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Model for the crystallization and sintering of unseeded and seeded boehmite gels

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Boehmite gels crystallize into α-alumina with a dendritic morphology and, in thin films, whiskers can be obtained. In bulk gels, vermicular morphologies are observed, their scale depending on the temperature of conversion to α-alumina. In seeded gels, where the phase change to α occurs at a lower temperature, the scale is much finer than in unseeded gels where a higher α-crystallization temperature is required. A model which explains the dendritic morphology is presented; it rests on the hypothesis that the porosity in the gel must be redistributed into the dense α-dendrite and the empty interdendritic space at the crystallization front. The dendrite spacing is then determined by the kinetic balance between the rate of crystallization and the rate at which the local porosity is redistributed. Measurements of the crystallization velocity, combined with the model, successfully explain the scale of the dendritic morphologies in the seeded and unseeded bulk gels, and in the seeded gel films. The model predicts that the scale of the dendritic structure should increase rapidly with crystallization temperature, also in agreement with experimental results. The model suggests processing paths for controlling the whisker diameter in seeded films, and for low-temperature sintering of seeded bulk gels.

1. Introduction

Our experiments [1] and those published in the literature [2–6] have convinced us that the sintering and crystallization behaviour of seeded or unseeded boehmite gels is controlled primarily by the morphology of the advancing crystallization front of the α-alumina grains as they grow into the boehmite gel. In our view, this morphology is nearly always dendritic: the α phase protrudes into the gel, like fingers, as it grows at the expense of the gel. While the dendrites themselves are dense α-alumina, the interdendritic space is occupied by elongated pores, the total volume of the dendrites and the interdendritic space being equal to the volume of the gel. This dendritic morphology can explain the following observations.

(i) The crystallization of unseeded, bulk boehmite gels into α alumina leads to a vermicular structure [2–4]. An example [1] is given in Fig. 1. The coarsening of the elongated interdendritic pores can be expected to give rise to this structure.
(ii) Films of boehmite gels, when seeded with grains of α-alumina, crystallize into whiskers [5] as shown by the micrographs in Figs 2 and 3. These whiskers may indeed be the dendrites which have not had an opportunity to coarsen because the number of nearest neighbours in two dimensions is less than in three dimensions.
(iii) The phase transformation of seeded boehmite gels into α-alumina is completed before the gel has sintered [6]. A micrograph of the grain structure prior to full sintering, but after the completion of the phase transformation, is shown in Fig. 4.
(iv) The micrograph in Fig. 5 shows the whisker morphology obtained in films that were deposited and then crystallized on single crystal sapphire.

In the following sections we begin by describing a model for the dendritic crystallization of α-alumina from the gels. Next, the applications of the model to the situations mentioned above are discussed.

2. A model for dendritic growth of α-alumina into the boehmite gel

2.1. Microstructure of the unseeded gel

When heated to 400 °C, simple boehmite loses 40% of its weight, mostly water. The remaining structure is a highly porous γ-alumina, with a grain size in the range 5–10 nm. When heated above 800 °C the γ-phase transforms to δ or θ phase [2, 3]; the grain size of these transitional phases coarsens to about 100 nm. Interestingly, in this state the structure remains fine-grained and equiaxed, and the porosity stays in the intergranular regions. Above 1200 °C the transitional

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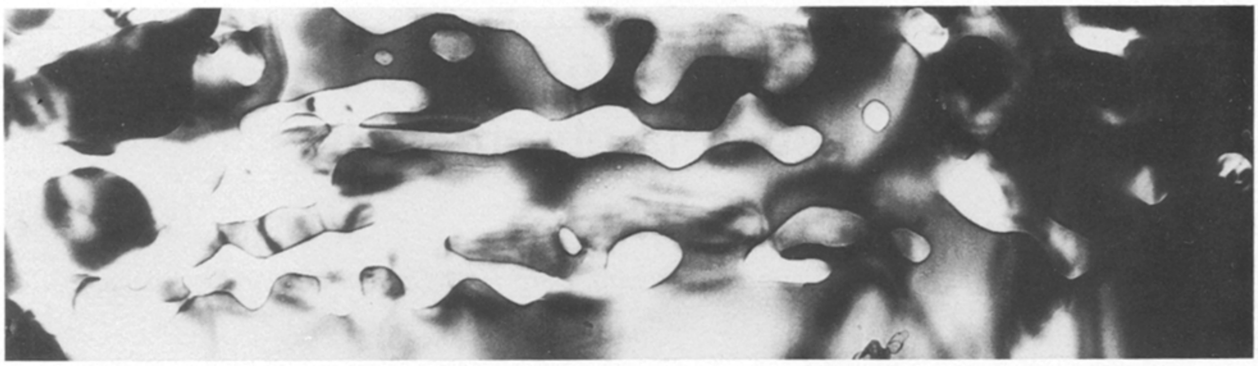

