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Microstructures of nanosized alumina powders synthesized by sol-gel method ①

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[Abstract] The microstructures of nanosized alumina powders prepared by sol-gel routine were systematically studied with transmission electron microscopy and X-ray diffractometer. It was found that the morphologies of alumina gel powders change in the orders of caterpillar- thorn- granular- dumbbell shaped structures during calcining at temperatures from 20 ℃ to 800 ℃, 1 200 ℃ and 1 300 ℃. The caterpillar shaped structure composed of strings with a diameter of 5 nm.

[Key words] nanosized; alumina powders; sol-gel; microstructure
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1 INTRODUCTION

Considerable attention has been focused on the synthesis of highly sinterable, nanosized, ceramic particles over the last decades[1, 2]. Numerous papers reported the preparation of alumina powders using different starting chemicals, such as nitrate, sulfate and other inorganic and(or) organic salts of aluminum through hydrolysis reaction or pyrolysis[3~ 7]. The aluminum alkoxides have the most advantages among the salts in the preparation of ultra-pure and superfine alumina powders. There are many reports involving in preparation processes, chemical reactions and properties of alumina powders obtained from the alkoxides[8~ 12], whereas no study on the microstructure of nanosized alumina powders so far.

The aims of the present work are mainly concentrated on preparing ultra-pure nanosize alumina powders by sol-gel method at first, and then tried to determine the microstructure of the alumina powders after calcining at different temperatures.

2 EXPERIMENTAL

The preparation process of alumina powders is shown in Fig. 1. As the starting material, 0.2 mol aluminum isopropoxide ($Al(OC_3H_7)_3$) was diluted with 300 mL of isopropoxide. Certain amount of water containing HCl was added into the solution. The molar ratio of alkoxide, water, isopropoxide and chlorate acid was kept as 1∶ 12∶ 20∶ 0.3.

During the hydrolysis at 20 ℃, the solution exhibited a white flocculent appearance at initial stage of the hydrolysis, then this flocculent product gradually disappeared under stirring, and finally turned to a translucent colloid sol after 20 min hydrolyzing. The gel powders (aluminum hydroxides containing different amounts of crystal water) were obtained by drying the sol at about 80 ℃. Calcining the dried gel to various temperatures could produce alumina powders. The morphologies and structures of the gel powders were examined using XRD (D/max-rB, Germany) and TEM (PHILIPS EM420, Holland).

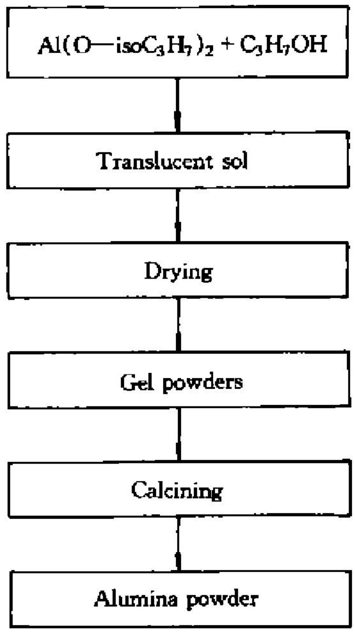

Fig. 1 Schematic diagram for preparation of nanosized alumina powders

3 RESULTS

The dried gel was fired from 20° up to 1 200 ℃ so as to investigate their phase transformation behavior and morphologies with XRD and TEM analysis. The results are shown in Figs. 2 and 3.

The bottom XRD pattern with broaden peaks in Fig. 2 indicates that the gel at 20 ℃ is Boehmite. It becomes amorphous after calcining at 350 ℃, but be-

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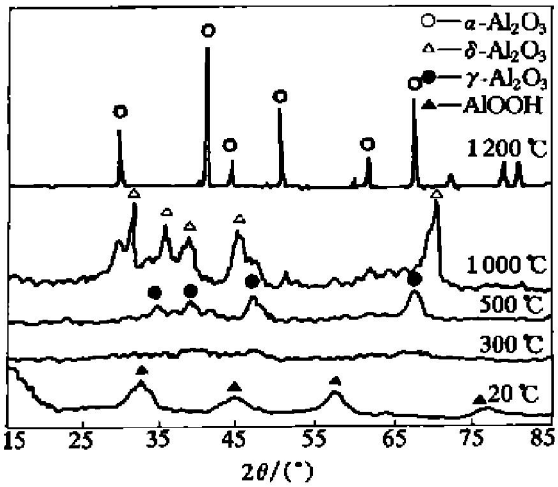


Fig. 2 XRD patterns of Al_2O_3 powder

gins to crystallize to γ-Al_2O_3 at 500 ℃, δ-Al_2O_3 at 1 000 ℃ and α-Al_2O_3 at 1 200 ℃ respectively.

