

The effect of an added seed on the phase transformation and the powder properties in the fabrication of Al_2O_3 powder by the sol–gel process

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$\alpha\text{-Al}_2\text{O}_3$ powder was produced by the sol–gel process. The prepared sol–gels were seeded with 1.5 wt% powder ($\leq 0.12\mu\text{m}$). The phase transformation of Boehmite into $\alpha\text{-Al}_2\text{O}_3$ and also the particle size distribution of the transformed $\alpha\text{-Al}_2\text{O}_3$ were strongly influenced by seeding and the heating rate during calcination. $\alpha\text{-Al}_2\text{O}_3$ seed particles have been shown to act as a nuclei for the transition of θ - to $\alpha\text{-Al}_2\text{O}_3$ and also to increase the driving force of the phase transformation, which consequently lowers the transformation temperature by about 200 °C. The particles derived from the seeded sol–gels retarded the formation of vermicular microstructures and were finer than those in the unseeded case. The seeding and the control of the heating rate during calcination could inhibit the grain growth due to transformation into $\alpha\text{-Al}_2\text{O}_3$. Fine particles which are homogeneous and have a high sinterability at lower temperatures could be obtained.

1. Introduction

Recently, considerable attention has been focused on the production of high density ceramic bodies with optimized microstructures. The microstructural morphology is determined by powder characteristics such as chemical composition, particle size and shape and agglomeration degree. This is because these factors determine sintering processes. Therefore, the preparation of highly sinterable ceramic particles is of considerable importance.

The fabrication of multiphase ceramics such as Al_2O_3 based systems by the sol–gel technique, offers the possibility of molecular-scale homogeneity and non-equilibrium phases. Recently attention has focused on the reduction of the sintering temperature as well as the homogeneous dispersion of second phases in an Al_2O_3 matrix.

Ceramic powders produced by sol–gel routes, generally, have the advantages of high purity and fine particle size, resulting in high sinterability. Unfortunately, in sol–gel derived Al_2O_3 ceramics, the temperature-sensitive phase transformation severely depletes these characteristics. The sol–gel route to Al_2O_3 initially consists of Boehmite which goes through various

modifications during calcination prior to transformation into the stable α -phase. The final stage in the transformation route generally has a high energy barrier, requiring the use of a high temperature of up to 1200 °C. This barrier is a major factor in influencing the calcination condition which is dependent on the particle size and shape, and agglomeration degree.

This work describes the influence of seeding the reaction and also variations in calcination conditions on the formation mechanisms via the sol–gel route of $\alpha\text{-Al}_2\text{O}_3$. This work is aimed at the preparation of an Al_2O_3 powder with excellent homogeneity and physical and chemical properties.

2. Experimental procedure

As is shown in Fig. 1, an Al_2O_3 sol was prepared by the Yoldas method. As-received aluminium alkoxide was slowly dripped into stirred water held at a temperature of 85 °C. The precipitation and the decomposition of hydrolysed alkoxide simultaneously occurred, resulting in a very opaque solution. When HNO_3 was added 30 min later, it became within a few minutes a transparent colloid solution.

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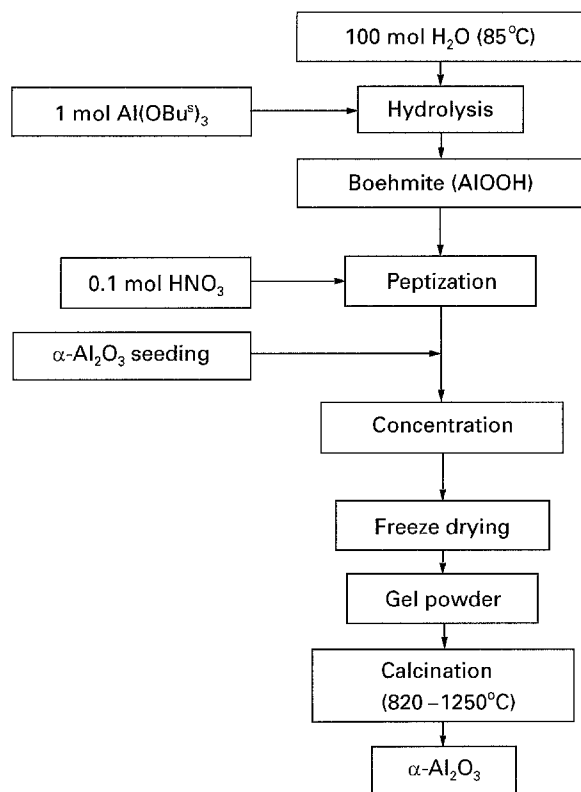