Figure 1 TEM micrograph of the vermicular structure of an α-alumina grain growing in an unseeded gel.

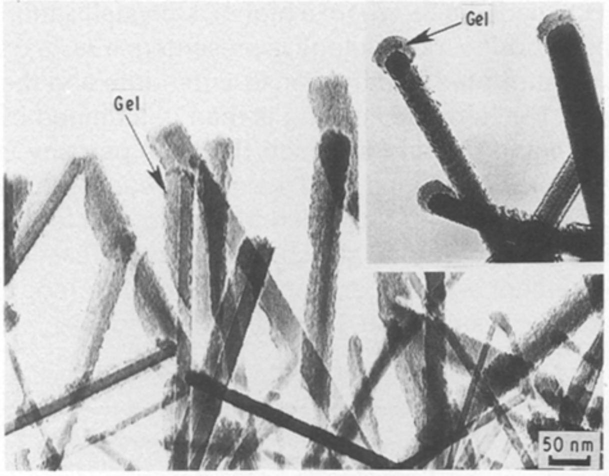

Figure 2 TEM micrograph of a seeded gel film calcined at 900 °C showing α-alumina whiskers with gel remnants along the sides of the whiskers and capping the tips.

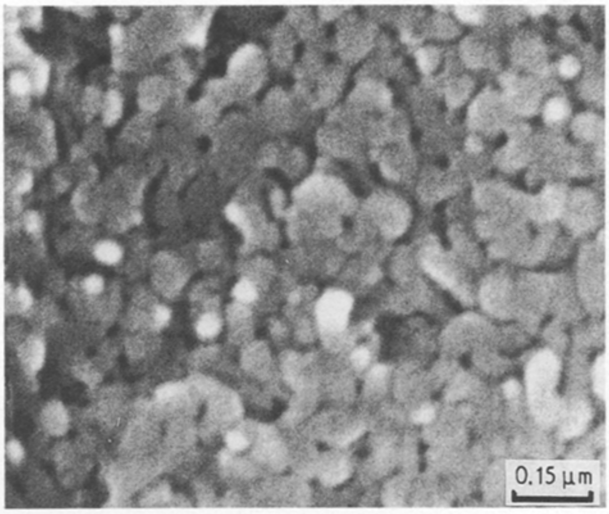

Figure 4 SEM micrograph showing microstructure of α-alumina in bulk boehmite gels seeded with 1.5 wt % α-alumina and heated at 1077 °C for 5 min. It shows the structure of the gel after complete phase transformation to α, but before complete sintering.

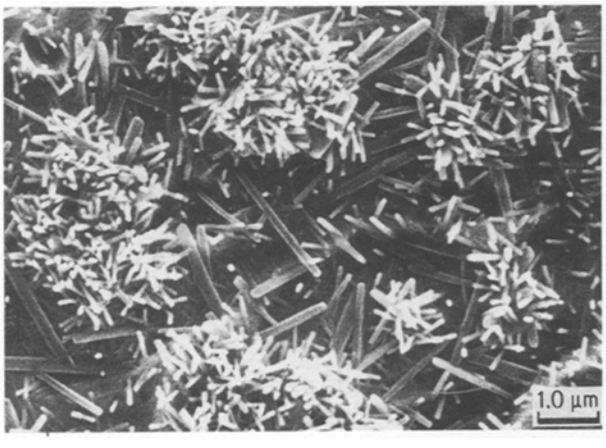

Figure 3 SEM photograph of a seeded gel film-crystallized at 1000 °C showing whiskers growing from the seeds into the plane of the film. Note that the seeds produce multiple nucleation, but only those that are aligned parallel to the film plane are able to grow [5].

