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Preparation of platelike nano alpha alumina particles

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Abstract

A novel synthesis process has been developed for producing high purity nonagglomerate nano platelike α-Al_2O_3 particles. The process mainly utilizes a seed-effect of fine α-Al_2O_3 grains, worn from the milling mediums and uniformly mixed with the hydrous alumina during grinding, and also utilizes ZnF_2 additive to reduce the transformation temperature and modify the alumina particle shape. The aspect ratio and the average size of Al_2O_3 particles prepared at 900°C for 1 h is 2–4 and 40 nm, respectively.

Keywords: A. Powder; B. Platelets; D. Al_2O_3; Nanometer

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, nanocrystalline ceramics can enhance their mechanical properties. So nanometer size powder processing is of great important in the range of nanotechnology since it affords to fabricate various kinds of nanocrystalline materials and the nanocomposite ceramics have such advantages over monolithic ceramics as high strength and high toughness [1]. Nano-sized platelike particles reinforcing ceramic nanocomposites in intragranular structure are promising to have exhibited excellent properties for structural materials in high performance applications, because platelike nano particles reinforced the grains of matrix ceramics in the intragranular structure can induce transgranular fracture, main cracks cannot propagate along the boundary of the grains, however into the matrix grains. In the matrix grains, platelike nanoparticles can make the main cracks to deflect, so the paths for the crack propagation are very tortuous and are impeded in many places, resulting in higher fracture energy, and enhance its strength and toughness [2].

For preparing nano alumina powder, a lot of approaches such as sol–gel, coprecipitation, hydrothermal, thermal spraying have been developed, it is known that heat treatment at 1100–1250°C is required for almost all those salt-derived aluminum hydroxides or hydrated aluminas to form α-Al_2O_3. During thermal treatment, it passes through the following series of phase transformation before conversion to α-Al_2O_3:

$$\text{hydrous alumina} \rightarrow \text{boehmite} \rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$$

the average crystallite size increase to >0.1 μm for α-Al_2O_3 at 1100–1250°C. So it is difficult to process nano α-Al_2O_3 powders which is less than 100 nm by conventional method [3].

In this paper, we report the preparation of the alumina gel from $Al(NO_3)_3{\cdot}9H_2O$ with NH_3OH, in which platelike nano α-Al_2O_3 is crystallized by heat-treating around 900°C. Messing [4] added 1.5 wt.% α-Al_2O_3 (0.1 μm) seeds with γ-Al_2O_3 to reduce the transformation temperature for α-Al_2O_3, but we used the processes of milling for in-situ introduction seeds to make the seeds uniformly mix with the hydrous alumina and also utilized ZnF_2 additive. Not only milling and ZnF_2 can significantly reduce the transformation temperature, but also ZnF_2 can modify the alumina particle shape.

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2. Experimental procedure

The hydrous alumina was prepared by adding $NH_3{\cdot}H_2O$ solution (0.2 mol l^{-1}) slowly to a rapidly stirred $Al(NO_3)_3{\cdot}9H_2O$ solution (4.5 mol l^{-1}). PEG (molecular weight 1000) solution was used as disperant to prevent the powder from agglomerating. When the slurry pH was adjusted to 9.0, the precipitate was aged in the container with constant stirring intensively for 1 h without removing the solution, then the slurry was filtered and kept without washing and dried at 70° for 24 h. After that, the dried gel was milled with alcohol by adding ZnF_2 (2 wt.%) in high purity alumina mediums for 24 h and then dried at 50°C for 12 h. The gel was calcined at different temperature for 1 h with fast or slow heating rate. A flow chart of the process was given in Fig. 1.

Differential thermal analysis (CDR-1, China) of the dried gel was carried out by heating the gel at a constant heating rate of 10 K min^{-1} from room temperature to 1200°C in air. The crystallize species was identified by X-ray diffraction (D/max-radiffractometer, Japan) with Ni filtered CuK_α radiation. The particle size and shape was characterized by transition electron microscopy (JEM-200CX, Japan).

3. Results and discussion

The DTA curves of the milled dried gel with ZnF_2 had four evident exothermic peaks and one endothermic peak as shown in Fig. 2. From DTA curve it can be seen that the intense exothermic peak (at about 300°C) was assigned to the PEG burnout and the 650, 720, 900°C peaks were associated with the phase transformation and the endothermic peak was due to the dehydration. It can be also known from DTA curve that no exothermic peaks after 900°C were observed. It was concluded that the exothermic peak at 900°C was due to the phase transformation and crystallization of α-Al_2O_3, which was in agreement with the XRD results in Fig. 3(d).