Figure 1 Schematic diagram of sol-gel process for synthesis of Al_2O_3 powder.

At this point, $\alpha\text{-Al}_2\text{O}_3$ seed particles ($\leq 0.12 \mu\text{m}$) prepared from Alcoa-A16 SG (99.8% $\alpha\text{-Al}_2\text{O}_3$, Alcoa Industrial Chemicals, Bauxite, AR.) were added to the sol solution. To ensure an homogeneous dispersion of the seed particles, the sol solution containing the seeds was powerfully agitated. A rotary vacuum dryer (Rotavapour-EL, Büchi Lab.-Technik AG., Switzerland) was used to dry to the viscous extent, in which the seed particles are not precipitated. This sol was dehydrated using a freeze dryer (Christ Delta 2-24, Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz, Germany) and then heat-treated at various calcination conditions. The gel powder characteristics were investigated using a differential thermal and thermo-gravimetric analysis (DTA-TGA) (STA 409, Netzsch-Gerätebau GmbH., Selb/Bayern, Germany) and a high-temperature X-Ray diffractometer (Philips, Eindhoven, The Netherlands). The particle size distribution for each calcination condition was observed with a disc-type centrifugal separator (BI-XDC, Brookhaven Instruments Corp., Holtsville, NY). Scanning electron microscopy (SEM: Cambridge Instruments, Buffalo, NY) was used for the microstructural analysis of the calcined specimens.

3. Results and discussion

In the fabrication of Al_2O_3 , various aluminium hydroxides containing varying amounts of crystalline water are produced. After the dehydration steps, the modified Al_2O_3 is produced [1] by calcination.

In the preparation of Al_2O_3 by the sol-gel processes, the first-observable phase is Boehmite. The phase transformation of Boehmite occurred at slightly

different temperatures, according to each experimental condition such as starting material, crystalline size, heating rate and pressure.

Fig. 2 (a and b) shows the high-temperature X-ray diffraction patterns of the Boehmite $\rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation routes in both the cases of seeding and non seeding. Up to 350°C , amorphous characteristics for Boehmite were observed in the mode of noticeably broad-diffraction peaks. Above 350°C , the various types of Al_2O_3 modification present prior to transformation into $\alpha\text{-Al}_2\text{O}_3$ could be investigated. Whereas in the non seeding case, the diffraction peaks of the α -phase were observed at 1150°C , in the 1.5 wt % seeding experiments they could be observed at 950°C . This effect illustrates the influence of the seed on the $\theta \rightarrow \alpha$ transformation.

From the X-ray diffraction patterns, it has been calculated that Al_2O_3 units modifications (γ -, δ -, θ - Al_2O_3) consists of about $40 \mu\text{m}$ size crystalline particles, which are considered to be a paracrystal. [2] The paracrystal is known to have a layer structure without a periodically repeated crystalline lattice. It has in effect the structure of the intermediate stage in the phase transformation from the amorphous phase into the ideal crystalline phase.