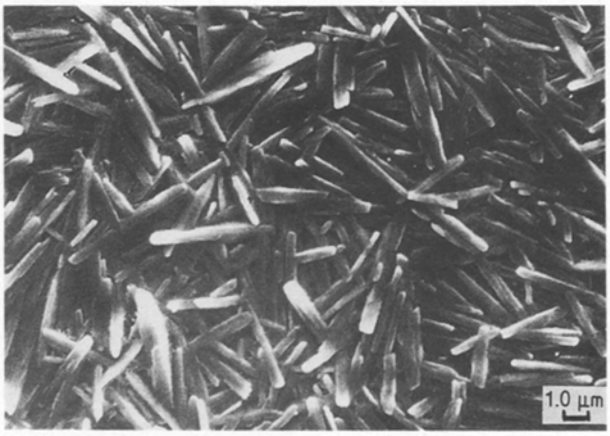

Figure 5 SEM micrograph of α-alumina whiskers grown from thin films of boehmite gel deposited on single crystal sapphire. Whiskers formed at 1200 °C.

phases transform to the stable α-phase which grows in the form of very large grains, nearly 10 000 nm in size, that have a vermicular microstructure. It is believed that the transitional phases contain molecularly bound water with a binding energy of 160 kJ mol^{-1} [7].

The sintering and crystallization behaviour of unseeded gels is illustrated in Fig. 6 [1, 3, 6, 8], which shows the densification of unseeded and seeded cases, ρ_u and ρ_s, the volume fraction of the α-phase, $\phi_{\alpha u}$ and $\phi_{\alpha s}$, and the change in the grain size of the α-phase $d_{\alpha u}$ and $d_{\alpha s}$, all as a function of time. The interesting

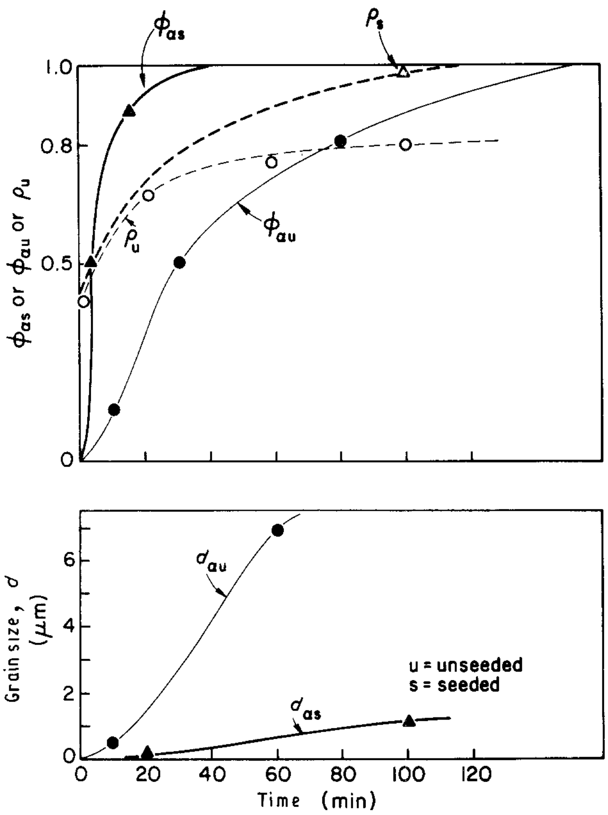

Figure 6 Densification (ρ), phase-change (ϕ_α) and grain-growth data for alumina gels and α-alumina. $\phi_{\alpha s}$ = volume fraction of α-alumina in seeded gels at 1100 °C; $\phi_{\alpha u}$ = volume fraction α-alumina in unseeded gels at 1300 °C; ρ_u and ρ_s = relative density of unseeded and seeded gels.

point is that the rate of sintering is strongly correlated to d_α. In the unseeded case, rapid grain growth in α impedes sintering, whereas in the seeded case d_α is smaller and sintering continues to completion.

