 mol% seed were also additionally presented for comparison. The used AlF_3 seeds and $Al(OH)_3$ particles had spherical shaped particles of 100 nm and polyhedrons of 0.5–1.0 μm, respectively. However, the particle shape of un-calcinated sample prepared using 1.0 mol% seed was not distinguishable because of strong aggregations among the particles. All of α-Al_2O_3 samples exhibited hexagonally shaped, except α-Al_2O_3 crystals prepared using 0.01 mol% seed. Particle size of α-Al_2O_3 significantly increased with an increase of seed concentration up to 2.0 mol% which average size was about 4.8 μm. However, the crystal size did not increase further, which is due to the increased number of nucleation sites.

Scheme 1 shows a putative mechanism for the synthesis of hexagonal-shaped α-Al_2O_3 in the presence of AlF_3 seeds. The crystallization process consists of four major events, such as super-saturation, nucleation, crystal growth, and crystal (solid state) phase transformation into more stable structures. When AlF_3 seed was not used, super-saturation involves the dispersion of $Al(OH)_3$ to form Al–F–Al–$(OH)_x(OR)_y$ complex by alcoholysis in ethanol. In the nucleation step, Al–F–Al–$(OH)_x(OR)_y$ complexes form stable clusters of [Al–F–Al–O–Al–O]$_n$ via the condensation of Al–F–Al–$(OH)_x(OR)_y$ complexes, and these then produced nuclei. These clusters need to reach a critical size in order to be stable nuclei, and the critical size is dictated by some operating conditions such as calcination temperatures and seed concentrations. Furthermore, during the induction stage of nucleation the atoms are arranged in a defined and periodic manner to produce the crystal structure. In the present study, super-saturation and nucleation process were carried out by liquid system. Crystal growth refers to the subsequent growth of nuclei that succeed in achieving critical size. Sometimes nucleation and growth continue to occur simultaneously in a super-saturated liquid system. Super-saturation and heating are the driving forces of crystallization and hence nucleation and growth rates are driven by super-saturation in solution. Depending on the conditions, nucleation or growth dominates crystals with different sizes and shapes are obtained. Furthermore, it is well known that presence of AlF_3 in supersaturated phase can significantly make changes in the crystal nucleation, growth, and aggregation of nuclei. During thermal treatment in the range 400–750 °C, the microscopic mechanism of crystal growth essentially involves dynamic balance between adsorption and desorption. The existence of AlF_3 can make the same crystal plane with seriously aggregated microstructure via crystal growth.

Table 1 shows the crystallite sizes calculated for all diffraction planes observed by XRD pattern of α-Al_2O_3 phases prepared at different AlF_3 seed concentrations after thermal treatment at 900 °C. The tabulated crystallite sizes were determined for the main peak of 43.39°. The table clearly shows that the crystallite size increases with increase of AlF_3 seed. The obtained results

