Effect of fluoride additives on production and characterization of nano- α - Al_2O_3 particles

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Abstract. Nano- α - Al_2O_3 particles were synthesized by a sol-gel method using aqueous solutions of aluminum isopropoxide and 0.5 M aluminum nitrate. Sodium dodecylbenzenesulfonate (SDBS) was used as surfactant stabilizing agents. The solution was stirred for 48 h at 60 °C. The microstructural observation showed that surfactant with 48 h stirring time nanoscale α - Al_2O_3 powder was produced at 1200 °C in the range of 20–30 nm in the presence of SDBS as a surfactant with 48 h stirring time. Temperature reduction of α - Al_2O_3 formation has been achieved by introducing fluoride in the alumina precursor. The effects of ZnF_2 additive and milling on the phase transformation as well as micrograph of the prepared α - Al_2O_3 particles were investigated. The samples were characterized by different techniques such as X-ray diffraction, thermogravimetry analysis, differential scanning calorimetry, Fourier transform infrared spectra, scanning electron microscopy and transmission electron microscopy. Results indicated that using zinc fluoride (ZnF_2) additive accompanied by milling led to retardation of the transformation temperature and modification of the alumina particle shape. The finest size for nonagglomerated nano-plate-like α - Al_2O_3 particles (15–20 nm) was achieved at 950 °C.

Keywords. α - Al_2O_3 ; X-ray diffraction; scanning electron microscopy.

1. Introduction

Ceramics have many applications in high technology from structural to electrical and electronic because of their excellent properties, but sometimes their low mechanical properties limit their wide applications. However, as nanocrystalline ceramics can enhance their mechanical properties, nanometer size powder processing is of great importance in the field of nanotechnology to provide high strength and high toughness (Karagedov and Lyakhov 1999; Mirjalili *et al* 2010). Alumina exists in a number of metastable transition phases as well as the thermodynamically stable α - Al_2O_3 or corundum (Karagedov and Lyakhov 1999; Trunov *et al* 2005; Mirjalili *et al* 2010). 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 (Xue and Chen 1992; Liu *et al* 2005; Yang *et al* 2007). Phase transformations is the process in which aluminum hydroxide is converted to aluminum oxide and is as shown in figure 1. It is indicated that temperature above 1200 °C is needed to obtain α - Al_2O_3 (Wang *et al* 1999; Li *et al* 2006; Ming *et al* 2007). One of the important challenges in thermal transformations of alumina ceramic systems has been attributed to

the reduction of the temperature in which α - Al_2O_3 phase is formed in order to impede the grain growth that occurs during high temperature calcination processes. Applying high temperature is technically energy consuming but may also initiate finger or vermicular grain growth for the α -particles. This makes it impossible to obtain well-dispersed and nano-sized α - Al_2O_3 powders (Hyuk-Joon and Kug 1999). Many scholars have tried to reduce the temperature for α -alumina formation in order to avoid coarsening of the α -particles occurring due to high-temperature calcination. Among these different techniques, using nucleation aids such as alumina (α - Al_2O_3) seeds, α - Fe_2O_3 , V_2O_5 and/or fluorides are reported to have significant influence on reducing the temperature needed for the α - Al_2O_3 phase formation. It is also indicated that the fluoride ions enhance the directional growth of the alumina nanostructures (Saito *et al* 1998; Li *et al* 2007; Arami *et al* 2008). Liu *et al* (2005) found that significant defects are generated by milling. However, the transformation temperature has been dramatically lowered by these defects as these defects enhance the diffusion phenomenon (Wang *et al* 2005).

This paper will present the results of the research conducted on preparing nano- α - Al_2O_3 with surfactant as well as applying zinc fluoride (ZnF_2) additive and milling to reduce the transformation temperature for α - Al_2O_3 formation. The novelty of this research is that it compares the characteristics of nano- α - Al_2O_3 in the presence and absence of ZnF_2 and sodium dodecylbenzenesulfonate (SDBS) as a surfactant.