The morphology of the dried gel powder is shown in Fig. 3(a). Individual caterpillar shaped structure in a size of several hundreds nm long and about 50~ 70 nm wide could obviously be seen. The caterpillar structure is composed of several granular sub-grains connecting with each other. Each of the granular sub-grains seems to be crossed by thorn shaped microstructures in it. It is very interesting that the individual subgrain is 50~ 80 nm in length and < 5 nm in width, which is about an order higher than atomic diameter. Fig. 3(b) shows the morphology of the gel powders after calcining at 300 ℃. The caterpillar structures mentioned above disperses and forms a large grain, whereas the thorn shaped microstructure and little granules remain.

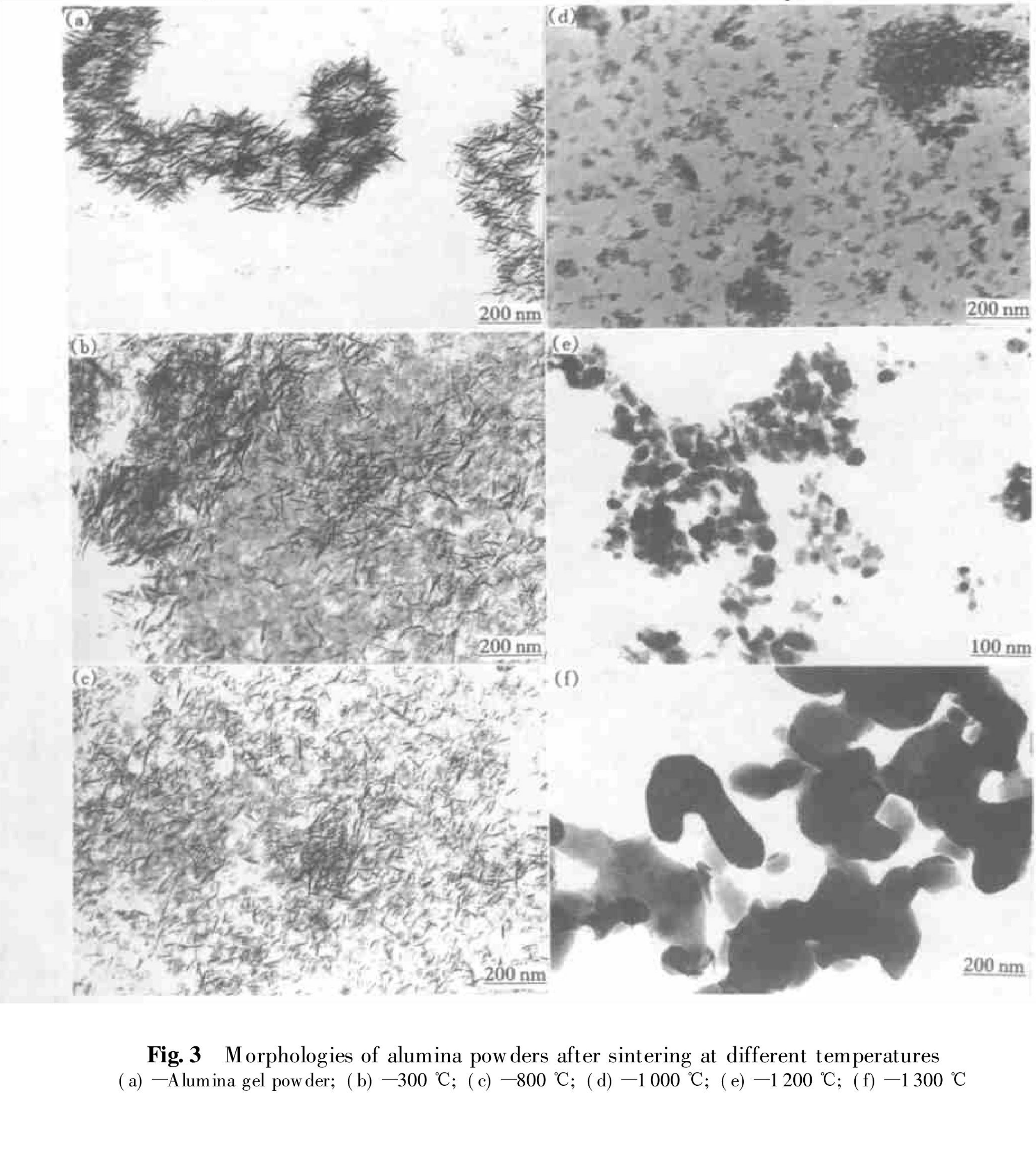


Fig. 3 Morphologies of alumina powders after sintering at different temperatures
(a) —Alumina gel powder; (b) —300 ℃; (c) —800 ℃; (d) —1 000 ℃; (e) —1 200 ℃; (f) —1 300 ℃

Increasing the calcining temperature to 800 ℃, uniform structure almost fill all the sight field of the TEM due to the dispersed big grains have already been connected and mixed with each other, but the characteristics of the thorn structures can still be found in the micrograph (Fig. 3(c)).

Significant changing in morphologies of the dried gel occurs as the calcining temperature reaches to 1 000 ℃ as shown in (Fig. 3(d)). All the characteristics of the caterpillar structure disappeared and new very fine irregular particles of 20 nm precipitate from the dispersed gel matrices. These irregular particles change to be clearer regular crystals as the calcining temperature increases to 1 200 ℃ (Fig. 3(e)). At 1 300 ℃, the regular crystals grow up and begin to join together and thus form the secondary agglomerates by the neck-bridge between the crystals (Fig. 3(f)). The powders grow to 300 nm or so after sintered at 1 300 ℃, about an order increased in size within only a 100 ℃ temperature range.

4 DISCUSSION

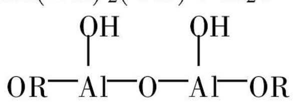