The transition routes from Boehmite to $\theta\text{-Al}_2\text{O}_3$ are generally caused by a topotactic phase transformation [3] during which a crystallographic vacancy is formed by dehydration due to the destruction of the Boehmite structure, and these phases, consequently, have high internal porosity. However the stable $\alpha\text{-Al}_2\text{O}_3$ phase is formed through nucleation and growth mechanisms from the Al_2O_3 modifications. Most ceramic materials are transformed into a stable phase via heterogeneous nucleation and growth processes [4, 5] and higher temperatures are, currently, required to overcome the energy barrier for the nucleation. In other words if the $\theta\text{-Al}_2\text{O}_3$ paracrystal is to act as a nuclei it must grow to the critical size that allows it to play a decisive role in being transformed into the $\alpha\text{-Al}_2\text{O}_3$ phase. In the transformation, vermicular-type grain growth of $\alpha\text{-Al}_2\text{O}_3$ causes a drastic reduction of specific surface area, which lowers the sinterability of the prepared $\alpha\text{-Al}_2\text{O}_3$ powders [6].

The fractions of transformed $\alpha\text{-Al}_2\text{O}_3$ at various calcination temperatures as a function of time are shown in Fig. 3. It has been shown that the transformation ($\theta \rightarrow \alpha$) is dependent on the temperatures and the seed concentration. In the unseeded case the required aging time for the transformation into $\alpha\text{-Al}_2\text{O}_3$ was shorter than in the seeded case and it has been concluded that $\alpha\text{-Al}_2\text{O}_3$ is hardly nucleated. For the seeded case however, the nucleation occurred heterogeneously and due to the seeding effect, the required activation energy and time for the nucleation were lower and shorter, respectively. In our experiments, the temperature for the transformation into $\alpha\text{-Al}_2\text{O}_3$ was significantly lower.

As mentioned above, the heating rate during calcination has an influence on the transformation ($\theta \rightarrow \alpha\text{-Al}_2\text{O}_3$) due to a time dependence of the nucleation rate. [7] As is shown in Fig. 4, the phase transformation temperature into $\alpha\text{-Al}_2\text{O}_3$ is more dependent on

