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Influence of annealing on properties and structure of alumina

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Alumina bodies were prepared from pure alumina powder (98.9% Al_2O_3 consisting of 82% > 53 μm). The powder was compacted by hot-pressing at 1200° C. Compacted bodies were annealed at 1300, 1400 and 1500° C. Annealing continued at each maximum temperature for 25, 50 and 100 h. Strong bodies were obtained with maximum bulk density of 2.32 g cm^{-3} and minimum apparent porosity of 30.21%. The change in sintering parameters with annealing was correlated with developed structure.

1. Introduction

As an oxide ceramic, alumina is characterized by chemical inertness, wear resistance, high temperature strength and low dielectric loss. It is well known that these advantages are connected with purity of the material. Therefore sintering an alumina ceramic in the absence of liquid constituents presents an important challenge. This is particularly so as alumina belongs to what may be called the stable oxides. Therefore, it has to be sintered at a temperature amounting to 0.8 to 0.9 of its absolute melting point [1]. Accordingly it became a tradition to sinter alumina bodies at 1800° C and higher. Moreover the material has to be ground to submicronic grain sizes [2]. Because of its hardness, contamination through milling can not be avoided.

Due to its technical importance, alumina has received careful attention especially during the 1950s. Most of the investigations were directed to thermal behaviour and sintering [3–6], as well as physico-chemical characteristics and catalysis [7–9]. A number of previous workers have stated that heating of alumina at the temperature range of γ–α transformation induced measurable changes in physical characteristics [5, 6, 8, 9]. Nevertheless, no explanation, based on structural studies, could be given. The structural changes occurring in alumina bodies through annealing at different temperatures have been discussed by the author elsewhere [10]. In the present work the influence of these structural changes on sintering parameters is investigated.

2. Experimental details

2.1. Materials

The starting material in the present work is γ-alumina powder produced by MERK (W. Germany). This powder has a specific gravity of 3.45 g cm^{-3} and a surface area of 1220 cm^2 g^{-1}. Chemical composition and grain size distribution are given in Tables I and II, respectively.

TABLE I Chemical analysis data of γ-alumina powder*

Constituents other than aluminium oxide	Wt %
Chloride (Cl)	0.015
Sulphate (SO_4)	0.05
Iron (Fe)	0.03
Arsenic (As)	0.0005
Loss on ignition	1.00

*Reagents Diagnostica Chemicals, MERK (1978).

2.2. Preparation of test samples

The alumina powder was precalcined for 1 h at 1000° C, and hot-pressed in a graphite die, heated by induction. Hot-pressing was induced at 1200° C and 450 kg cm^{-2} specific pressure. Maximum temperature and pressure were kept constant for 30 min and samples were obtained as pellets of 1.5 cm diameter and 1 cm height.

2.2.1. Heat treatment

Samples were annealed on a platinum boat in an electrical tubular furnace. Annealing was induced at 1300, 1400 and 1500° C. Heating was continued for 25, 50 and 100 h at each maximum temperature. Samples were removed after cooling down slowly to room temperature.

2.2.2. Sintering parameters and structure

The bulk density, apparent porosity and water adsorption were taken as measures for densification. They were determined by the evacuation method [11], where kerosene was used as the immersion liquid.

The changes in microstructure were studied in freshly broken surfaces, by means of a type Nanolab-7 SEM manufactured by SEMCO-Canada.

TABLE II Grain size distribution in γ-alumina powder

Grain size (μm)	Wt %
+180	0.03
+150	0.66
+125	2.04
+63	64.64
+53	14.63
−53	17.94

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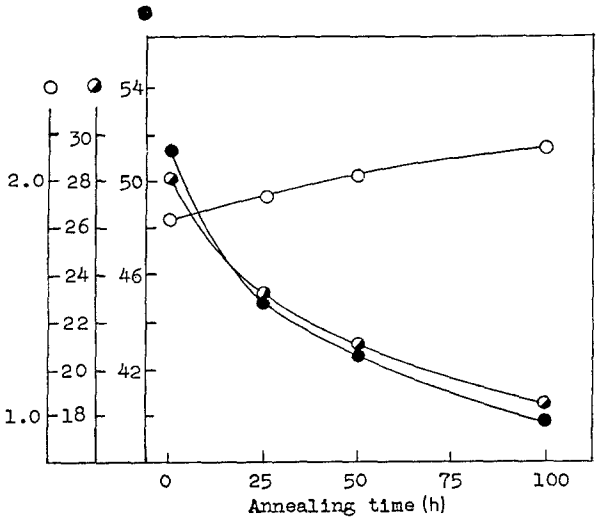


Figure 1 Sintering parameters of 1300° C alumina bodies in relation to their annealing time. (○) bulk density, (◑) water adsorption, (●) apparent porosity.

