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Study on α-alumina precursors prepared using different ammonium salt precipitants

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ABSTRACT

Nano-sized α-Al_2O_3 platelets have been produced by the precipitation method employing the starting material of $Al(NO_3)_3 \cdot 9H_2O$ and ammonium salt precipitants, such as the NH_4OH, $(NH_4)_2CO_3$ and NH_4HCO_3. The effects of chemical composition of ammonium salt precipitants and aging time of precipitated product on the formation of precursor and final product of α-Al_2O_3 particles were studied. The precursors with different crystal structures were formed depending on the chemical composition of precipitant and the agglomeration of final α-Al_2O_3 particles was found to be greatly affected by the precipitant. The aging time of precipitated precursor also influenced the agglomeration of final α-alumina particles.

1. Introduction

It is well known that the mechanical, optical and electrical properties of ceramics strongly depend on their microstructure including shape and size. It has been shown that the performance of ceramics can be improved by producing nano-scale structure [1]. In recent years, therefore, the synthesis of nanocrystalline ceramics has received much attention since the ceramics have considerable potential in many fields such as aerospace, automotive, and electronics.

Among various ceramics, the nanocrystalline α-alumina is currently one of the most widely used ceramic materials because it has considerable applications in a wide range of modern industries including electronics, metallurgy, high strength materials and ceramic composites [2,3]. It was also demonstrated that the morphology of alumina particles affects the engineering properties [4]. For example, nano-sized alumina, as compared with micron-sized particle, has many advantages in various applications such as catalyst, abrasive and coatings. In addition, it was also observed that nano-sized plate-like alumina grains can increase fracture toughness more significantly than the ball-like grains because the plate-like grains can form crack bridging easily in ceramics matrix [5,6].

Nanocrystalline α-alumina can be obtained by various processes such as precipitation, gas phase deposition, sol–gel, hydrothermal and combustion methods [3,7]. Among them, the precipitation is the most widely used and low-cost process for preparing nano-sized alumina powders [4]. However, the powders with small size prepared by the aqueous precipitation process are often heavily agglomerated [8,9]. Moreover, nano-sized particles tend to strongly agglomerate because of their high ratio of surface-area to particle size. Thus, the agglomeration of α-Al_2O_3 crystallite is very common in the industrial α-Al_2O_3 powders [10].

Recently it was demonstrated that, in the precipitation process to synthesize ceramic materials, the chemical composition and physical properties of precursor have dramatic effects on the properties of the resultant oxide powders [11]. It was also reported that the properties of γ-Al_2O_3 powders prepared by precipitation method were changed depending on the chemical composition of precipitant [7].

In this work, several types of precursors to nano-sized α-Al_2O_3 platelets were prepared in precipitation process by using different ammonium salt precipitants. We identified the phase of these precursors and studied the effect of precursor phase on formation of resultant α-Al_2O_3 powders. The effect of aging time of precipitate during the synthesis of precursor was also investigated

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since the aging time affects the crystallinity of precipitate and the characteristic of final ceramic materials can be influenced by the physico-chemical properties of precursor [11–13].

Although many studies have been done on the preparation of alumina powders via chemical process, no significant result is reported on the production of highly-dispersed α-Al_2O_3 nanopowders by using a low-cost and simple route like the precipitation method with a short processing time and the low calcination temperature. This is why the effects of chemical composition of ammonium salt precipitant and aging time of precipitate on the preparation of nano-sized α-Al_2O_3 platelets via precipitation process are investigated in this study.

2. Experimental

2.1. Sample preparation

The nano-sized α-alumina particles were prepared using a method similar to that described in literature [5]. All the reagents used in this study were analytical grade and used without further purification. $Al(NO_3)_3\cdot 9H_2O$ was used as the starting materials for nano-sized α-alumina particles and NH_4OH, $(NH_4)_2CO_3$ and NH_4HCO_3 were used as precipitants. AlF_3 was also used to induce platelet morphology and to decrease phase transition temperature.

The concentrations of precipitant solutions were adjusted according to the typical values reported in the literatures, and the chosen concentrations for the solutions of NH_4OH [2,5], $(NH_4)_2CO_3$ [14] and NH_4HCO_3 [11,15] were 0.2, 0.4 and 1.4 mol L^{-1}, respectively. Aqueous solution of precipitant was added slowly (0.33 mL min^{-1}) into 100 mL of $Al(NO_3)_3\cdot 9H_2O$ solution (0.8 mol L^{-1}) under rapid stirring. When the final pH of slurry was adjusted to 9.0 and then the precipitate was aged with constant stirring for 1 h. The slurry was filtered and dried at 70 °C for 24 h. After that, the dried gel was mixed with AlF_3 (2 wt%) to induce platelet morphology and to decrease phase transition temperature. The mixture was milled with alcohol in high purity alumina medium for 24 h. Then gel was dried at 55 °C for 24 h and calcined at 900 °C for 2 h with heating rate of 10 °C min^{-1}. To examine the effect of aging time, only the aging times were varied from 1 to 24 h under equivalent reaction conditions.