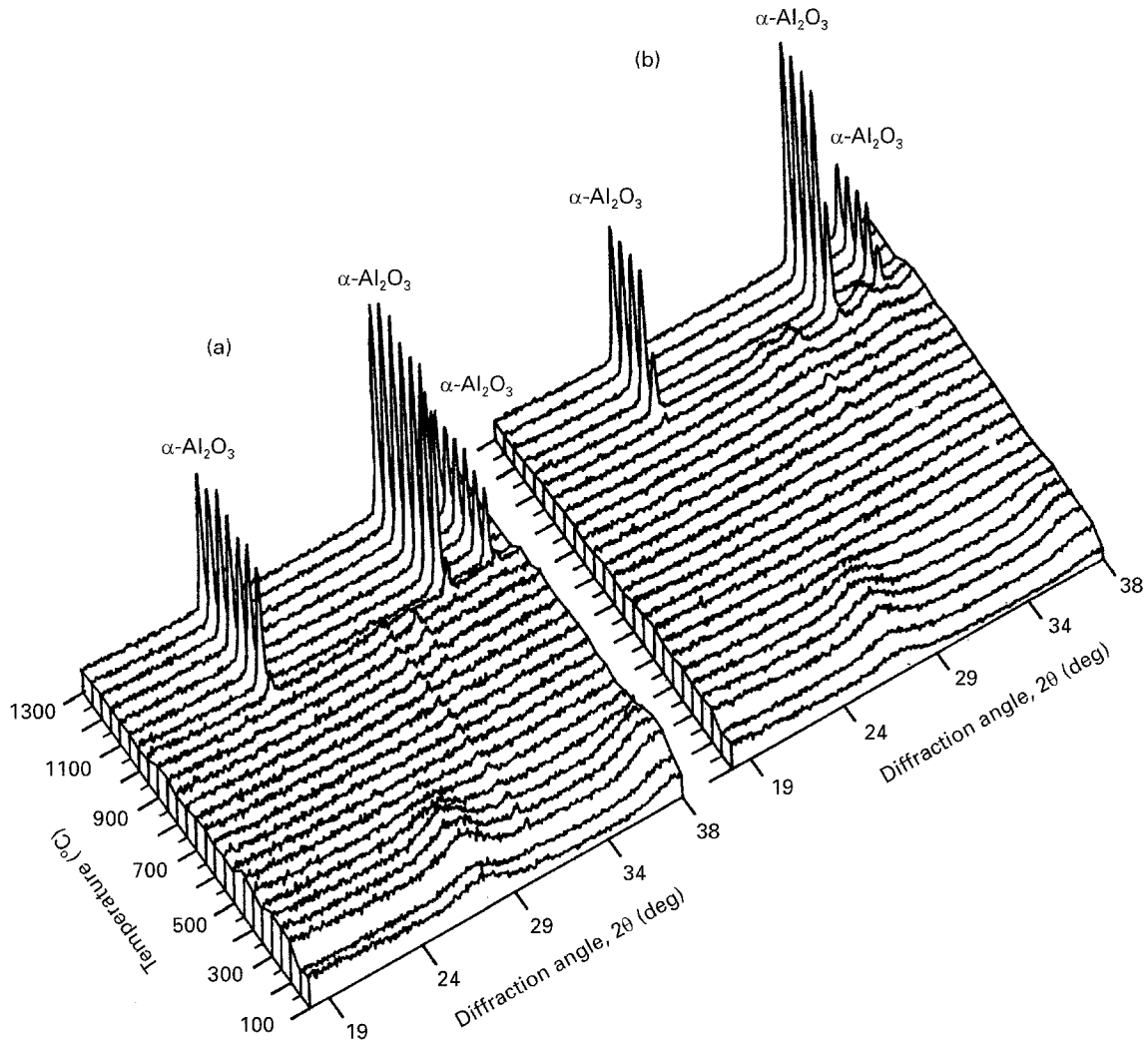


Figure 2 High temperature X-ray diffraction patterns of α - Al_2O_3 gels (a) 1.5 wt % seeded and (b) unseeded.

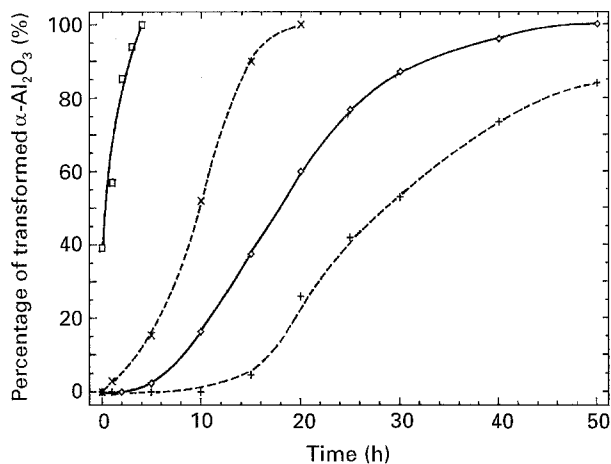


Figure 3 Comparison of transformation kinetics at 900°C and 1000°C for α - Al_2O_3 seeded and unseeded gels. The data are: (+) 900°C unseeded, (o) 1000°C unseeded, (x) 900°C seeded and (□) 1000°C seeded.

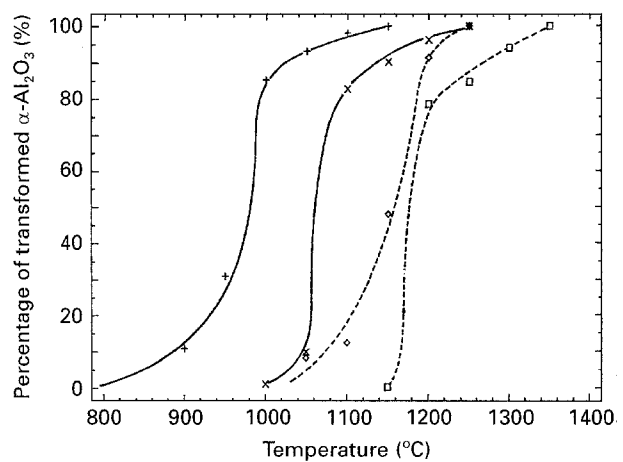


Figure 4 Comparison of transformation kinetics at heating rates of 50°C per h for: (-x-) an unseeded gel; (-+-) a 1.5 wt % seeded gel and at 2000°C per h for (-□-) an unseeded gel and (-◇-) a 1.5 wt % seeded gel.

the heating rate than on seed concentration. Consequently, as the heating rate became faster the transformation temperature moved to higher temperatures.