The dried gel with and without ZnF_2 calcined at 700 and 900°C respectively were identified by XRD, as shown in Fig. 3. The dried gel with ZnF_2, milled in high purity alumina mediums and calcined at 900°C, can be converted to α-Al_2O_3, but when calcined at 700°C, the XRD only gave diffraction peaks of γ-Al_2O_3 and amorphous background. The γ-Al_2O_3 XRD pattern was very broad indicating the existence of fine crystallite, which can be observed from Fig. 4. The dried gel without milling and adding ZnF_2 calcined at 900°C also gave γ-Al_2O_3 peak and amorphous background, because in this condition at 900°C transition alumina cannot be converted to α-Al_2O_3. Milling with high purity alumina mediums and ZnF_2 additive have potential synergistic effects for reduction in the transformation temperature. Fluorides have the ability of reducing the transition alumina transformation temperature and of modifying the grain morphology, because an intermediate compound, AlOF, may be formed in the case of the phase transformation and AlOF can accelerate the mass transportation from transition alumina to α-Al_2O_3 [5]. In milling conditions the alumina hydroxide in the abrasion powder can be transformed into a single phase of α-Al_2O_3 without forming γ- and θ-Al_2O_3 phases at a relatively low temperature of about 900°C [6] and the fine α-Al_2O_3 particles can act as seeds for the dry gel nucleation sites, but the milling time must be controlled carefully. Seeds have been reported to reduce the θ- to α-Al_2O_3 conversion temperature because they can reduce the activation energy barrier involved in the thermally activated nucleation process. In addition, the reaction production of ammonium nitrate can also reduce the transformation temperature

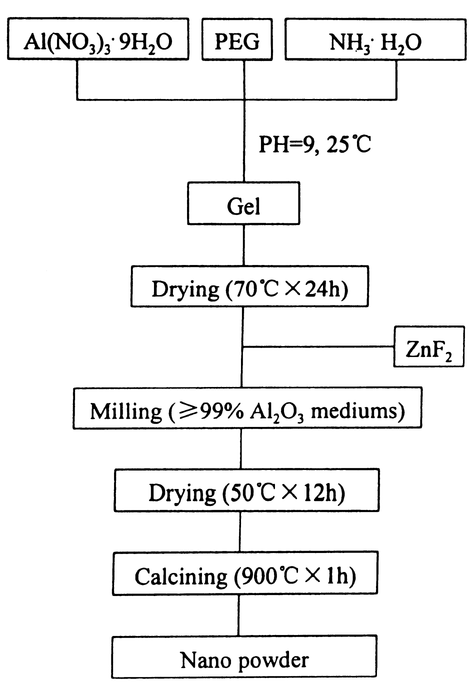


Fig. 1. Flow diagram for synthesizing powder.

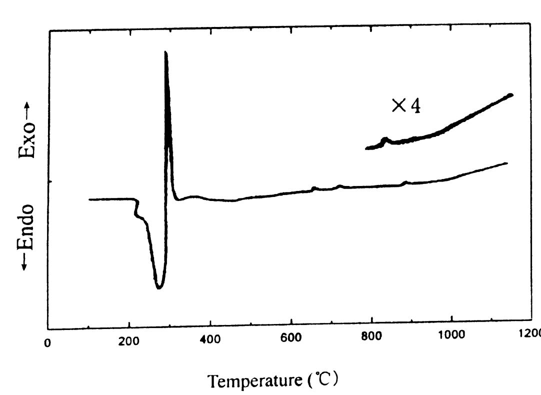


Fig. 2. DTA curve of dried gel with milling and ZnF_2 additive (heating rate 10 K min^{-1}).

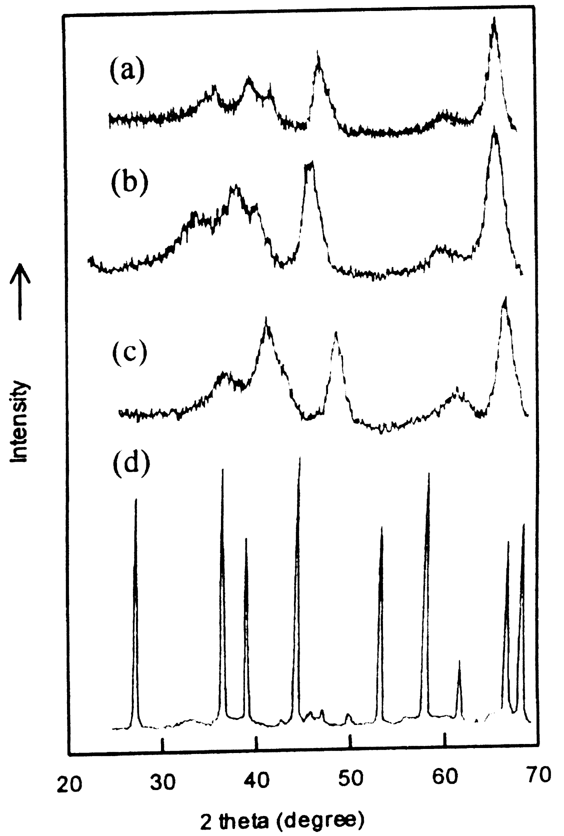
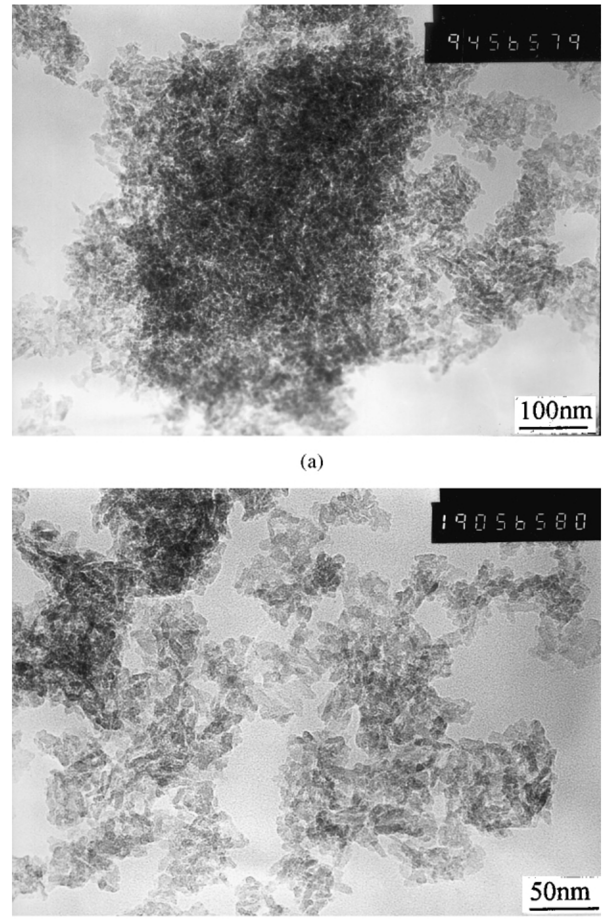


