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A simple method in particle size reduction of nano-crystalline alumina powder

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A grinding process is well known for size reduction of a bulk material. However, the efficiency of the method is limited and not considerable. In this study, a simple method is proposed for reducing the particle size of nano-crystalline alumina powder. The principle of the procedure lies in a localized etching caused by the chlorine released from molten aluminum tetra chloride. In comparison with a grinding process, the proposed method claims a higher efficiency and time saving. Results from X-ray diffraction have indicated that no appreciable changes, in the alpha Al_2O_3 phase used as the raw material, have occurred. The effects of the experimental conditions such as the heat treatment time and the $AlCl_3/Al_2O_3$ weight ratio have been investigated and results have shown that the $AlCl_3/Al_2O_3$ weight ratio has an important influence on the size reduction efficiency of the method.

Key word: grinding, alumina powder, localized etching, size reduction.

Introduction

Size reduction of bulk material can be achieved by thoroughly grinding a bulk solid of the given material by a grinding process employing a planetary ball mill [1-2]. However, the grinding process has some disadvantages such as a broad particle size distribution and the introduction of the impurities. The most important inconvenience is the limitation in particle size reduction and the low efficiency in long grinding periods. This can be partly related to a high tendency of the particles to agglomerate. For alumina powder the phenomena is related to the hydration of alumina particles, especially in an aqueous media [3]. In order to increase or improve the efficiency or effectiveness of the technique, a chemical reaction may be introduced to help particle size reduction by cracking or fracturing powder grains, in which less energy for grain breakdown is required. Dutta *et al.* presented an etching process as an efficient method of making nanoparticles by contacting a powder having particles of an initial size with an etchant and heating the powder and the etchant to reduce the particles of the initial size to nanoparticles having a smaller size than initially [4].

The etching process is well known for surface treatment of the thin films [5], decontamination of the metal oxide surfaces [6] or preparation of SiO_2 wafers in the semiconductor industry [7]. Recently, an etching process was used for the synthesis of uniform hollow oxide nanoparticles [8-9].

In this study, using the principles of the etching process a method is proposed for reducing the particle size of the flakes of synthesized nano-crystalline alumina powder. The principle of the procedure lies in a localized etching caused by the chlorine released from molten aluminum tetra chloride. Results of this procedure are compared with a simple grinding process using a planetary ball mill. The synthesized alumina powder was prepared by a solution combustion method in which the particles obtained are in a flake-like shape. The products were characterized by an X-ray diffractometer, scanning electron microscope and particle size analyzer.

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Experimental

Raw materials used in this study were: ammonium acetate (CH_3COONH_4) and aluminum chloride ($AlCl_3{\cdot}6H_2O$) from Merck.

The combustion procedure for the preparation of nano-crystalline alpha alumina is well known [10-11]. The materials were dissolved in deionized water and were transferred into a microwave oven (Samsung, Korea, 900 W, 2.45 GHz frequency). After 10 minutes a gel like structure was obtained which then swelled, with the evolution of a large volume of gases and self propagating solution combustion occurred. The heat treatment was performed at 900 ºC for1 hour to obtain pure alpha alumina phase.

The particle size of the as-synthesized powder was reduced by two procedures; (I) by a simple grinding process in a planetary ball mill for 4 hours and (II) by our proposed procedure in which the synthesized alumina powder and $AlCl_3$ were measured and were mixed in weight ratios from 1 to 1.5. Then the mixture was added to a planetary mill and milling was performed for 30 minutes. After complete mixing, the mixture was transferred to a furnace for heat treatment at 600 ºC for a time varying from 30 to 90 minutes. The powder obtained was crushed, washed,

filtered and dried in an oven at 100 ºC, in order to remove the residual water.

For the procedure (I) the sample was wet milled at 400 rpm in air in a planetary mono mill pulverisette 6 (Fritsch, Germany) with zirconium dioxide grinding bowls (500 ml) containing 20 balls 20 mm diameter.

The crystallinity and phase identification of the powders were measured by a Philips Xpert X-ray diffractometer using Cu Kα as the radiation source and Ni as the filter. The crystallite size of the particles was calculated by the Scherer formula [5]. The morphology of the powders was determined by a LEO 1455VP scanning electron microscope. A laser diffraction particle size analyzer (LDpsa Mastersizer 2000 Malvern instrument Ltd., Malvern, UK) was used to investigate the particle size distribution of the samples after and before procedures (I) and (II).

Results and Discussions

Fig. 1(a) shows the XRD patterns of the alumina prepared powder by the microwave-assisted combustion method. It is observed that the powder is in an amorphous state and the alpha phase has not been obtained as yet. The heat treatment of the powder at 900 ºC leads to the pure α-alumina phase being confirmed by Fig. 1(b). The crystallite size of the particles has been calculated by the Scherer formula to be in the range of 37 nm.