Fig. 5 (a and b) shows the particle size distributions with the calcination conditions in which the freeze-dried Boehmite powders were fully calcined into

α - Al_2O_3 . When the unseeded samples were calcined at 50°C per h and at 950°C for 150 h, there was a very broad particle size distribution due to particle agglomerations, which frequently appear in powders produced by sol-gel processes. When the unseeded powders were calcined at a very rapid heating rate

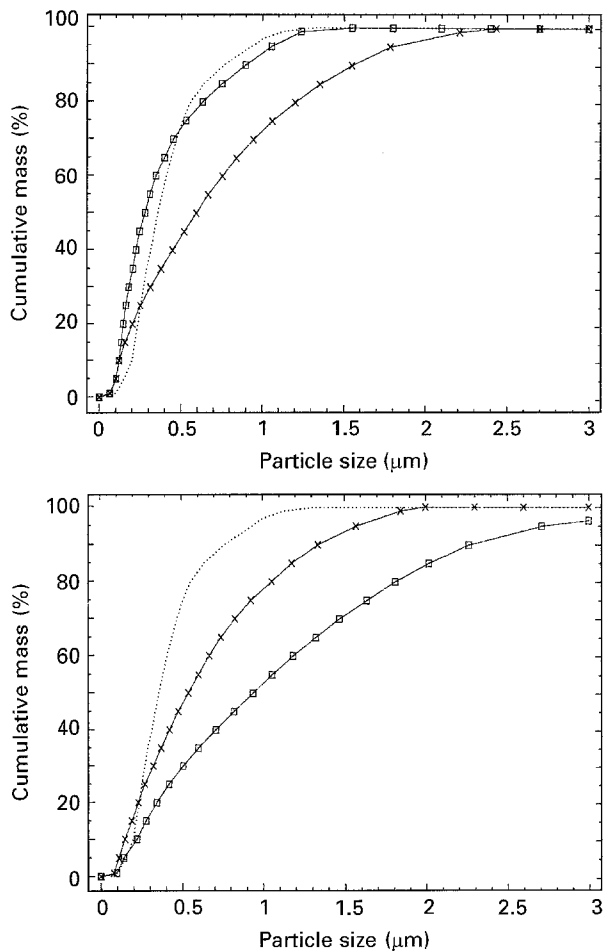


Figure 5 Particle size distributions of calcined $\alpha\text{-Al}_2\text{O}_3$. (a) data taken for a 1.5 wt % seeded sample at (\square) 820 °C 150 h (slow firing) and (\times) 1100 °C for 0.1 h (fast firing). Data shown as (----) is for Alcoa A16SG material and is included for comparison. (b) is data taken for an unseeded sample at (\square) 950 °C 150 h (slow firing) and (\times) 1250 °C 0.1 h (fast firing). Data shown as (----) is for Alcoa A16SG material and is included for comparison.

(3000 °C per h) and at the maximum temperature for a very short holding time (1250 °C for 0.1 h), the particle size distributions of $\alpha\text{-Al}_2\text{O}_3$ became predominantly narrow. At this time, the mean particle size was about 0.55 μm .

In the seeded powder, it has been shown that the characteristics of the particle size distributions with heating rate were very different to the seeded case. That is to say, the calcined powder at 50 °C per h had a more homogeneous particle size distribution than at 2000 °C per h, with a mean particle size of about 0.33 μm . From this result, it has been concluded that seed additives had a significant influence on the fine particle size as well as the homogeneity of the particle size caused by homogeneous nucleation and growth. We also conclude that by altering the calcination conditions such as heating rate and temperature, that the particle size distribution could be controlled. In addition, the nuclei concentration has been shown to be a major factor in influencing the transformation mechanisms of Al_2O_3 .