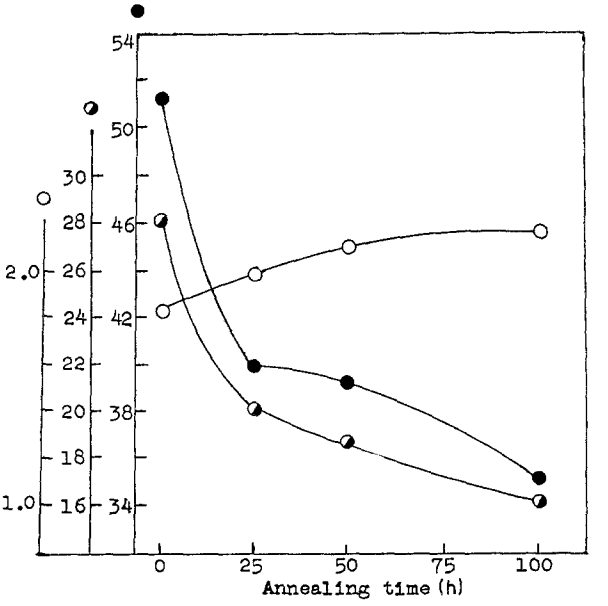


Figure 3 Sintering parameters of 1400° C alumina bodies in relation to their annealing time. (○) bulk density, (◑) water adsorption, (●) apparent porosity.

3. Results

3.1. Samples annealed at 1300° C

Sintering parameters of these samples are graphically represented in Fig. 1. The data reveal that increase in annealing time resulted in a gradual increase in bulk density. The decrease in apparent porosity and water adsorption was remarkable after 25 h annealing and then became relatively steady.

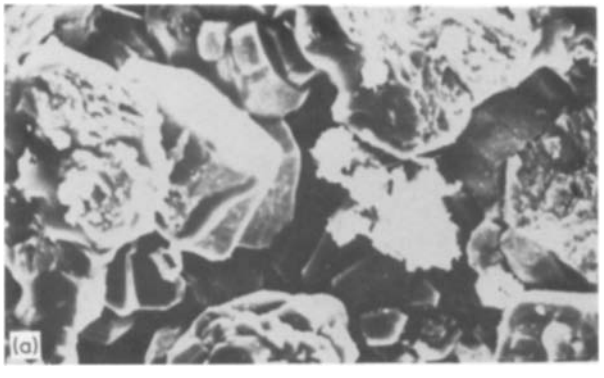
The photomicrographs of these samples are shown in Fig. 2. The sample annealed for 25 h seemed to be more affected by hot-pressing. Some grains are fractured (lower part), and most of the grains are pressed together.

As annealing time increased to 50 and 100 h the intergranular porosity decreased obviously. This occurs side by side with conversion of γ-alumina to irregular grains. After 100 h annealing a sort of micro-porosity and microfissures started to appear in the altered grains.

3.2. Samples annealed at 1400° C

Sintering parameters of these samples are graphically represented in Fig. 3. The data reveal a noticeable increase in bulk density up to 50 h annealing. This increase became relatively slight as time increased from 50 to 100 h. Both apparent porosity and water adsorption decreased remarkably after 25 h annealing. From 25 to 100 h the decrease became gradual and steady.