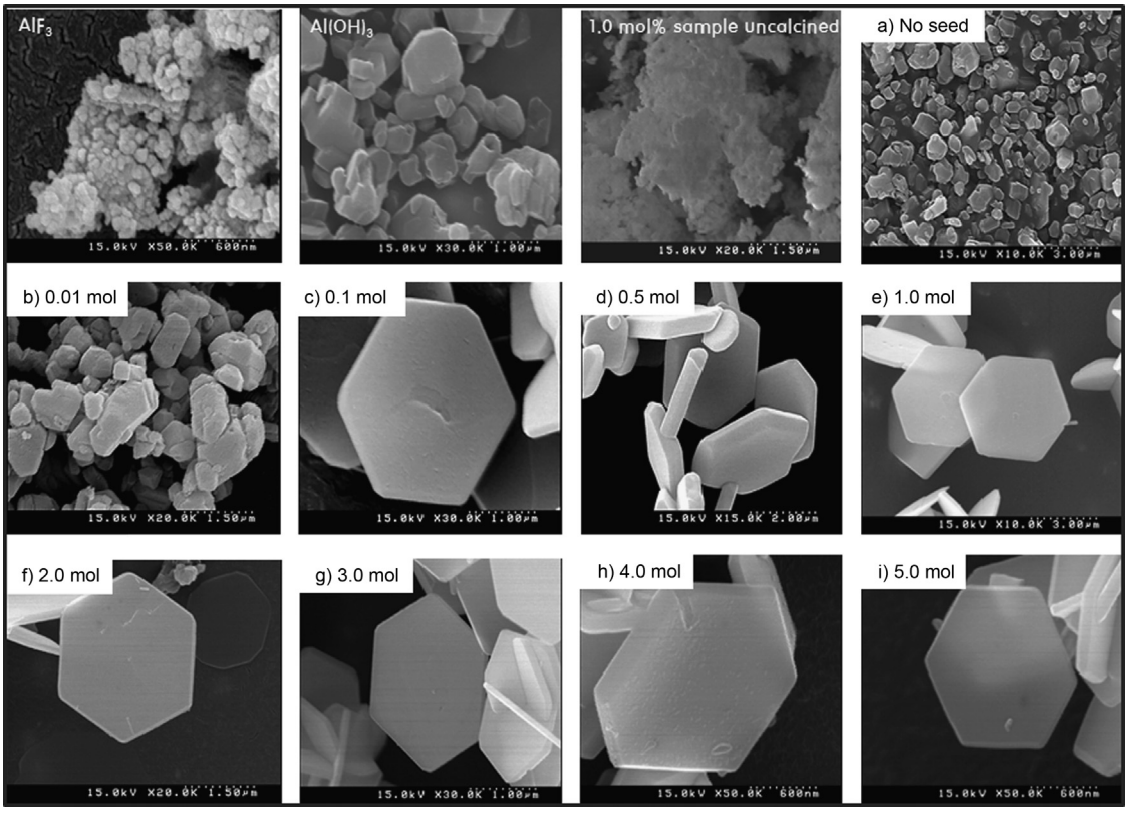
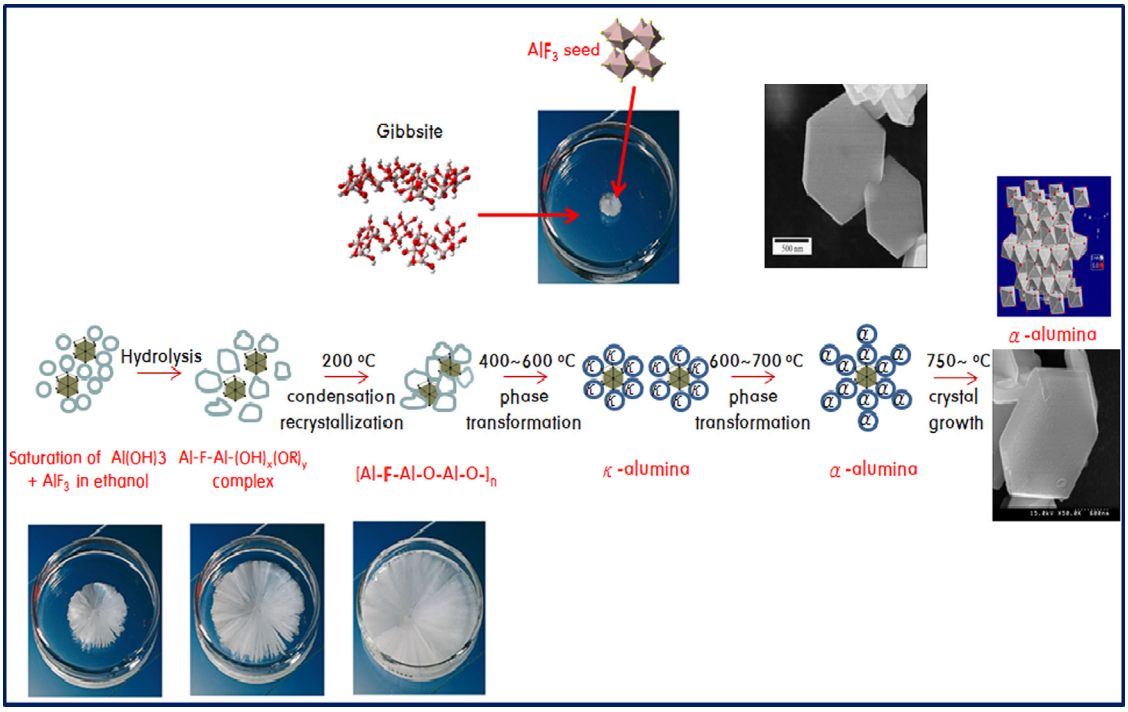