The consolidation behaviours of the calcined $\alpha\text{-Al}_2\text{O}_3$ powders were observed with a horizontal-type dilatometer ($T_{\text{max}} = 1600$ °C, Netzsch-Gerätebau GmbH, Selb/Bayern, Germany). As is shown in Fig. 6,

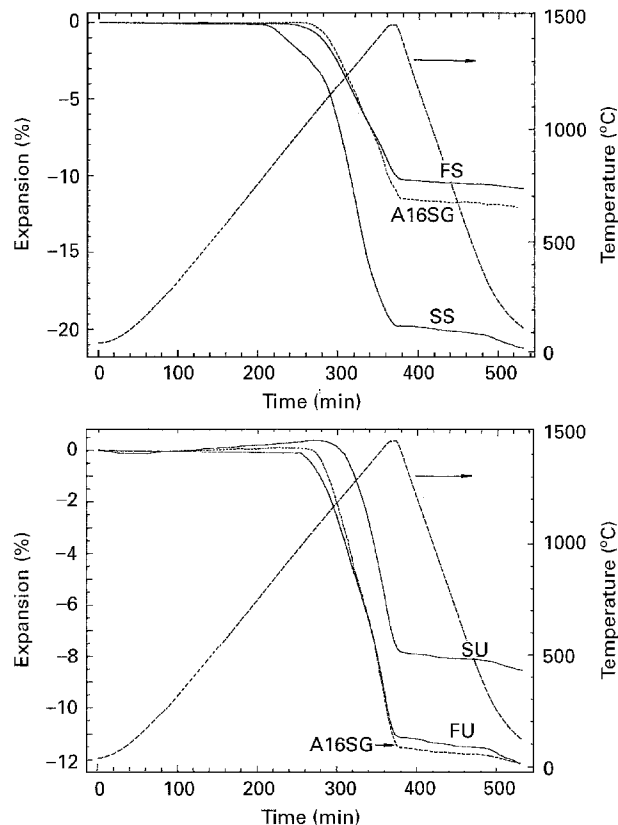


Figure 6 Dilatometer profiles of $\alpha\text{-Al}_2\text{O}_3$ green specimens. (a) The label SS represents the conditions for slow firing and seeding namely 820 °C for 150 h whilst FS represents the conditions for fast firing and seeding namely 1100 °C for 0.1 h. In (b) the label SU represents the conditions for slow firing with no seeding namely 950 °C for 150 h whilst FU represents the conditions for fast firing without seeding namely 1250 °C for 0.1 h. For both (a) and (b) the dashed line represents data taken on Alcoa A16SG which is included for comparison.

(a and b) sinterability is heavily dependent on particle size. The seeded powder started to be densified at a lower temperature, about 150 °C, than any of the other specimens. It is thought that high sinterability like this, is mainly induced by a fine particle size of the powder.

The effects of heating rates on the microstructures are shown in Fig. 7 (a–d). In the seeded case (Fig. 7 (a and c)), the particle size distribution of the specimen heat-treated at 50 °C per h is shown to be more homogeneous than that heated at 2000 °C per h.

In the seeded specimen heat-treated at the very slow heating rate, the growth of the seed as a nuclei occurred gradually which is thought to result from a reaction between the seed and the matrix phase. While, since the very fast heating rate does is only applied for a time shorter than that required for the reaction between the seed and the matrix, the added seed grows very fast. In addition, nucleation and growth within the matrix phase have been thought to cause the broad particle size distribution.