The photomicrographs of these samples are shown in Fig. 4. The photomicrograph of the sample annealed for 25 h reveals a well marked decrease in intergranular porosity (relative to the 1300° C, 25 h sample). As the time increased to 50 h the individual grains impinged noticeably against each other, and the intergranular porosity decreased. Most of the γ-alumina in the examined sample was converted to irregular grains with internal microporosity. Nevertheless, some cubic γ-alumina crystals were encountered (upper right). In the sample annealed for 100 h the cubic form



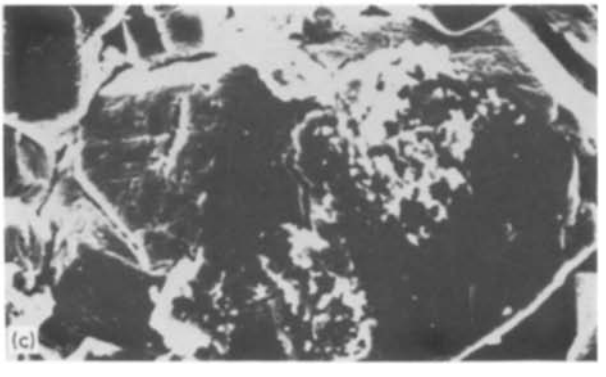
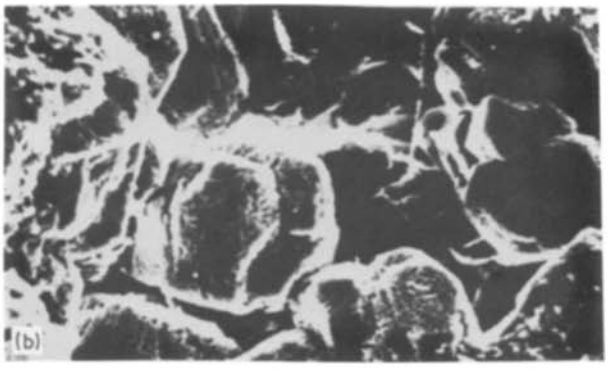


Figure 2 Scanning electron microscope photomicrographs of alumina bodies annealed at 1300° C for (a) 25 h, (b) 50 h, (c) 100 h. Magnification: (a) × 850, (b) and (c) × 1700.



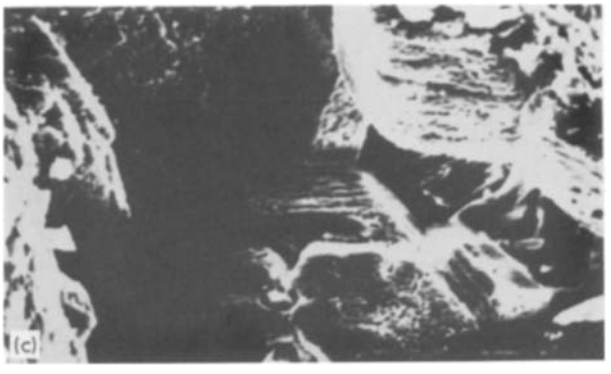


Figure 4 Scanning electron photomicrograph of alumina bodies annealed at 1400° C for (a) 25 h, (b) 50 h, (c) 100 h. Magnification × 1700.

characterizing γ-alumina was almost absent. The intergranular porosity decreased and remarkable recrystallization in the hexagonal α-form occurred. This recrystallization was accompanied by the appearance of some microcracks within the individual crystals.

3.3. Samples annealed at 1500° C

Sintering parameters of these samples are shown in Fig. 5. The data reveal a noticeable increase in bulk density with increase of annealing time up to 50 h. From 50 to 100 h the increase in bulk density was slight. Annealing for 25 h at this temperature resulted in a sharp decrease in apparent porosity and water adsorption. This decrease was less intense when the time increased from 25 to 50 h, and became slight when the time increased from 50 to 100 h.