Fig. 2. The FESEM photos of α-Al_2O_3 powders produced using different seed concentrations after calcination at 900 °C.



Scheme 1. Suggested mechanism for the synthesis of hexagonally shaped α-Al_2O_3 in the presence of AlF_3 seeds .

are confirmed from the particle sizes observed in FESEM photos. Depending on the conditions, either nucleation or crystal growth may predominate, and as a result crystals with different sizes and shapes are obtained. The control of crystal size and shape is one

Table 1
The crystallite sizes calculated at all diffraction planes detected by XRD patterns of α-Al_2O_3 phases which prepared at different AlF_3 seed concentrations after thermal treatment at 900 °C.

2θ	d(h, k, l)	0.1 mol	0.5 mol	1.0 mol	2.0 mol	3.0 mol	4.0 mol	5.0 mol
25.59	(0, 1, 2)	[a]2146.63	2402.35	2350.53	2506.42	2335.24	2404.73	2425.04
35.16	(1, 0, 4)	2909.28	3300.95	3076.43	3564.54	3080.64	3201.60	3217.63
37.81	(1, 1, 0)	1321.79	1568.85	1440.75	1522.46	1475.17	1529.00	1588.12
43.39	(1, 1, 3)	3417.71	3641.25	3508.33	3732.44	3382.12	3728.70	3731.14
52.59	(0, 2, 4)	1356.54	1512.62	1386.17	1587.86	1440.02	1518.62	1491.08
57.53	(1, 1, 6)	2611.17	2865.95	2672.30	2890.03	2610.83	2753.36	2770.83
66.58	(2, 1, 4)	970.64	1172.32	1018.43	1157.38	1048.83	1130.56	1102.91
68.29	(3, 0, 0)	1514.74	1796.70	1706.98	1793.82	1599.09	1758.31	1665.96
76.89	(1, 0, 10)	426.54	386.17	412.23	398.92	401.47	404.24	395.31

[a]D (crystallite size)=0.9λ/β cos θ (nm), at 900 °C.