The shape and size of the particles have been investigated by SEM and the laser particles size analyser and the results are presented in Figs. 2(a) and 2(b). Fig. 2(a) demonstrates a flake-like shape for the particles, and the particle size analysis results from Fig. 2(b) indicate a broad size distribution with a mean value of 34 μm.

The particle size reducing operation has been made by the two procedures (I) and (II) and the laser particle size curves are shown in Fig. 3. After 4 hours of grinding by a simple milling procedure in a planetary ball mill (I) the particle size is reduced to about 16 μm (Fig. 3 I) whereas the particle size from procedure method (II) is reduced to 3.5 μm (Fig. 3 II). The SEM micrograph shown in Fig. 4, presents the size reduced particles with an irregular shape (not yet flake-shape).

The mechanism of procedure (II) is shown in Fig. 5. It is based on the fact that when Al_2O_3 and $AlCl_3$ are

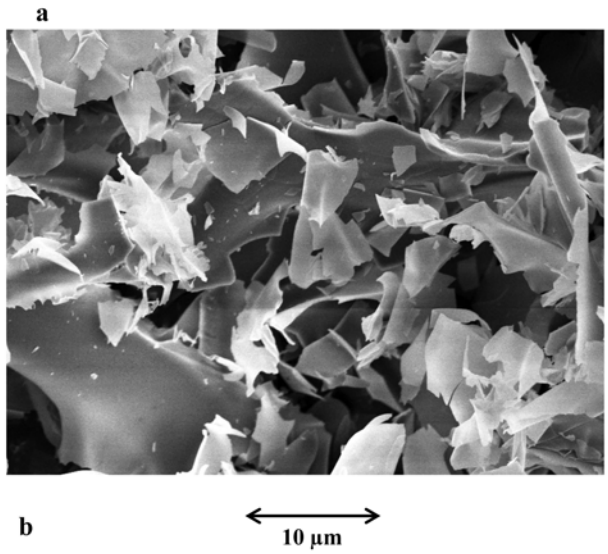

Fig. 2. Characteristics of the synthesized alumina powder, a) SEM micrograph of the particles and b) particle size distribution of the powder.

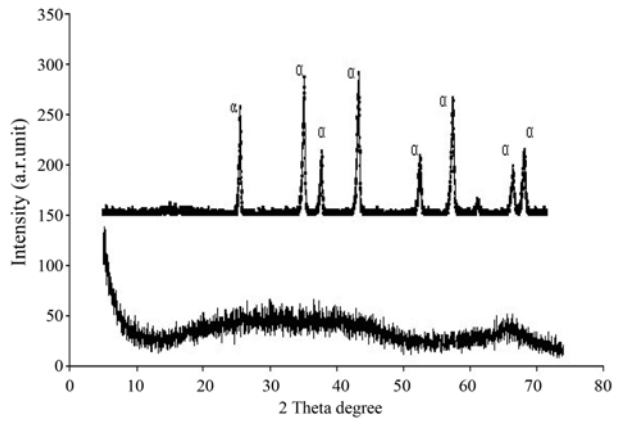

Fig. 1. The XRD patterns of the synthesized alumina powder, a) before heat treatment and b) after heat treatment.

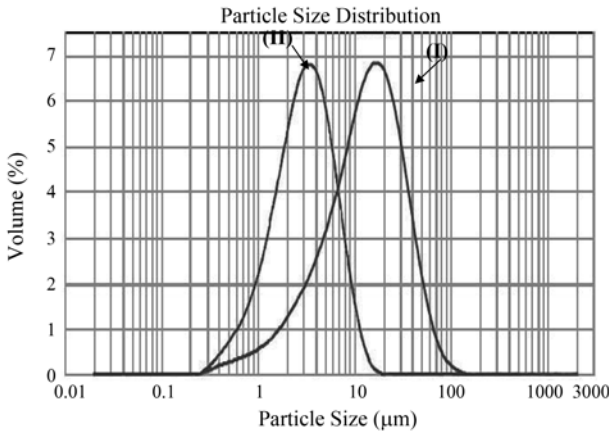

Fig. 3. Comparison of the particle size analysis for two procedures, a) procedure (I) and b) procedure (II).

