

# PREPARATION OF ULTRAFINE ALUMINA POWDERS BY ALUMINUM ISOPROPOXIDE<sup>①</sup>

Yu, Zhongqing Zhao, Qinsheng Zhang, Qixiu

*Department of Nonferrous Metallurgy,  
Central South University of Technology, Changsha 410083*

## ABSTRACT

The porous  $\gamma$ -AlOOH powders were obtained by the hydrolysis of aluminum isopropoxide in the alkaline (C<sub>6-9</sub>) solutions. The disperse  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders, with the mean diameter of 70 nm and apparent density of 0.14 g/cm<sup>3</sup>, were obtained by the calcination of said  $\gamma$ -AlOOH powders at suitable temperature. The thermal behavior and changes in powder morphology of AlOOH during the calcination process were also discussed.

**Key words:** aluminum Isopropoxide alumina ultrafine powders hydrolysis calcination

## 1 INTRODUCTION

Alumina ceramic has been extensively used as structural, biological and optical materials, based on its intrinsic properties such as wear, corrosion, oxidation and high temperature resistances. However, its application was restricted by its inferior brittleness at room temperature and its susceptibility to thermal shock. The way to overcome this disadvantage is preparation of nanocrystal ceramic<sup>[1]</sup>, which needs nanometer size alumina powders as raw materials.

The method for preparing nanometer size alumina powders, such as gas-phase methods of MOCVD, electric-arc evaporation, electric-arc plasma, solid-phase method, solution-methods with thermal decomposition and supercritical solutions, are feasible. Among all the above methods for preparing ultra-high-purity alumina powders except for MOCVD, hydrolysis or sol-gel process, aluminum alkoxides are used as precursor since it is easy to be purified. Unfortunately, the average diameter of alumina powders prepared by these processes<sup>[2-6]</sup>, is more than 0.2  $\mu$ m. Using the sol-gel method and aluminum ethoxide as precursor, the authors of this article have obtained disperse spheri-

cal  $\gamma$ - and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders with mean particle size of 40 and 100 nm, respectively. The aim of this research is to prepare ultrafine alumina powders using aluminum isopropoxide through hydrolysis and calcination process.

## 2 RAW MATERIALS

Aluminum isopropoxide used is a chemical reagent grade (Shanghai, No. 1 Chemical Reagent Factory) with a content of 24.7%, which was purified before use. Water used in hydrolysis process was double distilled. Solvent with analysis reagent grade, which is used to dilute aluminum alkoxide, is the linear chain alkaline with carbon number of 6~9. In addition, the reagent A was also used.

## 3 EXPERIMENTAL PROCEDURE AND TEST METHOD

Before hydrolysis of aluminum isopropoxide in a proper way, it was mixed with linear chain alkaline solutions, the alkoxide concentration being 0.12~0.2 mol/l. The water temperature was kept in the range of 70~80 C during hydrolysis process. The upper solvent were decanted and recov-

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ered after hydrolysis. The addition of small amount of reagent A into the under solvent is necessary before recovery of precipitate. The as-prepared precipitate was changed into the loose aluminum hydroxide powders after keeping at 80 °C under vacuum for 8 h.

The thermal behavior of aluminum hydroxide in calcination process was tested by Dupont 9900 thermal analyzer at a heating rate of 15 °C/min. Powder morphology and size were determined by H-600 transmission electronic microscopy. The crystalline structure of powders was tested by X-ray diffraction. The apparent density of powders was tested by the funnel method, whose hole diameter is 2.5 mm.