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Figure 1. Thermal transformation sequence for boehmite. Transition alumina is denoted by appropriate Greek symbols.

2. Experimental

Aluminum isopropoxide $\text{Al}(\text{OC}_3\text{H}_7)_3$ (Merck, Germany), aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, Germany), and sodium dodecylbenzenesulfonate (SDBS) (Merck, Germany) were used as raw materials to prepare nano- $\alpha\text{-Al}_2\text{O}_3$. The starting solution was prepared using aluminum isopropoxide while 0.5 M aluminum nitrate aqueous solution as a solvent with distilled water and aluminum isopropoxide powder gradually added to it. The molar ratio of alumina sol (aluminum isopropoxide (AIP)/aluminum nitrate (AIN) nonahydrate) was 3, so that the raw materials could be completely dissolved and provide clear solution. The solution was continuously stirred for 48 h. Later, sodium dodecylbenzenesulfonate was added to adjust the molar ratio between alkoxide and surfactant to 0.1. The solution was then stirred for 1 h. This was considered to be the optimal time for the addition of the surfactant which occurred prior to the onset of the nucleation and growth step. The solution was heated to 60 °C and stirred constantly for an evaporation process. The viscosity and colour changed as the sol turned into a transparent thick gel. The gel was then heat treated at 90 °C for 8 h. Dried gels were calcined at 1000–1200 °C.

The next step for temperature reduction of nano- $\alpha\text{-Al}_2\text{O}_3$ formation is to prepare the solution through implementing aluminum isopropoxide (AIP) and aluminum nitrate (AIN) as well as SDBS as a surfactant. The solution was stirred for 24 h continuously and heated up to 60 °C for evaporation process. The gel was then heat treated at 90 °C for 8 h. Then, alcohol was applied to be milled with dried gels for 24 h after ZnF_2 additive (2 wt%) was added to the solution. After the gelled mass was dried at 60 °C, it was calcined at 650, 750, 850 and 950 °C for 1 h. In the final stage, mortar and pestle were used in order to crush the calcined powders. Phase identification was carried out by X-ray diffraction (XRD) applying nickel filtered $\text{CuK}\alpha$ radiation in the range of $2\theta = 10^\circ\text{--}80^\circ$ with a scanning speed of 5° per minute. Fourier transform infrared spectrometer (FTIR) by Perkin Elmer Spectrum 100 series was used by universal ATR sampling accessory. DTA analysis was carried out using Mettler Toledo TGA/SDTA 851. Measurements were taken under a continuous flow of air (10 ml min^{-1}). Samples were heated

at $10^\circ\text{C min}^{-1}$ to 1200 °C and then cooled to room temperature. The DSC analysis was performed by using the Mettler Toledo DSC 823.

The samples were encapsulated in aluminum pans and were heated from 35 to 1000 °C at a heating rate of 10°C/min in air atmosphere with a flow rate of 10 ml/min . The morphology of the gained $\alpha\text{-Al}_2\text{O}_3$ powder was observed by Phillips CM12 transmission electron microscopy and Cambridge Stereoscan 200 and Leica Cambridge S-360 Scanning Electron Microscopy.

3. Results and discussion

The synthesis of nano- $\alpha\text{-Al}_2\text{O}_3$ was carried out with the concurrent addition of SDBS and increasing the stirring time, to prevent excessive grain growth and aggregation of nanoparticles. The overall reaction scheme is shown below (Mirjalili *et al* 2011)

This is a multi-step process that involves the transformation of aluminum alkoxide to aluminum hydroxide ($\text{Al}(\text{OH})_3$) followed by the dehydration to form an oxo-hydroxide aluminum intermediate, $\text{AlO}(\text{OH})$ (boehmite), that will constitute the precursor in the sol-gel process and involve the following chemical transformation (Mirjalili *et al* 2010):

The XRD analysis in figure 2 showed the most stable phase, $\alpha\text{-Al}_2\text{O}_3$ occurred at 1200 °C. The observation reported by Hyuk-Joon and Kug (1999) indicated that completion of the most stable phase, α -alumina occurred at this temperature. Although the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ phase could be obtained through a reconstructive transformations (boehmite), the morphology remains unchanged and the final products have the same shape as in the initial phases (Wu *et al* 2001; Mirjalili *et al* 2011).