2.2. Microstructure evolution in the seeded gels

The seeding of gels increases the number density of α-nuclei. The number of nuclei can be even greater than the number of seeds because of multiple nucleation. For example, the addition of 1.5 wt % seeds of α-alumina, having a particle size of 0.3 μm, leads to grain size in the fully transformed — but yet unsintered — material of approximately 0.1 μm. Thus the particle size of α-alumina in seeded gels can be a factor of 10–100 smaller than in seeded gels; recognizing that the sintering rate varies inversely as the third or the fourth power of the particle size, that translates into a very large increase in the sintering rate of the seeded gels relative to the unseeded gels, as observed.

The grain growth, phase transformation and sintering behaviour of seeded gels, illustrated in Fig. 6, show that phase transformation precedes densification. A possible inference is that seeding promotes sintering, by reducing the grain size of the α phase.

Micrographic evidence suggests that seeding does not suppress the vermicular structure. Instead, it produces a fine vermicular structure which coarsens rapidly. We believe that the wavy pattern of the grain shapes in Fig. 4 is a result of the dendritic growth of the α phase in seeded gels.

In thin films the seeding of gels produces whiskers. When the films are seeded by particles of α-alumina, then (as shown in Fig. 3) many whiskers are nucleated at one seed which grow in all directions. However, because of the constraint of the film, only those whiskers that lie in the plane of the film are able to grow, and this growth distance is approximately equal to one half of the spacing between the seeds. Thus whisker length depends on seed concentration. The diameter of the whiskers increases with the crystallization temperature, as shown in Fig. 7; in the model presented later, the whisker diameter depends on the grain size of the gel material. The larger grain size of the gel is believed to increase the whisker diameter.

2.3. A model for dendritic growth

The mechanism for dendritic growth proposed here arises from the following requirement: the growth of the α-phase into the gel matrix occurs without significant external shrinkage because the α-alumina grains act like non-sintering inclusions which constrain the sintering of the gel matrix. In the case of unseeded gels, the α-phase grows into a nanograin gel matrix consisting of transitional phases of alumina. Because of its ultrafine grain size, this matrix can sinter very quickly. The hypothesis is that rapid growth of α-grains in this matrix pre-empts and constrains [9] the sintering of the gel. The dendritic growth of the α-phase satisfies the need for redistribution of the porosity in the gel into the spaces between the dendrites, so that the geometrical condition of conservation of mass is satisfied.

The proposed mechanism for dendritic growth is illustrated schematically in Fig. 8 and a TEM micrograph is shown in Fig. 9. The schematic diagram shows that as the dendrites of α-alumina grow into the porous gel, the porosity in the gel is redistributed as

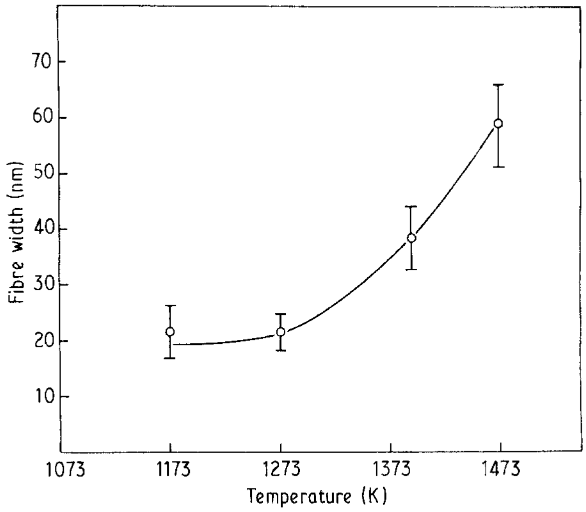

Figure 7 Change in whisker diameter with temperature [5]. (Time = 20 min.)