The sophisticated caterpillar shaped structure (Fig. 3(a)) in the Al_2O_3 dried gel after calcining at different temperatures has never been reported before. Individual thorn needle of 5 nm in diameter on the caterpillar structures is almost the same order to the length of the chemical bond. This structure can be referred to as linear molecular or one-dimensional structure of the Boehmite.

As already known, the initial hydrolysis reaction for the aluminum alkoxides can be described by

$$Al(OR)_3 + H_2O \longrightarrow Al(OR)_2(OH) + R(OH)$$

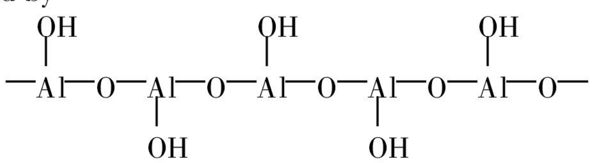
where OR is the alkyl, OH the hydroxyl. This reaction proceeds rapidly and soon becomes a co-reaction of a hydrolyzation and a polymerization.

$$2Al(OR)_2(OH) + H_2O \longrightarrow$$



+ 2ROH

Assuming that all the reactions above are linear ones, the medium product of these reactions is $Al_nO_{n-1}(OH)_{(n+2)-x}(OR)_x$. Where n is the number of aluminum ion and x the OR groups. x decreases until it drops to zero as the reaction continues. The final product will be the Boehmite (AlOOH) with linear molecular structure and schematically described by



Structure water escaped from Boehmite. This results the chemical bonds among the linear molecular of the Boehmite being broken down and the length of the linear molecular becoming shorter and shorter. Thus the morphologies of alumina gel powder changed from a caterpillar structure at 20 ℃ to a fluffy structure at 300~ 800 ℃ (Fig. 3 (a) ~ (c)) with a thorn characteristics still remaining.

The surface area for a linear particle of 100 nm in length and 2 nm in diameter is 1.02 nm^2/nm^3, while for a sphere particle of 6.7 nm in diameter with the same volume as the linear one, is only about 0.45 nm^2/nm^3. The gel powders intend strongly to change from a thorn shaped structure with more surface areas to a spherical one with less surface areas automatically. Another reason of this change belongs to phase transformation. At 500~ 1 000 ℃ phase of alumina powders changes from α-Al_2O_3 to δ-Al_2O_3. This can be seen in Figs. 2, 3(c) and (d).

The morphologies of alumina powders completely change to sphere shape after sintering at 1 200 ℃ for 3 h (Fig. 3(e)). The nanosized alumina granular powders of 20~ 30 nm in diameter can be obtained after 1 200 ℃ calcining.

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