The addition of the surfactant resulted in the formation of an amorphous boehmite phase coupled with some hydrates of surfactant. This might be the result of the absorption of surfactant layer on the surface of the initial boehmite nuclei, which prevented the aggregation and grain growth of boehmite in the absence of surfactant that would allow the formation of crystalline phase (Yong and Wang 2001; Li *et al* 2006).

Figure 3 shows the synthesis of nano- $\alpha\text{-Al}_2\text{O}_3$ with the addition of ZnF_2 as an additive and milling on the phase transformation of $\alpha\text{-Al}_2\text{O}_3$ at different temperatures. As it is shown, the precursors are amorphous when the powders are calcined at both 650 and 750 °C temperatures.

The characteristic peaks of $\alpha\text{-Al}_2\text{O}_3$ emerged at 850 °C with a quite weak intensity and amorphous background. The

Figure 2. XRD pattern of Al_2O_3 at 1200 °C.

Figure 3. XRD patterns of the as-synthesized precursor calcined at different temperatures.

particle size of the prepared alumina powders was estimated at about 14.5 nm through the Scherrer formula. By increasing the calcination temperature up to 950 °C, high intensities of α - Al_2O_3 were observed, and the amount of α - Al_2O_3 was considerably improved. It was shown that α - Al_2O_3 crystallite rapidly grew up to ~ 21.6 nm as transformation was completed. This is in consistent with the work of Wang *et al* (2005), which showed that the α - Al_2O_3 particle size slightly increased during the phase transformation. The phase structure and crystallite size of the prepared Al_2O_3 powder which

Table 1. Phase structure and crystallite size of the prepared Al_2O_3 calcined at different temperatures.

	Calcination temperature (°C)			
	650	750	850	950
Crystallite size (nm)	—	—	14.5	21.6
Phase structure	Amorphous	Amorphous	α	α

is calculated through the Scherrer formula are presented in table 1.

FTIR analysis was also carried out for the aluminum oxide precursor in the wave number region of 4000–280 cm^{-1} . The related spectra are presented in figure 4. The absorption was recorded at about 3500 and ~ 650 cm^{-1} , and this is because of the stretching vibration as well as deformation vibration characteristics of hydroxylate (O–H) (Park *et al* 2005). The absorption peaks presented in figure 4 at 1556.73 cm^{-1} might indicate that there was some SBDS impregnated on the sample and the bands at 1121–1328 cm^{-1} were due to the typical signals of C–N (Wang *et al* 2006). There were wide and high peaks of Al–O stretching (AlO_4 or AlO_6 vibration) in the range of 500–1000 cm^{-1} . These peaks were attributed to the transitional phases of alumina and stable phase of alumina (Alpha). For the sample calcined at 1200 °C, significant spectroscopic bands at about 900, 568.15, 499.19 and 431.99 cm^{-1} emerge, which are recognized as characteristic absorption bands of α - Al_2O_3 (Wen and Yen 2000). These observations were in good agreement with XRD observation.

According to figure 5 with increase of ZnF_2 additive and milling, the absorption band of γ - Al_2O_3 appeared at 863.37 cm^{-1} at 750 °C and by increasing the temperature

Figure 4. FTIR spectra of Al_2O_3 precursor: (a) enlarged at the region of $400\text{--}1600\text{ cm}^{-1}$ and (b) normal spectra.