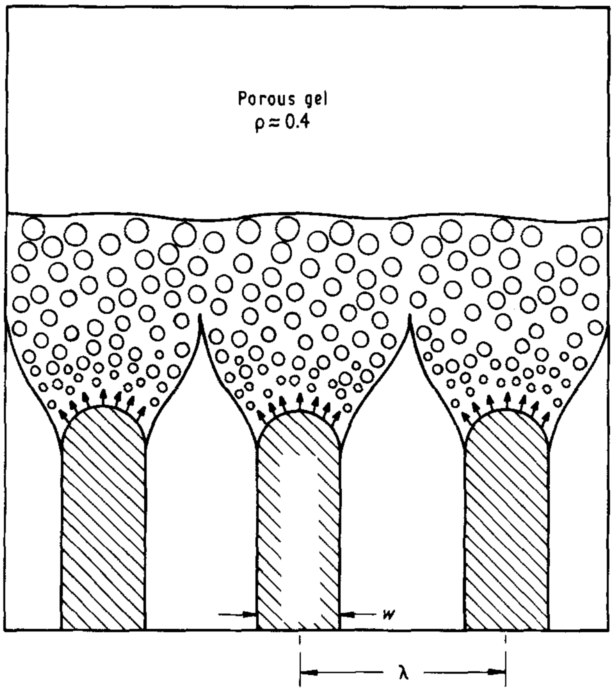

Figure 8 Schematic diagram of the growth of α-alumina dendrites on transformation of boehmite gels to α-alumina due to a coupling between sintering rates in the gel and crystallization of α-alumina.

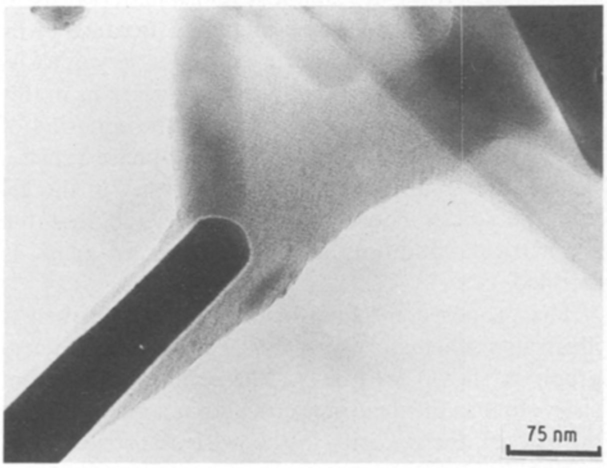

Figure 9 TEM micrograph of an α-dendrite or a whisker growing into the gel.

empty spaces between the dendrites by gradual sintering adjacent to the interface. The region near the interface is able to sinter, while the material well into the gel cannot, because the separation of the gel into free columns near the dendrites removes the constraint to sintering that is otherwise imposed by α-grains on the gel in regions remote from the crystallization front. The condition of conservation of matter immediately leads to the following equation

$$\rho_{\text{gel}} = \frac{w^2}{\lambda^2} \tag{1}$$

where ρ_{gel} is the relative density of the gel, w is the width of the dendrites (assumed to have a circular cross-section) and λ is the spacing between the dendrites.

The magnitude of λ is determined by a kinetic equilibrium such that the time taken by the gel to sinter just ahead of the crystal front, defined to be τ_s, is equal to the time for the α-crystal to advance by a distance 0.5 λ, which we call τ_α. The quantity τ_α can be obtained experimentally by studying the kinetics of crystal growth of α in the boehmite gels. If v_α is the velocity of the crystal growth front, then we have

$$\tau_\alpha = \frac{\lambda}{2v_\alpha} \tag{2}$$

Now consider the time required for sintering of the gel ahead of the crystal growth front. We take the approach that the sintering of the gel can be described by the Mackenzie and Shuttleworth [10] model for sintering of glass, where the viscosity of the glass is replaced by the viscosity of a fine-grained polycrystalline solid which is deforming by diffusional Coble or Nabarro Herring creep. In view of the ultrafine grain size of the gel, which consists of transitional phases with a grain size in the range 10–100 nm, we assume that Coble creep [11] will dominate, which leads to the following equation for the viscosity of the gel

$$\eta_0 = \frac{d_{\text{gel}}^3 kT}{42\pi\Omega\delta D_b^{\text{gel}}} \tag{3}$$

where η_0 is the viscosity of the fully dense material. d_{gel} is the grain size of the crystallites in the gel, Ω is the molecular volume and δD_b^{gel} is the grain-boundary diffusion width multiplied by the grain-boundary diffusion coefficient. The porosity in the gel will lower the viscosity. Sinter-forging data [12], where the shear viscosity of porous polycrystals deforming by Coble creep was measured, show that the following equation is a satisfactory first-order description of the viscosity

$$\eta = \rho\eta_0 \tag{4}$$

when η is the viscosity of the gel, and ρ is the relative density of the gel.

