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Hydrothermal synthesis of boehmites with various particle sizes and transition to α-Al_2O_3 powders by calcination*

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Abstract: Boehmite powders with various particle sizes have been prepared by hydrothermal method and the α-Al_2O_3 powders yielded after subsequent calcination have been studied. Dispersive crystalline boehmite powders of 30-100 nm, 0.4-0.6μm and 1μm in size were obtained respectively by changing the hydrothermal precursors and the *pH* value of hydrothermal slurry. Calcination of boehmite powders of 30-100 nm at 1250℃ for 1h resulted in the formation of single-phase α-Al_2O_3, and the products consisted of vermicular particles. The boehmite powders of 0.4-0.6μm were also fully converted to α-Al_2O_3 at 1250℃, and the products consisted of plate-like particles with the same size of 0.4-0.6μm. The boehmite powders of 1μm calcined at 1350℃ for 2h were still composed of a little proportions of transition aluminas besides α-Al_2O_3, and the particles sintered severely. The reaction processes for the formation of crystalline boehmites under hydrothermal conditions and α-Al_2O_3 powders during calcination have been discussed.

Key words: hydrothermal; boehmite; α-Al_2O_3 powder; particle size

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1 Introduction

Boehmite (γ-AlOOH) is an important starting material for preparation of both active alumina (γ-Al_2O_3) and corundum (α-Al_2O_3). The properties of γ-Al_2O_3 and α-Al_2O_3 are related to the characteristics of boehmite which depend on its preparation conditions. Okada *et al.* [1,2,3] studied the effect of the crystallinity of nano size boehmite on the properties of γ-Al_2O_3 and α-Al_2O_3 prepared from it. Powders of submicron and several microns in size are used more common in practice. α-Al_2O_3 powders formed by calcination of nano size boehmite are usually consisted of strongly bonded aggregates because the transformation temperature to alpha phase is high and nano size particles have great surface energy. In this paper, boehmite crystallites with various particle sizes have been prepared by hydrothermal method, and the α-Al_2O_3 powders yielded after subsequent calcination have been compared.

2 Experimental

Firstly the fresh aluminum hydroxide gel was prepared by adding aluminum nitrate solution into am-

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monia solution until pH=9. The precipitation was filtered and washed repeatedly with deionized water.

Boehmite crystalline powders were prepared by hydrothermal treatment of the fresh aluminum hydroxide gel or aluminum hydroxide reagent at 200℃ in the autoclave. After hydrothermal treatment, the slurry was filtered, washed repeatedly with deionized water and the anhydrous ethanol, and dried.

Alumina powders were obtained by calcination of above boehmite powders at various temperatures.

Crystalline phases of powders were identified by an X-ray powder diffractometer (XRD, PANalytical, X'Pert Pro, Holland). The morphology of particles was observed by a transmission electron microscopy (TEM, HITACHI, H-600A, Japan) or scanning electron microscopy (SEM, JEOL, JSM-35CF, Japan).

3 Results and discussion

3.1 Properties of boehmite samples by hydrothermal treatment

The XRD analysis confirmed that the fresh aluminum hydroxide gel prepared by precipitation was amorphous structure, the phase of aluminum hydroxide reagent was highly crystalline bayerite, and the hydrothermal products were single-phase crystalline boehmite. The preparation conditions for various boehmite samples are listed in Table 1. The XRD peaks for the boehmite sample BG1 obtained by hydrothermal treatment of fresh aluminum hydroxide gel are weak and broad; the XRD peaks for the boehmite sample BR3 obtained by hydrothermal treatment of aluminum hydroxide reagent are comparatively strong. This shows the crystallite size of the sample BG1is smaller than that of BR3.

Table 1 Preparation conditions of various boehmite samples at hydrothermal temperature of 200℃

Sample	Hydrothermal precursor	pH value of hydrothermal slurry	Hydrothermal period/h	Appearance of samples after drying
BG1	Wet gel of aluminum hydroxide	2.5	12	Gel
BR2	Aluminum hydroxide reagent	3.0	3	Fluffy powder
BR3	Aluminum hydroxide reagent	7.0	12	Fluffy powder

The TEM of some typical boehmite samples are shown in Fig. 1. It shows that the crystallite size of boehmite samples depended on the hydrothermal precursor and the pH value of the hydrothermal medium. The crystallite size of boehmite samples obtained by hydrothermal treatment of fresh aluminum hydroxide gel was smaller than 100 nm(Fig. 1a). The crystallite size of boehmite samples obtained by hydrothermal treatment of aluminum hydroxide reagent was larger than 100 nm. In the weak acidic hydrothermal medium, the submicronic particles of 0.4-0.6μm were obtained(Fig. 1b). In the neutral hydrothermal medium, the crystallites were of rhombic plates with a particle size of about 1μm (Fig. 1c).