2.2. Characterization

The phase and crystallinity of particles were analyzed using an X-ray diffractometer (XRD; PHILIPS, X'Pert-MPD System) with Ni filtered Cu Kα radiation. The morphology and agglomeration of particle were observed by transmission electron microscopy (TEM; JEOL, JEM-2010). The nature of bonding in precursor was identified by infrared spectroscopy (FTIR, Bruker, IFS-88). The size of the particles/aggregates of final products suspended in ethanol was determined using particle size analyzer (PSA; Beckman Coulter, LS 13320) and before this measurement the samples were sonicated for 20 min.

3. Results and discussion

3.1. Effect of precipitant on the formation of particles

It was reported that, during the precipitation reaction, the precipitation conditions such as the charging rate of reactants, pH and temperature, affect greatly the morphology and chemical composition of precipitates [15,16]. In this study, three different precipitants were used to produce precipitate as the precursor to α-Al_2O_3 and the X-ray diffraction analysis results for the three precipitated precursors obtained using different precipitants were shown in Fig. 1.

As can be seen in Fig. 1, the three precipitate precursors have different crystal structure. The XRD analysis results reveal that the precursor obtained using NH_4OH is composed of the mixture of poorly crystallized pseudo-boehmite (AlOOH) and bayerite ($Al(OH)_3$), while that by NH_4HCO_3 precipitant has the pseudo-boehmite phase only. On the contrary, the XRD pattern for the precursor formed by $(NH_4)_2CO_3$ precipitant indicates the formation of ammonium aluminum carbonate hydroxide (AACH; $NH_4AlO(OH)HCO_3$) phase with low crystallinity.

It was reported that, during the precipitation reaction between aqueous $Al(NO_3)_3$ solution and ammonium salt precipitant for preparing α-Al_2O_3, different types of precursors can be formed depending experimental conditions [16,17]. In the case of using NH_4OH as a precipitant, the precipitate should be hydroxide since only OH^- anions generated by the dissociation of NH_4OH can participate in the precipitation [11]. Du et al. [17] reported that the main precipitate products obtained using NH_4OH precipitant are amorphous aluminum hydroxide, boehmite and bayerite. They also found that acidic, neutral and alkaline conditions are favorable for the formation of amorphous aluminum hydroxide, boehmite and bayerite, respectively. On the other hand, Okada et al. [12], who studied the effect of pH on precipitation of aluminum hydroxide, observed the formation of boehmite in the pH range of 7–10 and they ascribed the change in the phase of aluminum hydroxide as a function of pH to the difference of the alumina solubility in solution. In this work, the poorly crystallized pseudo-boehmite and bayerite were formed by the precipitation reaction between aqueous $Al(NO_3)_3$ solution and NH_4OH at pH = 9, and these results are a little different from those reported by Du et al. [17]. This difference could be due to the difference in reaction conditions, such as the concentration of aqueous $Al(NO_3)_3$ solution and charging rate of reactant.

When NH_4HCO_3 is used as a precipitant, various cations and anions, for example H^+, NH^{4+}, OH^-, HCO_3^-, CO_3^{2-}, can be formed by hydrolysis in the solution. Therefore, various precipitate products with different chemical structure can be obtained by using NH_4HCO_3 precipitant. Among them, the most common precipitate products are known to be boehmite and AACH, and the chemical structure of precipitate can be decided by the competition between OH^- and carbonate species [13,16]. It was also proposed that the possibility of AACH formation increases with

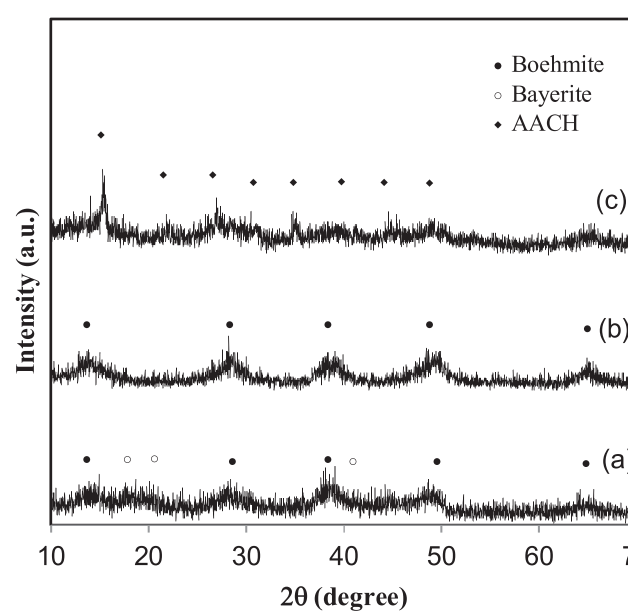

Fig. 1. XRD patterns of the precipitated precursors obtained using different precipitants: (a) NH_4OH, (b) NH_4HCO_3 and (c) $(NH_4)_2CO_3$.