The Mackenzie and Shuttleworth model for sintering gives the following equation for the sintering rate

$$\dot{\rho} = \frac{3}{4\eta}\frac{2\gamma}{a}(1-\rho)^{2/3}\rho^{1/3} \tag{5}$$

where γ is the surface energy of the gel, and a is the radius of the pores in the gel. The pore radius is related to the grain size in the gel, d_{gel}, by the equation $(1-\rho) = (2a/d_{\text{gel}})^3$. Substituting this and Equation 4 in Equation 5, and integrating, we obtain

$$\tau_s = \frac{\eta_0}{3\gamma} d_{\text{gel}} \int_{\rho_{\text{gel}}}^{1} \frac{\rho^{2/3}}{(1-\rho)^{1/3}}\,d\rho. \tag{6}$$

The integral on the right-hand side varies from 1.5 to 2.0 when ρ_{gel} is changed from 0.3 to 0.6. We assume it to be equal to 1.5. Making this substitution, and also substituting Equation 3 into Equation 6

$$\tau_s = \frac{d_{\text{gel}}^4}{84\pi\delta D_b^{\text{gel}}}\frac{kT}{\gamma\Omega} \tag{7}$$

Enforcing the steady-state growth condition that $\tau_s = \tau_\alpha$ and substituting from Equation 2 for τ_α we obtain an expression for dendrite spacing

$$\lambda = \frac{1}{42\pi} \frac{v_\alpha d_{\text{gel}}^4}{\delta D_{\text{b}}^{\text{gel}}} \frac{kT}{\gamma\Omega} \tag{8}$$

Most noteworthy is the strong dependence of λ on the grain size in the gel: the grain size can increase from an initial value of ~ 10 nm to ~ 100 nm during the growth of the α-phase. The implication is that the dendrites which form at lower temperatures, when d_{gel} is smaller, will be much finer than those forming at higher temperatures when d_{gel} is larger. In unseeded gels, the need for nucleation of the α-grain delays transformation to α, allowing d_{gel} to increase, while in the seeded gels the crystal growth of the α phase occurs much sooner. For this reason, dendrite spacing in unseeded gels is likely to be much greater than in the seeded gels.

3. Application of the model

The final microstructure of the unseeded or the seeded gels consists of the α-phase in different morphologies. In the unseeded case the α-grain size is very large, of the order of about 10–100 μm; the grain structure is vermicular; and the highest possible sintered densities are about 0.80. In the seeded gels the α-grain size is much smaller, about 1 μm, and the material sinters to full density; however in the early stages of sintering the α-grain structure is wavy and resembles the vermicular structure, although its scale is much finer than the scale of the vermicular structure in the unseeded gels. In films, the formation of whiskers is strong evidence for dendritic growth; the whiskers are seen when the spacing between the seeds is large, the length of the whiskers being about equal to one half the spacing between the seeds [5].

In the following sections, we attempt to estimate the magnitude of the dendrite spacing, λ. The estimates are approximate because of the lack of information for some of the parameters in Equation 8. For example, the best estimate of the diffusion coefficient would be to assume the value for α-alumina, but that may be an underestimate because in the gel the transitional phases of alumina not only have a more open structure, but may also contain OH bonds.

3.1. Estimate of the velocity of the crystallization front in seeded gels

The velocity of the α-crystal front can be estimated from the data for phase transformation of seeded gels; this was obtained by X-ray diffraction (XRD). These data, given in Fig. 10, show the volume fraction of the transformed gel at different temperatures at various times. We use the following procedure for obtaining the crystal velocity, v_α, from these data.