3.2 Phase changes during calcination

The crystalline phases present in the alumina powders formed by calcination of boehmite samples at various temperatures were examined by XRD and the results are presented in Table 2. It shows that the conversion to α-phase for boehmites with a particles size smaller than 100 nm and 0.4—0.6μm could be completed by calcination at 1250℃ for 1 h. The conversion of boehmite powders with a size of 1μm to α-phase was still incomplete by calcination at 1350℃ for 2h, and a few amount of powders were of θ-phase.

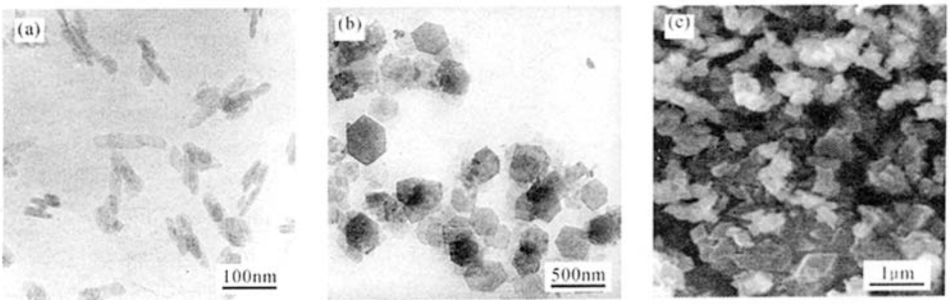

Fig. 1 Morphologies of boehmites powders formed under various conditions
(a)—TEM micrograph of samples BG1; (b)—TEM micrograph of samples BR2; (c)—SEM micrograph of samples BR3

Table 2 Crystalline phases of alumina powders formed by calcination of boehmites at various temperatures

Boehmite samples	Calcination conditions			
	1150℃, 1 h	1200℃, 1 h	1250℃, 1 h	1350℃, 2 h
BG1	θ, traces of α	α	α	
BR2		α, traces of θ	α	
BR3		δ, θ, a few of α	δ, θ, a few of α	α, a few of θ

3.3 Morphology changes of powders during calcination

Morphologies of powders formed by calcination of boehmites with various particle sizes are shown in Fig. 2. Nano size boehmites were fully converted to α-Al_2O_3 by calcination at 1250℃ for 1h and the obtained powders had vermicular shape, which indicated that some particles sintered together (Fig. 2a). α-Al_2O_3 powders formed by calcination of boehmite crystallites consisted of hexagonal-like plates of 0.4—0.6μm still maintained plate-like particles with the same size of 0.4—0.6μm, although the hexagon shape of the precursor boehmite has been distorted(Fig. 2b). Boehmite crystallites consisted of rhombic plates of 1μm have not been fully converted to α-Al_2O_3 but most of particles were sintered when calcination at 1350℃ for 2 h (Fig. 2c).

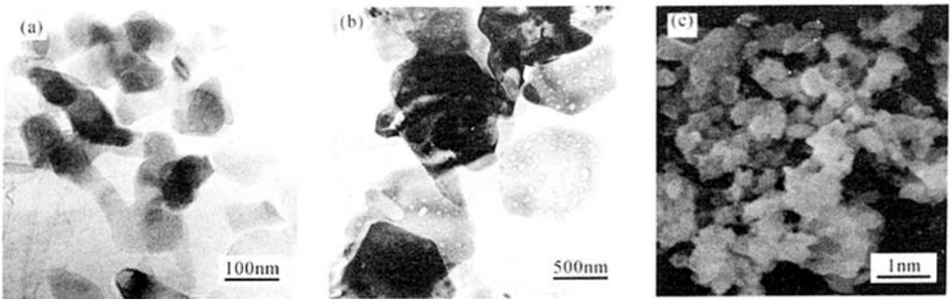

Fig. 2 Morphologies of alumina powders formed by calcination of boehmites with various particle sizes
(a)—TEM micrograph of sample BG1 heated at 1250℃ for 1 h; (b)—TEM micrograph of sample BR2 heated at 1250℃ for 1 h; (c)—SEM micrograph of sample BR3 heated at 1350℃ for 2 h