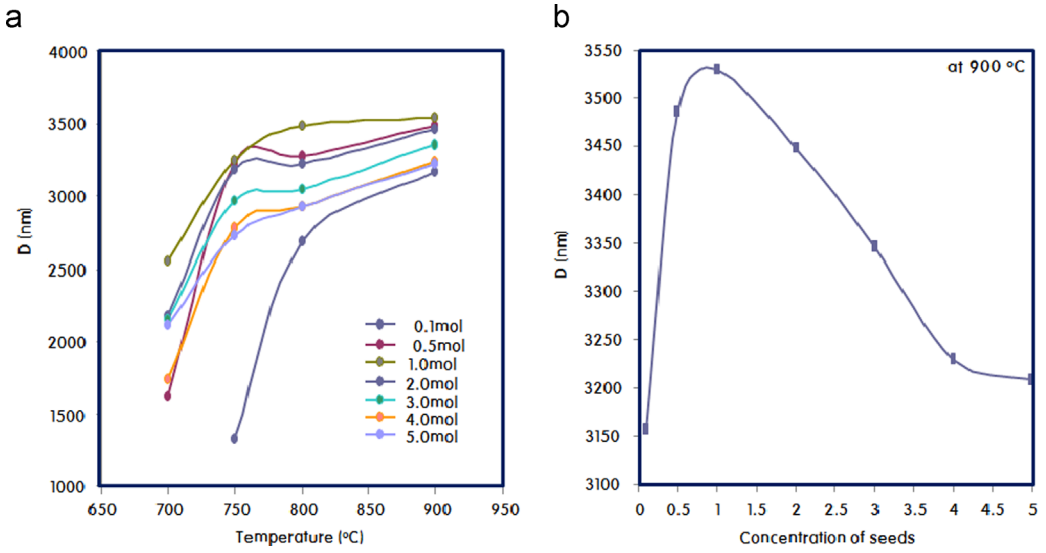


Fig. 3. The relationship between the calcination temperatures (a) and seed concentration (b) verse the crystallite sizes calculated from the Scherrer's equation based on a main peak at 2θ=43.39° (corresponding to the (113) plane).

of the main challenges for the industrial manufactures especially pharmaceutical manufactures. In the present study, the rate of crystal growth was driven by the existing AlF_3 seeds in solution.

Fig. 3(a) shows the relation between calcination temperature and the crystallite size. Fig. 3(b) shows the relation between the concentration of seed and the crystallite size. The crystallite size was calculated by using the Scherrer's equation based on a main peak at 2θ=43.39° which corresponds (113) plane. The temperatures in the range of 700 (the temperature firstly shown α-Al_2O_3 structure)~900 (the temperature no any growth in α-Al_2O_3 crystallite sizes) °C were selected. In our previous study [11], we found that if AlOOH was used as the Al precursor the most appropriate temperature for growing alumina is 750 °C. Moreover, depending on the Al starting material, the α-Al_2O_3 crystallization temperature was different and different alumina phase intermediates were produced at each calcination temperatures. So in this study wide range of temperatures has been given, which can lead to complete α-alumina. But the temperature more than 1000 °C were excepted because those did not adequate for the purpose of this study, growing the hexagonal shaped α-alumina at low-temperatures. From the relationship between crystal growth temperature and crystallite size shown in Fig. 3a, crystallite size ranged from 1200 to 3700 nm were produced using various AlF_3 seed concentrations and the calcination temperature ranges from 700 to 900 °C. This shows that the crystal growth of produced α-Al_2O_3 samples are depending on AlF_3 seed concentrations and calcinations temperatures. The α-formations in other samples were produced at lower temperature of 700 °C than that of the sample with use of 0.1 mol % AlF_3 seed. Many factors affect the reaction rate, such as reactant concentration, temperature, pressure, and catalyst

type. For the α-Al_2O_3 samples produced using different seed concentrations, the crystallite size increases linearly with the calcination temperature. Except for the sample prepared using 0.1 mol% AlF_3 seed, the crystallite size rapidly increased with calcination temperature up to 750 °C but did not beyond 800 °C. It meant that not only calcination temperature dominate for crystal growth in the temperature ranges of > 800 °C and < 700 °C other factor such as seed concentration also important. As shown in Fig. 3b, the crystallite size for α-Al_2O_3 was large when 1.0 mol% AlF_3 seed was used. We suggest that the use of an optimum amount of AlF_3 seed promotes α-Al_2O_3 crystal growth at lower temperatures and controls crystal morphology.

4. Conclusions

XRD result indicates that α-Al_2O_3 rhombohedral structures were successfully fabricated at 700 °C using AlF_3 seed concentrations of 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mol% per mol of Al $(OH)_3$ precursor. The result also shows that the α-phased alumina was observed for seed concentrations of 0.01–0.1 mol% above 750 °C. FESEM image shows that the addition of seed could control the hexagonal shape in α-Al_2O_3 crystals. The hexagonal particle size of α-Al_2O_3 were significantly increased with seed concentration up to 2.0 mol%, however, the crystal size did not increase further more than 2.0 mol%. The crystallite size increases with the calcination temperature from 700 to 900 °C. However, the α-crystallizations were formed at lower temperature less than 700 °C when 1.0–2.0 mol% AlF_3 seeds were used. These results gives an evident that 1.0–2.0 mol% is the optimum amount of seed for α-formation at lower temperatures less than 700 °C. Eventually, this study demonstrates that AlF_3 seed addition affects α-Al_2O_3 crystal growth and morphology.

Acknowledgments

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