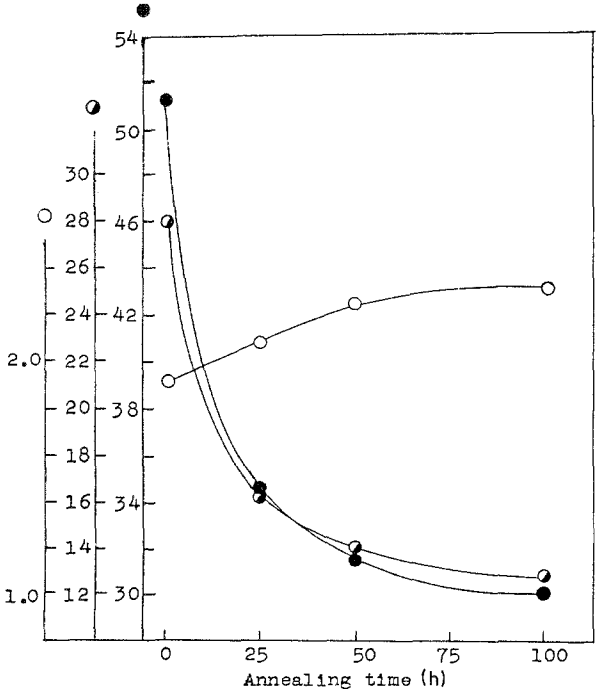


Figure 5 Sintering parameters of 1500° C alumina bodies in relation to their annealing time (○) bulk density, (◑) water adsorption, (●) apparent porosity.

The photomicrographs of these samples are shown in Fig. 6. The photomicrograph of the 25 h sample reveals that intergranular porosity is almost entirely restricted to the grain boundary surfaces. After 50 h annealing the intergranular cracks were still occurring but some parts of the examined sample showed a sort of massive structure set up from union of the individual crystals (left side of the micrograph). This massive structure was relatively prevalent in the 100 h annealed sample.

4. Discussion

From the above results and observations it is clear that the increase in annealing time at 1300° C caused a continuous increase in density and a decrease in apparent porosity as well as water adsorption. This gradual densification occurred while the material was still unchanged intensively into the α-form. On the other hand the 1400 and 1500° C samples behaved somewhat differently. The annealing for 25 h brought about remarkable decrease in apparent porosity and water adsorption. The increase of time from 25 to 100 h induced relatively steady reduction in porosity and water adsorption. In both the 1400 and 1500° C samples the bulk density values showed remarkable increase up to 50 h annealing time. This density increase ceased when annealing time increased from 50 to 100 h.

As shown from the SEM micrographs two main events affected the microstructure through annealing. One is densification according to the well-known concepts of sintering, and the other is transformation of γ-alumina to the α-form. This transformation started to occur in samples annealed 50 h at 1300° C. In the 100 h sample slight formation of micropores and microfissures occurred. In case of 1400 and 1500° C samples the recrystallization in α-alumina was remarkable after 50 and 100 h annealing. This recrystallization was accompanied by progressive development of a sort of microporosity in the individual crystals, while they were becoming impinged to each other through sintering. The induced micropore structure