**4 RESULTS AND DISCUSSION**

**4.1 Determination of powder crystalline structure and Thermal Analysis**

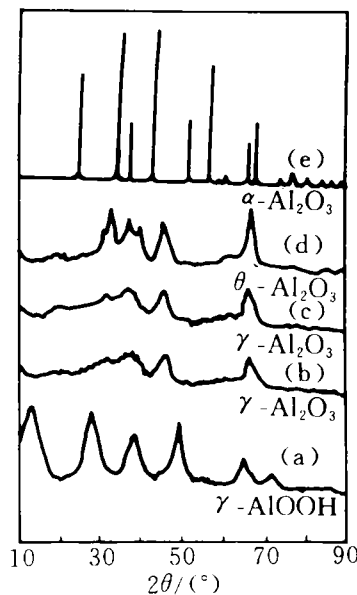
X-ray diffraction patterns of aluminum hydroxide and calcined powders at different conditions are shown in Fig. 1. In Fig. 1, (a) is corresponding to  $\gamma$ -AlOOH; (b) demonstrated that  $\gamma$ -AlOOH could change into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 500 °C completely; (c) is the X-ray patterns of powders calcined at 800 °C for 3 h, which still showed that the powder remains to be  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; (d) showed that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders were partially transformed into  $\theta$ -Al<sub>2</sub>O<sub>3</sub> after the powders were calcined at 900 °C for 3 h; (e) is obtained after calcination at 1 200 °C for 1 h, which showed that transition phase of alumina transformed into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> completely.

The curve of weight loss corresponding to temperature during the heating process of  $\gamma$ -AlOOH powder shown in Fig. 2. The total weight loss is about 32.92% and is 2.92% more than the theoretical dehydration value of aluminum hydroxide.

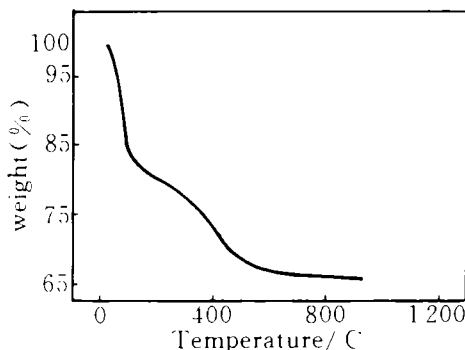
Fig. 3 is DTA curve of  $\gamma$ -AlOOH powders, in which an endothermic peak at 100 °C is linked to the departure of the adsorbed water. An indistinct endothermic peak near to 400 °C may correspond to the dehydration of  $\gamma$ -AlOOH through condensation reaction and formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. A sharp endothermic peak at 985.46 °C might relate to the a-

lumina crystalline transformation. A sharp exothermic peak at 1 193.55 °C corresponds to the transformation of intermediate phase into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This is consistent with the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation temperature shown in Fig. 1.

**4.2 Variation of AlOOH powder Morphology After Calcination under Different Conditions**



**Fig. 1 X-ray diffraction patterns of the powder samples after calcination at different temperature for different time**  
 (a) --  $\gamma$ -AlOOH ; (b) -- 500 °C, 3 h; (c) -- 800 °C, 3 h;  
 (d) -- 900 °C, 3 h; (e) -- 1200 °C, 1 h



**Fig. 2 TGA curve of  $\gamma$ -AlOOH powders**

The TEM morphologies of as-prepared and calcined powders under different conditions are shown in Fig. 4. In Fig. 4, (a) is the morphology of  $\gamma$ -AlOOH powders with porous appearance; (b) and (c) show that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders take the shape of dendritic crystalline with a mean length less than 70 nm and a width about 10 nm; (d) is the morphology of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with particle size of 70 nm in which the amount of dendritic powders is reduced and spheroidization occurred partially.