Let the concentration of the α-nuclei be equal to n_α per unit volume. Then the volume fraction of α phase, ϕ_α, is given by

$$\phi_\alpha = \frac{4}{3}\pi r^3 n_\alpha \tag{9}$$

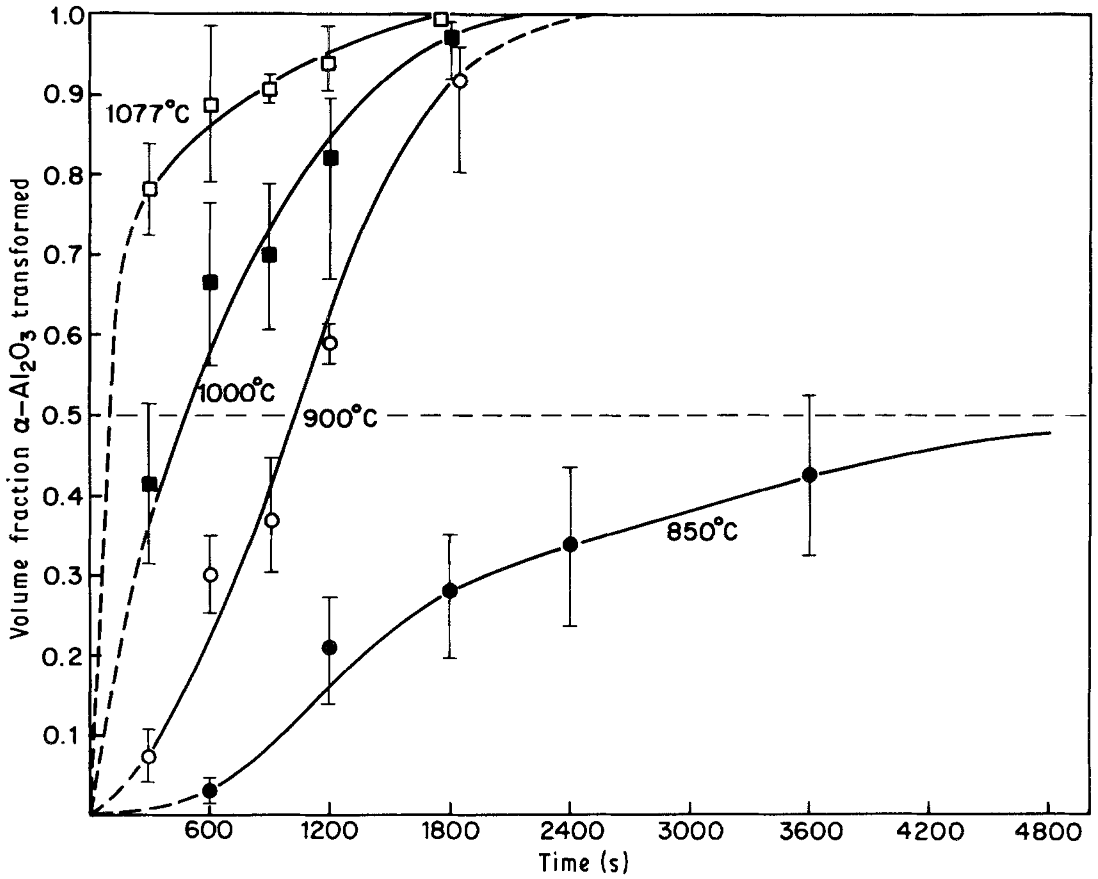

Figure 10 Isothermal transformation curves showing volume fraction ϕ of α-alumina transformed against time in boehmite gel seeded with 1.5 wt % α-alumina seeds and heated at 850, 900, 1000 and 1077 °C.

where r is the average radius of the α-grains. The velocity of the crystal front, v_α, is given by

$$v_\alpha = \dot{r} \tag{10}$$

Equations 9 and 10 lead to the following expression for v_α:

$$v_\alpha = \frac{0.2}{n_\alpha^{1/3}\phi_\alpha^{2/3}}\dot{\phi}_\alpha \tag{11}$$

Note that all quantities on the right-hand side in Equation 11 are experimental, ϕ_α and $\dot{\phi}_\alpha$ are obtained from Fig. 10, and n_α is known from the composition of the seeded gel. For the data in Fig. 10, n_α was equal to 6.4×10^{16} m^{-3}. The application of these data to Equation 11 leads to the curves for v_α which are shown in Fig. 11.