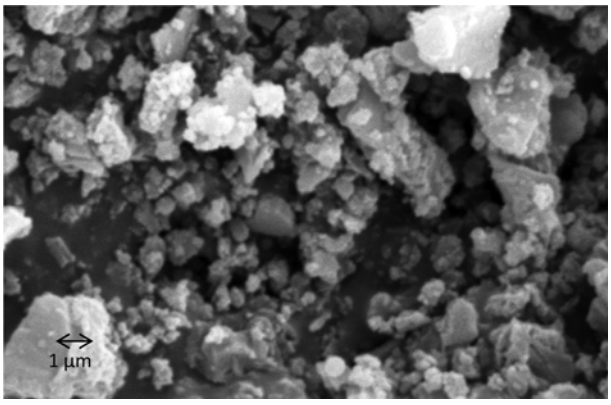

Fig. 4. SEM micrograph of the alumina flakes after procedure (II)

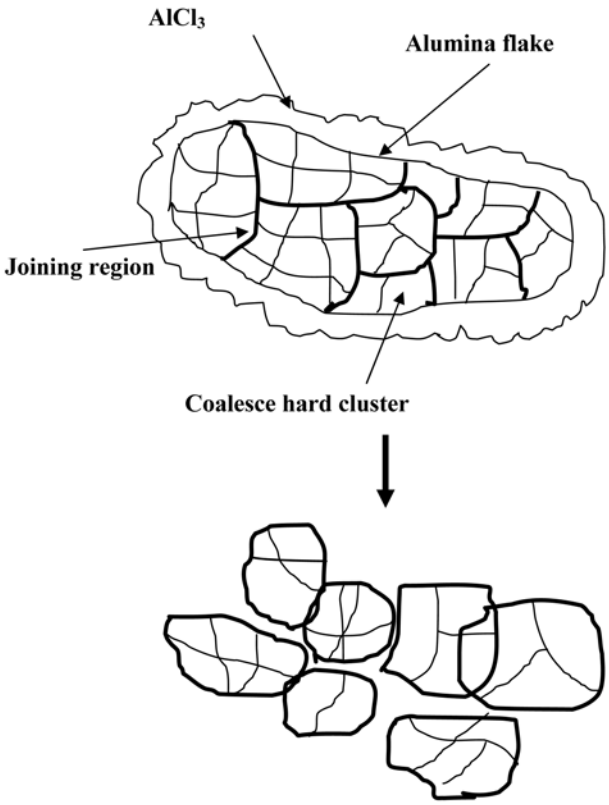

Fig. 5. The mechanism of procedure (II).

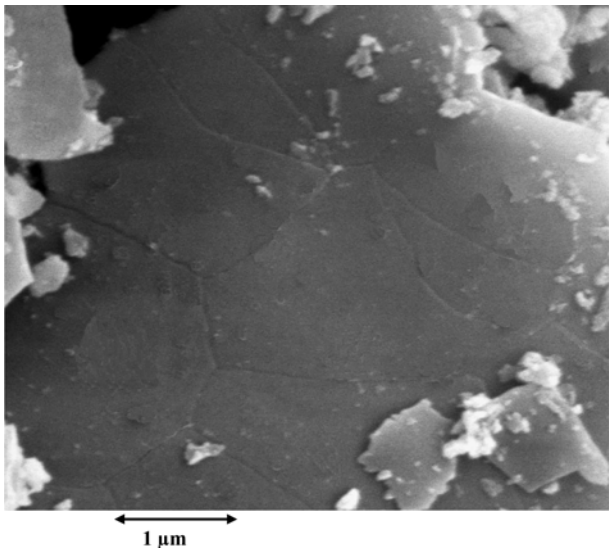

Fig. 6. SEM micrograph of the joined regions on the alumina flakes and the hard clusters colonies.

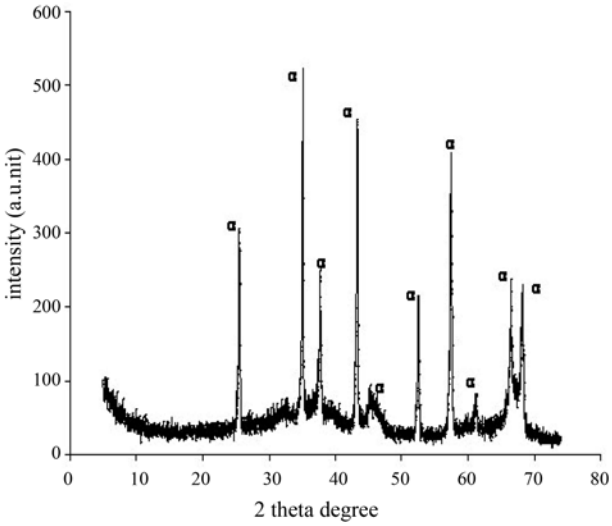

Fig. 7. The XRD pattern of the synthesized alumina powder after performing procedure (II).

mixed together by ball milling, $AlCl_3$ covers the surfaces of the flake-like particles. Each flake is composed of hard cluster colonies, obtained at high temperature during powder synthesis and calcination. The hard cluster colonies are separated by the joined regions as shown in Fig. 6. At 600 ºC $AlCl_3$ melts and covers the Al_2O_3 flakes. The chlorine from the $AlCl_3$ is removed in a gaseous state while some remains in the material as HCl and trapped Cl_2 gas. This promotes localized etching in the regions of the clusters where particles had originally been joined. In these regions etching is faster which leads to seperation of the particles and leads to the size reduction of the flakes. Although the melting point of $AlCl_3$ is 190 ºC the temperature of the heat treatment has been set at 600 ºC to allow complete melting of the $AlCl_3$ powder in a short time. The flake-like form of the particles, which increases the contact surface area between the Al_2O_3 flakes and the $AlCl_3$ melt, can be a good parameter for increasing the efficiency of the procedure.