However the unseeded powder heated at a rate of 2000 °C per h consisted of finer grains than the powder heated at 50 °C per h, and had no in-grain pores. The unseeded sample heated at 50 °C per h, however, was shown to have many pores in the grains. The vermicular-type transformed α -phases are thought to begin

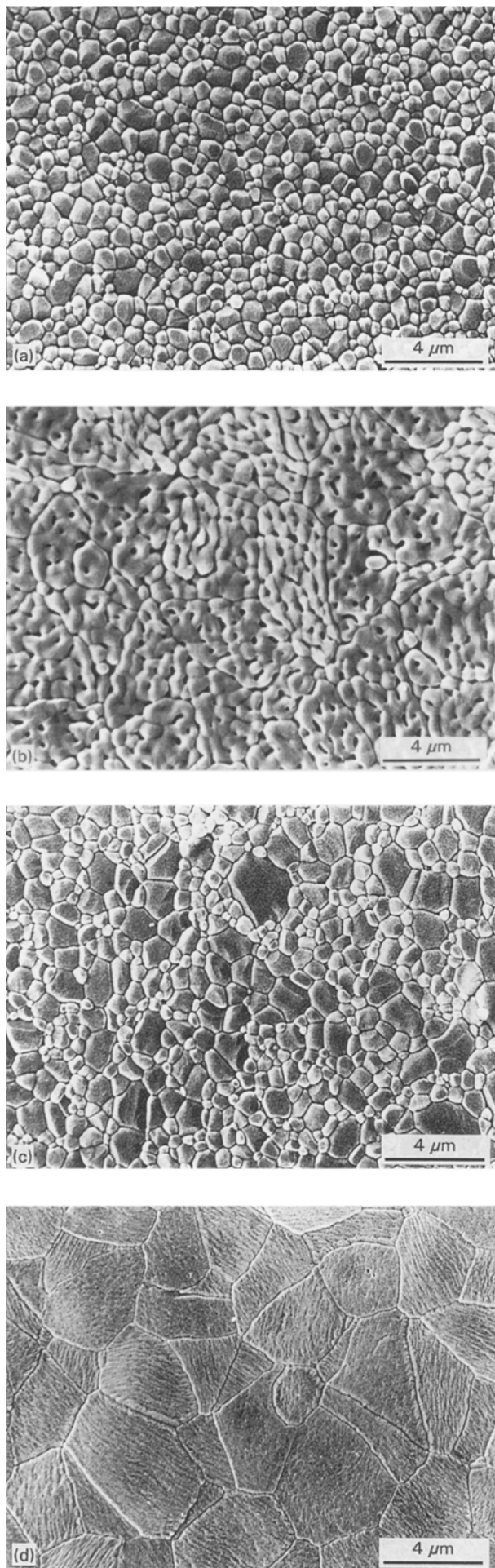


Figure 7 Microstructure of unseeded and seeded gels sintered at 1400 °C for 1 h (a) and (b) at 50 °C per h, (c) and (d) at 2000 °C per h.

densification in the contacted regions, and this ultimately causes the closed pores in the grains.

As a consequence, there are various modified structures created by nucleation and growth mechanisms of Al_2O_3 which result from whether the powder was or was not seeded [8]. To obtain a fine Al_2O_3 powder, the $\theta \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation mechanisms operating during the heat-treatment processes of Boehmite gels must be thoroughly investigated.

4. Conclusions

This work has described a fabrication technique for Al_2O_3 powders based on the sol-gel process. Particular attention was focused on the transformation mechanisms ($\theta \rightarrow \alpha\text{-Al}_2\text{O}_3$) and the effects of seeding on the transformation temperature and transformed α -phase morphology. In the preparation of $\alpha\text{-Al}_2\text{O}_3$ powders, the control of the $\theta \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation is the major factor, and this is in turn influenced by the seed concentration, the heating rate and the calcination temperature. The required temperature for α -phase formation could be decreased by about 200 °C with a 1.5 wt % $\alpha\text{-Al}_2\text{O}_3$ seed addition.

A requirement for the fabrication of fine $\alpha\text{-Al}_2\text{O}_3$ with seed additives, is a calcination condition capable of producing the $\alpha\text{-Al}_2\text{O}_3$ at a temperature as low as possible and for a long holding time. The unseeded powder must be calcined at as rapid a heating rate as possible so that the θ -phase is quickly transformed into the α -phase.

These facts, resulting from the transformation mechanisms of Al_2O_3 , could be altered by whether or not seeding was used. It has been shown that each transformation of Al_2O_3 occurred by nucleation and growth mechanisms different to one another.

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