3.4 Discussion

TEM shows that the fresh gel of amorphous aluminum hydroxide was flocculent mass and the aluminum hydroxide reagent consisted of irregular particles of about 10μm in size. After hydrothermal treatment the morphology and the particle size of the yielded products were clearly different from those of the precursor materials. Therefore, it can be thought that the boehmite crystallites were formed by dissolution-nucleation-growth reaction under hydrothermal conditions. The solubility of amorphous aluminum hydroxide is the highest of all the aluminum hydroxide and alumina phases. A lot of nuclei would be formed at one time. Fine crystalline boehmite particles were obtained by many nuclei growth simultaneously. The solubility of crystalline aluminum hydroxide reagent is low, and only a small quantity of nuclei could be formed. Larger crystalline boehmite particles were obtained by a few nuclei growth gradually. The relative growth rate of each plane of boehmite crystal is different under various pH solutions because the interaction with hydrogen ion is different. This difference could result in different morphologies of boehmite crystallites.

The transformation of boehmite to stable α-Al_2O_3 through the following sequence: γ-AlOOH → γ-$Al_2O_3 \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$ upon heating. Conversion of boehmite to γ-Al_2O_3, γ to δ and θ-Al_2O_3 proceed topotactically because of the similar cubic close-packed oxygen sublattice. Therefore, the resulting transition aluminas possess some properties of the boehmite precursor such as crystallinity and crystallite size. The transition of θ- to α-Al_2O_3, however, involves a change in the oxygen sublattice from cubic to hexagonal with simultaneous movement of metal ions and occurs by a nucleation and growth mechanism[4]. The crystal structure of boehmite consists of $Al(O,OH)_6$ octahedral layers. There are many imperfections in the fine particles because of the limited layer stacking number and excess interlayer water[5], and the structure of the resulting transition aluminas will have many imperfections too. The nucleation of α-Al_2O_3 occurs preferentially at active sites such as surface and defects. θ-Al_2O_3 derived from boehmites with a size less than 100 nm possessed more nucleation sites due to more imperfections and more surface areas in nano scale boehmite crystallites, thus the nucleation density of α-Al_2O_3 was high. As the crystal growing, they were impinging and coalesced because of high surface energy of nano size particles. Therefore, sintered α-Al_2O_3 particles with vermicular shape were obtained. Boehmite crystallites prepared by hydrothermal treatment of aluminum hydroxide reagent in neutral medium were large and well crystalline. The activation barrier for the nucleation of α-Al_2O_3 in the corresponding θ-Al_2O_3 was high. On the other hand, mass diffusion was accelerated with increasing temperature. Thus sintering among particles occurred by mass diffusion. Crystalline boehmite powders with a size of 0.4-0.6μm prepared by hydrothermal method contained a considerable amount of defects in the structure. These defects were retained in the resulting transition alumina particles and provided sufficient number of sites for nucleation at temperature as relative low as that of particles with a size less than 100 nm. Besides, water absorbed in the boehmite particles had been removed by alcohol washing before drying and aggregation of particles during calcination was minimized. The process of surface diffusion was inhibited and the crystal growth was restricted to the original powder particles through interphase interface migration. Thus α-Al_2O_3 powders obtained had the plate-like shape as the precursor boehmite particles.

4 Conclusions

(1) Dispersive crystalline boehmite powders of 30-100 nm, 0.4-0.6μm and 1μm in size were obtained respectively by changing the hydrothermal precursors and the pH value of hydrothermal slurry.

(2) Calcination of plate-like boehmite powders of 30—100 nm at 1250℃ for 1h resulted in the forma-

tion of single-phase α-Al_2O_3, and the products consisted of vermicular particles.

(3) The plate-like boehmite powders of 0. 4-0. 6μm were also fully converted to α-Al_2O_3 at 1250℃, and the products maintained the plate-like shape with the same size of 0. 4-0. 6μm.

(4) The boehmite powders of 1μm calcined at 1350℃ for 2 h were still composed of a little proportions of transition aluminas besides α-Al_2O_3, and the particles sintered severely.

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