Figure 5. FTIR spectra of Al_2O_3 precursor calcined at different temperatures: (a) enlarged at the region of $400\text{--}1600\text{ cm}^{-1}$ and (b) normal spectra.

to $950\text{ }^{\circ}\text{C}$, this band shifted to about 820 cm^{-1} . Moreover, the significant absorption bands of $\alpha\text{-Al}_2\text{O}_3$ at 583.15 and 517.19 cm^{-1} to 572 and 482 cm^{-1} , respectively. This showed that the phase transformation of $\alpha\text{-Al}_2\text{O}_3$ was promoted by the addition of ZnF_2 additive and milling.

DSC curves of the precursor are illustrated in figure 6. In the absence of ZnF_2 at temperature region of $25\text{--}370\text{ }^{\circ}\text{C}$, a broadened endothermic peak emerges. This peak was associated with the vaporization of physically bound absorbed water (Arami *et al* 2008). Three small peaks at 443 , 492 and $545\text{ }^{\circ}\text{C}$ were attributed to the pseudomorphic phase

transformation of boehmite to $\gamma\text{-Al}_2\text{O}_3$ (Park *et al* 2005). The endothermic peak at $582\text{ }^{\circ}\text{C}$ was attributed to the transitional phases of alumina and $\alpha\text{-Al}_2\text{O}_3$ (Wang *et al* 2006). However, in the presence of ZnF_2 , it could be observed that the peaks related to transitional phases of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ shifted to lower temperatures at 307 , 339 and $521\text{ }^{\circ}\text{C}$, respectively, suggesting that the phase transformation became easier for alumina powders.

This was in consistent with DTA curves of the as-synthesized precursor in the absence of ZnF_2 additive which showed that the intensive exothermic peak of about $270\text{ }^{\circ}\text{C}$

Figure 6. DSC curve of the as-synthesized precursor: (a) enlarged at the region of 300–600 °C and (b) normal curve.

Figure 7. DTA curve of the as-synthesized precursor.

Figure 8. DTA curves of the milled dried gel with ZnF₂ additive.

was assigned to the SDBS burnout, the 800 and 1100 °C peaks were associated with the phase transformation, and, finally, the endothermic peak was due to dehydration (figure 7). However, by adding the ZnF₂ additive, the exothermic peaks of phase transformation shifted to 404 and 744 °C, as a result of the reduction of transformation temperatures (figure 8).

Milling and ZnF₂ additive have the potential synergistic property to reduce the transformation temperature. Fluorides can cause the capability to reduce the transition alumina transformation temperature as well as the ability to modify the grain morphology. This is because, in the case of the phase transformation, Orthorhombic aluminium oxyfluoride (ALOF) may be formed as an intermediate compound, and it can step up the mass transportation from transition alumina to α - Al_2O_3 . The alumina hydroxide in the abrasion powder

Figure 9. SEM micrograph of α - Al_2O_3 after 48 h in the presence of SDBS calcined at 1200 °C.

Figure 10. SEM micrograph of the as-synthesized precursor calcined at different temperatures: (a) 650 °C, (b) 750 °C, (c) 850 °C and (d) 950 °C.

can be transformed into a single phase of α - Al_2O_3 without forming γ - and θ - Al_2O_3 phases at a reasonably low temperature of about 900 °C in the milling conditions (Park *et al* 2005; Wang *et al* 2006).

Figure 9 shows SEM micrograph of α - Al_2O_3 after 48 h stirring time. As it can be seen the particles are fine with less agglomeration and good dispersion.