#### 4.3 Change Mechanism of Powder Morphology

Single porous  $\gamma$ -AlOOH powders could be induced to occur the dehydration condensation reaction and bring out several  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nuclei in the matrices at a suitable temperature. There is a non-coherent boundary between the nuclei and matrices. The non-coherent boundary is in a tensile state on account of their difference of thermal expansion coefficient. The atom of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> formed from  $\gamma$ -AlOOH could depart from matrices and arrange in

the direction of closest-packed direction  $\langle 110 \rangle$  at the closest-packed face  $\{111\}$  of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> lattice. So the  $\{111\}$  face becomes superior growing face, the  $\langle 110 \rangle$  direction becomes superior growing direction, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystalline become dendrite finally. Certainly, the growth of dendrite is not unlimited. When the boundary being in a tensile state couldn't sustain the connection between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystalline and matrices, several  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crys-

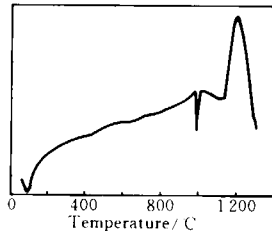


Fig. 3 DTA curve of  $\gamma$ -AlOOH powders



Fig. 4 TEM micrographs of  $\gamma$ -AlOOH and alumina powders obtained by calcination of  $\gamma$ -AlOOH powders under different conditions

(a)  $\gamma$ -AlOOH powders; (b) 500 °C, 1h; (c) 800 °C, 1h; (d) 1200 °C, 1h

tallines will be free from matrices. This is the reason why the dendritic  $\gamma$ - $\text{Al}_2\text{O}_3$  powders is more disperse than the porous  $\gamma$ - $\text{AlOOH}$  powders.

When the calcination temperature is up to 1200 °C, the atom of alumina intermediate phase being activated by heating, could rearrange into  $\gamma$ - $\text{Al}_2\text{O}_3$  lattice in order to reduce the lattice energy. On the other hand, the rearrangement of atom and a tendency to cut down the surface energy of powder, could urge the dendrite to shrink into spherical powders. That the spheroidization of ultrafine powders means the accelerating growth of powders, is one of difficulties for preparing ultrafine  $\alpha$ - $\text{Al}_2\text{O}_3$  powder. There is a tendency for powders in Fig. 4 (d) to spheroidize, but this tendency is not so distinct because the amount of reagent A added was controlled suitably. So the spheroidization of  $\text{Al}_2\text{O}_3$  powders could be controlled by the amount of reagent A added. This is significant for preparation of nanocrystalline alumina ceramic. As for the mechanism of reagent A in the spheroidization, it needs to be studied extensively.

#### 4.4 Determination of Apparent Density

The apparent density of powder obtained under different test conditions and percentage of apparent density to theoretical density were measured, as shown in Table 1. (The theoretical density of  $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$  are 3.5 and 4.0 g/cm<sup>3</sup> respectively).

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imply the non-linear characteristics of these chemical processes. Both the decomposition and carbonization involve complex anionic polymerization process with autocatalytic amplification mechanism. In the mixing and dilution process, the local instantaneous composition of solution is different. After autocatalytic amplification, these very small difference may induce the non-reproducibility of the reaction kinetics.

**Table 1 Apparent density of alumina powders prepared under different test conditions**

test condition	600 °C, 3h	800 °C, 3h	1200 °C, 3h
apparent density	0.0864	0.0923	0.1444
percentage to theoretical density, %	2.47	2.64	3.61

## 5 CONCLUSIONS

(1) The porous  $\gamma$ - $\text{AlOOH}$  powders were obtained by hydrolysis of aluminum isopropoxide.

(2) After calcination of  $\gamma$ - $\text{AlOOH}$  powders, disperse dendritic  $\gamma$ - $\text{Al}_2\text{O}_3$  powders with mean length less than 70 nm and width about 10 nm were produced. The apparent density of  $\gamma$ - $\text{Al}_2\text{O}_3$  at 600 °C and 800 °C were 0.086 and 0.092 g/cm<sup>3</sup>, respectively.

(3)  $\gamma$ - $\text{Al}_2\text{O}_3$  powders transformed into  $\alpha$ - $\text{Al}_2\text{O}_3$  with mean particle size of 70 nm and apparent density about 0.14 g/cm<sup>3</sup> after calcination at 1200 °C for 1 h.

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