The structure of the α-alumina flakes after performing procedure (II) has been investigated to verify ultimate phase changes. The result is shown in Fig. 7. From the XRD pattern it has been observed that no phase changes occur during procedure (II).

To verify the effect of the experimental conditions on the efficiency of procedure (II) the heat treatment time in the furnace and the $AlCl_3/Al_2O_3$ weight ratio, have been investigated as the main parameters.

Influence of the heat treatment time

Two experiments were carried at 60 and 90 minutes and

the results were compared with that for 30 minutes as shown Fig. 8. From Fig. 8 it is observed that increasing the heat treatment time in the furnace affects the size reduction efficiency of the method and the particle size of the samples are 2.8 and 2.15 μm for 60 and 90 minutes respectively. However, this influence is not large and when the heat treatment time is two or three times greater, the size reduction changes a little. This can be explained by the fact that the majority of the $AlCl_3$ melts in the first 30 minutes, and causes the localized etching. So, in an extera time there is not an important quantity of released chlorine from the $AlCl_3$ which promotes more localized etching.

Influence of the $AlCl_3/Al_2O_3$ weight ratio

Two experiments were carried with $AlCl_3/Al_2O_3$ weight ratios 1.25 and 1.5 and the results were compared with a $AlCl_3/Al_2O_3$ weight ratio 1 in Fig. 9. The results demonstrate that increasing the $AlCl_3/Al_2O_3$ weight ratio has a significant influence on the size reduction efficiency of the method. The particle size of the samples is 900 and 500 nm for $AlCl_3/Al_2O_3$ weight ratios 1.25 and 1.5 respectively. This is caused by the extra quantity of chlorine released from the $AlCl_3$.

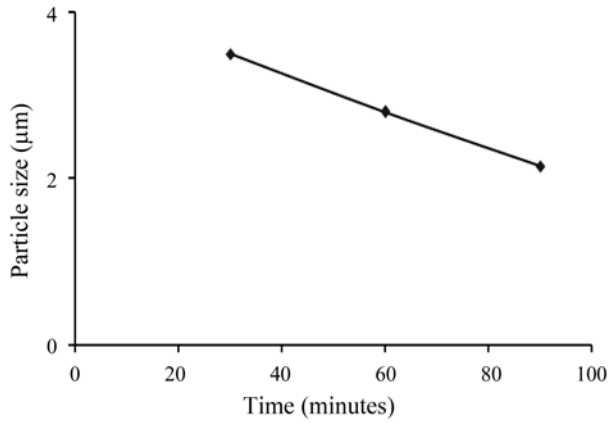

Fig. 8. Effect of the heat treatment time on the size reduction efficiency.

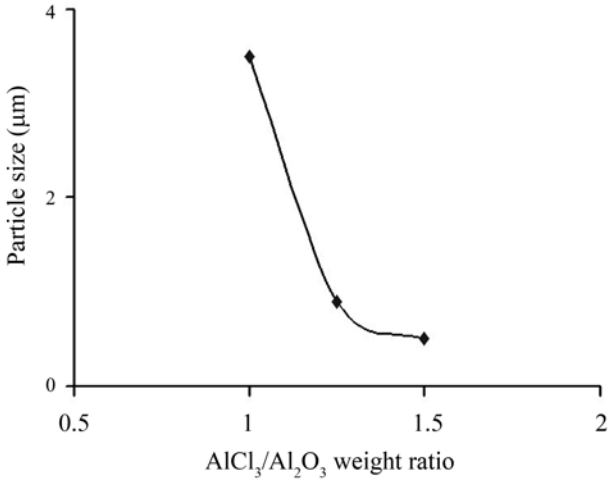

Fig. 9. Effect of the $Al_2O_3/AlCl_3$ weight ratio on the size reduction efficiency.

Conclusions

In this study, a simple method is proposed to reducing particle size of the flaky nano-crystalline alumina powder. In comparison to the grinding process the proposed method is more efficient and time saving. Results have shown the $AlCl_3/Al_2O_3$ weight ratio has an important influence on the size reduction efficiency of the method. It can be suggested that this method can be applicable to others metal oxides.

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