Figure 10 shows SEM micrographs of the synthesized precursors with the addition of ZnF_2 at different temperatures. The SEM images of 650 and 750 °C calcined Al_2O_3 powder show large irregularly shaped particles. The amorphous raw powder provided micrometer-sized agglomerated particles with a greatly porous structure. On the contrary, by raising the calcined temperature, well-faceted grains made up of several little crystallites appeared (Wang *et al* 2005). In this case, for the Al_2O_3 powder calcined at 650 and 750 °C, α - Al_2O_3 crystallite could not be nucleated. This was due to the low temperature and only the amorphous background was observed. However, with the raising of calcination temperature up to 850 °C, fine crystallites of α - Al_2O_3 appeared. This indicated amorphous to α - Al_2O_3 transition. At this time, nano- α - Al_2O_3

Figure 11. TEM micrograph of α - Al_2O_3 after 48 h in the presence of SDBS calcined at 1200 °C.

grains made up of several tiny crystallites also appeared (figure 10c). At the temperatures higher than 950 °C crystallite growth of grains were observed. As shown in

Figure 12. TEM micrograph of the as-synthesized precursor calcined at different temperatures: (a, b) 650 °C, 750 °C, (c, d) 850 °C and (e, f) 950 °C.

figure 10(d), the particle size of α - Al_2O_3 crystallite became larger with the spherical shape. This results were confirmed by TEM figures which shown in figures 11 and 12.

Therefore, milling and adding of ZnF_2 connect the property of reduced transformation temperature. Fluorides have a capability to reduce the transition alumina transformation

temperature and modify the grain morphology (Wang *et al* 2005). This research concluded that the plate-like nano- α - Al_2O_3 particles could be fabricated by adding ZnF_2 , where as Zn^{2+} could provide solid solution with Al_2O_3 , and the integration of limited Zn^{2+} in solid solution might control oxide ion mobility and create interfacial energy difference. The interfacial energy difference improved the interface reaction of alumina and speeded up the grain growth in some directions (Wen and Yen 2000).

Liu *et al* (2005) investigated the effect of mechanical milling on the phase transformation of nanoscale α - Al_2O_3 particles. They had particle size distribution ranging from 40 to 200 nm with a lot of agglomeration after 50 h milling. Li *et al* (2006) synthesized nanoscale α - Al_2O_3 particles by introducing fluorides in the alumina precursor. It is also indicated that the fluoride ions enhance the directional growth of the alumina nanostructures. In summary, liquid-forming additives enhance the γ -to- α transformation of alumina. ZnF_2 was found to be the strongest enhancing agent. Additive effects on sintering/shrinkage were similar except for the added effect of reaction sintering and faster transformation kinetics due to the better contact between powders in a compact (Wen and Yen 2000; Wang *et al* 2005).

In the proposed method, nanoscale α - Al_2O_3 powder was synthesized at about 950 °C when milling and ZnF_2 additive were used together. Consequently, in this research, the size of the particles formed was in the range of 15–20 nm when SDBS surfactant and ZnF_2 additive were applied in 24 h milling. Nano- α - Al_2O_3 particles were plate-like in shape with a good quality of dispersion. Therefore, the presence of surfactant and ZnF_2 control the size of the particles, their degree of aggregation, and their shape.

4. Conclusions

The sol-gel method was used for the synthesis of nano- α - Al_2O_3 from aluminum alkoxide complexes which were coupled with the presence of surface active agents, like SDBS. The micro-structural observation showed that with 48 h stirring time nanoscale α - Al_2O_3 powder was produced in the range of 20–30 nm. Moreover, the nanoplate α - Al_2O_3 powders with average size of 20 nm was fabricated using the process of milling and the introduction of ZnF_2 that could reduce the transformation temperature. ZnF_2 could also modify the shape of the alumina particle and caused the morphology of the α - Al_2O_3 particles to be plate-like.

Its calcination temperature was about 950 °C, which was 250 °C lower than general calcination temperature for

preparing α - Al_2O_3 particles. α - Al_2O_3 particles were also obtained without forming γ - and θ - Al_2O_3 phases at a reasonably low temperature of about 950 °C in the milling conditions. This process was available for preparing a number of compounds to provide ultra-fine powders at relatively low temperature. With its great simplicity, the process would provide ultra-fine powders at relatively low temperature.

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