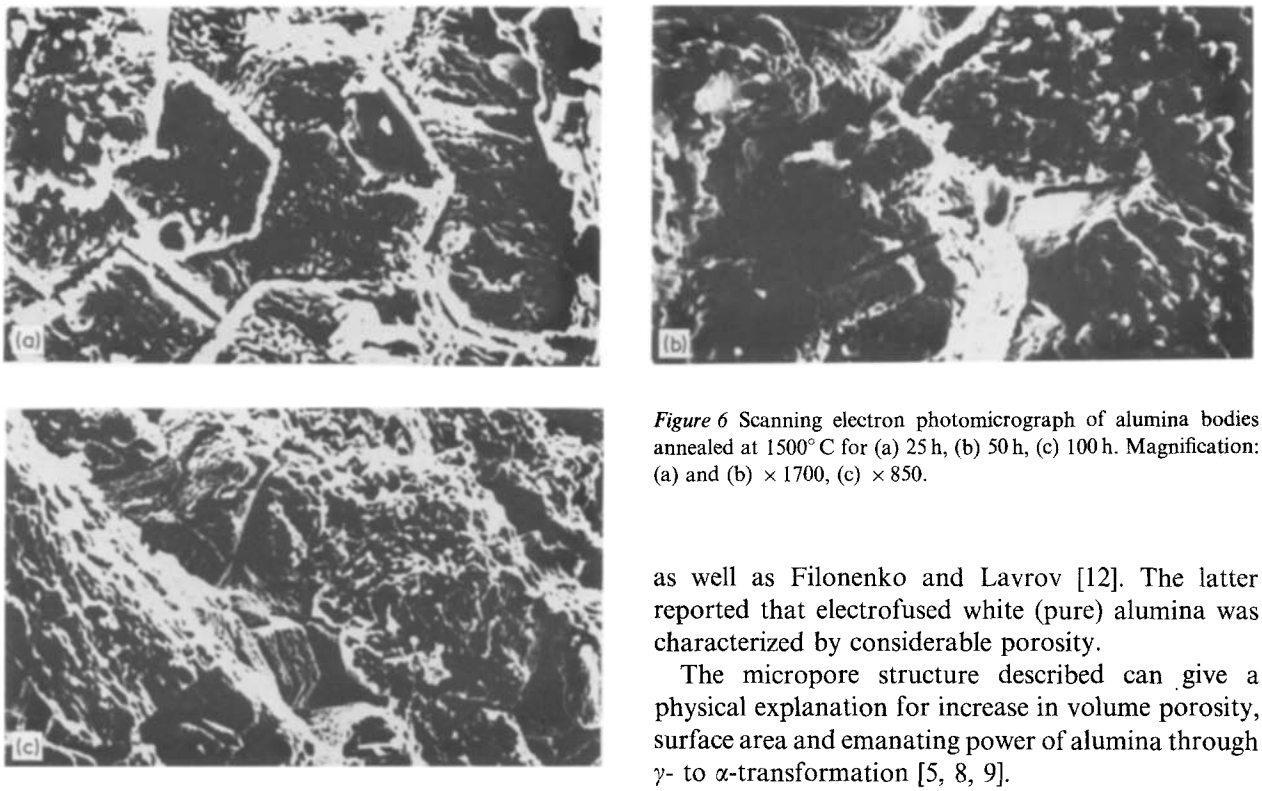


Figure 6 Scanning electron photomicrograph of alumina bodies annealed at 1500° C for (a) 25 h, (b) 50 h, (c) 100 h. Magnification: (a) and (b) × 1700, (c) × 850.

became more clearly defined with both increase of time and temperature of annealing. The development of this micropore structure provided a partial compensation for the densifying effect induced through sintering which is reflected in the cessation of increased density and decreased porosity as well as water adsorption as time increased from 50 to 100 and from 25 to 100 h, respectively.

Although alumina is an important and relatively well studied ceramic oxide, the microstructural changes accompanying its transformation from the γ- to the α-form have not been disclosed until now. Several works in the literature pointed out some changes taking place during transformation, but no clear picture has been given. According to Burke [6], a sample of aluminium oxide with an initial fine pore distribution was heated 1 h at 1800° C and 1 h at 1900° C for recrystallization. The recrystallization almost left the same amount of porosity as was in the initial compact. In a study of sintering alumina, Clark and White [5], detected an increase in percentage volume porosity greater than that theoretically expected. This was in the temperature range of transformation of γ-alumina to the α-form. When catalytic properties of alumina were investigated, the observations about change in surface area during γ–α transformation were contradictory. Such changes in surface area were reported by some authors [8, 9], while some others could not detect it [3]. The emanating power of alumina has been reported to increase to a highly reproducible peak at the temperature range of γ-α transformation [9]. This peak has been attributed to the increase in self diffusion of atoms, and the effect of surface area has been overlooked.

The development of the above described micropore structure during transformation of alumina from γ- to the α-form is in harmony with observations of Burk [6] as well as Filonenko and Lavrov [12]. The latter reported that electrofused white (pure) alumina was characterized by considerable porosity.

The micropore structure described can give a physical explanation for increase in volume porosity, surface area and emanating power of alumina through γ- to α-transformation [5, 8, 9].

5. Conclusions

1. The hot-pressing of alumina powder (82% > 53 μm) brought about good compactness. This was effective in helping densification in subsequent heat treatments.

2. The increase of annealing temperature to 1400 and 1500° C effected more improvement in sintering parameters. Relative remarkable increase in density occurred up to 50 h annealing. A sharp decrease in porosity and water adsorption occurred after 25 h annealing.

3. A sort of micropore structure was associated with transformation of γ-alumina to the α-form. This micropore structure, developed in the individual crystals, compensated partially for the solid state sintering process. This caused a cessation of density increase, and porosity and water adsorption decrease. This effect was more obvious in samples annealed at 1400 and 1500° C. The density increase ceased in the range of 50 to 100 h annealing. The cessation of porosity and water adsorption decrease occurred in the range of 25 to 100 h annealing.

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