Fig. 3. XRD patterns for dried gel: (a) without milling and ZnF_2 at 10 K min $^{-1}$ at 900°C; (b) without milling and ZnF_2 at 3 K min $^{-1}$ at 900°C; (c) with milling and ZnF_2 at 10 K min^{-1} at 700°C; (d) with milling and ZnF_2 at 10 K min^{-1} at 900°C.



(a)

(b)

Fig. 4. TEM micrographs of γ-Al_2O_3.

due to its decomposition and oxides with releasing of a large mount of energy [7]. From the XRD curve it was shown that fast heating and slow heating have no affection on the transformation temperature, Fig. 3(a) and (b) almost have the same XRD peak patterns.

TEM investigations in Fig. 4 showed that the size of the particles, calcined at 700°C with ZnF_2 and 900°C without ZnF_2, were very large, but the crystallites were very fine with average size of 5 nm. It is probably that in those conditions hydrous alumina can be converted into γ-Al_2O_3, but cannot be α-Al_2O_3 due to low temperature for transformation. So fine γ-Al_2O_3 grains sinter and form relatively larger grains composed of strongly bonded aggregates, necking can be seen from Fig. 4(b). The particles calcined at 900°C with ZnF_2 showed that the size of the grains was nanometer and the morphology of the particles was non-agglomerate platelike, the aspect ratio was 2–4 and also with a small amount of fine crystallites, the largest grains are less than 100 nm and the average size is about 40 nm as shown in Fig. 5. Previous research [7–12] demonstrated that the nano-sized alumina particles were almost spherical by only adding alumina seeds, so this research appears to be the first time reported in the literature to fabricate the platelike nano α-Al_2O_3 particles by adding ZnF_2, because Zn^{2+} can form solid solution with Al_2O_3 and the incorporation of limited Zn^{2+} in solid solution may influence oxide ion mobility and make interfacial energy difference which improves the interface reaction of alumina, then accelerate the grain growth in some directions.

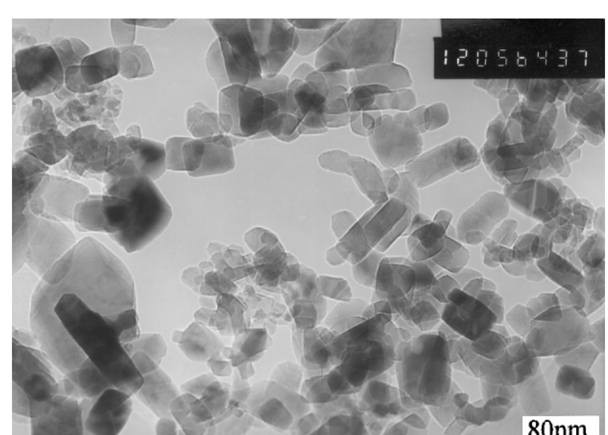


Fig. 5. TEM micrograph of α-Al_2O_3.

Generally, in intragranular structure materials, the grain size of matrix is about 0.5–5 μ and the reinforcement grain is about 10–200 nm, so the nano α-Al_2O_3 platelike particles is suitable for the intragranular reinforcement of nanocomposites. This work is in progress.

4. Summary

The nano platelike α-Al_2O_3 powders with average size of 40 nm and aspect ratio of 2–4 can be fabricated from $Al(NO_3)_3{\cdot}9H_2O$ and NH_3OH, based on gel technology, by in-situ introduction seeds and adding ZnF_2 for reducing the transformation temperature. The ZnF_2 additive can also modify the shape of α-Al_2O_3 particles and make the morphology of particles to be platelike.

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