3.2. Estimation of velocity of growth v_α in unseeded gels

The kinetic data for transformation to α-alumina in unseeded gels [13] can be used to estimate the velocity of growth of α-alumina in unseeded gels. The homogeneous nucleation density can be found from the observed grain size of the α-phase, and is estimated to be 10 μm [13]. Then n_α—the number of seeds per unit volume—will be approximately $n_\alpha = 10^{15}$ m^{-3}. Using data in the literature for 1150 °C [13], we can calculate v_α from Equation 11, leading to the estimate that $v_\alpha = 3.44 \times 10^{-9}$ m s^{-1} when $\phi_\alpha = 0.5$.

3.3. Estimate of the dendrite spacing

The dendrite spacing, λ, is estimated from Equation 8. This equation contains parameters that are poorly known. Thus only approximate, perhaps even speculative estimates are possible. We assume the grain-boundary diffusion coefficient to be equal to that for grain-boundary diffusion-controlled creep in MgO-doped alumina [14] which gives $\delta D_b = 2.5 \times 10^{-10} \exp(-421$ kJ mol^{-1}/RT) m^3 s^{-1}. Note that this value for the diffusivity is expected to be the lower bound, because the relative open structure of the transitional phases, which may also incorporate some OH bonds, is likely to support faster rates of self diffusion. For the other parameters we assume the following values: $\gamma = 0.9$ J m^{-2}, and $\Omega = 4.0 \times 10^{-29}$ m^3.

The estimates of λ for different values of d_{gel} at various temperatures are shown in Fig. 12. We now consider how the expression for the dendrite size, λ, may apply to the observed α-morphologies.

3.4. Dendrite spacing in unseeded gels

We estimate the dendrite spacing from Fig. 12. The gel grain size, d_{gel}, at 1200 °C was measured [1] to be 0.05–0.1 μm. This gives a dendrite spacing, λ, of 0.15–2.4 μm.

The micrograph in Fig. 1 shows that the vermicular structure of the grains arises from the elongated, wavy pores. The spacing between these pores may be considered as the dendrite spacing, λ. This is seen to be of the order of 0.3–0.7 μm, and agrees well with the model.

Note that long, cylindrical pores are likely to be unstable and to break up or spheroidize into more equiaxed shapes, as observed [15].

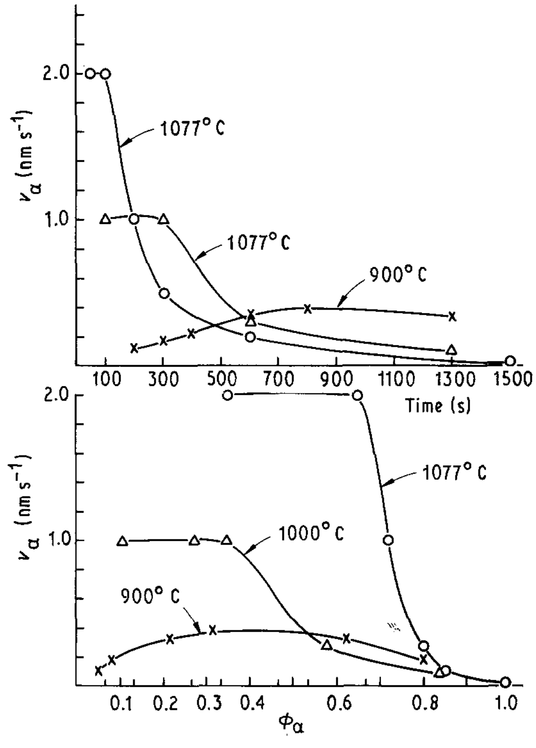

Figure 11 Velocity, v_α, of α-alumina crystals grown from boehmite gels seeded with 1.5 wt % α-alumina seeds at 900, 1000 and 1077 °C plotted as a function of time and volume fraction of α.

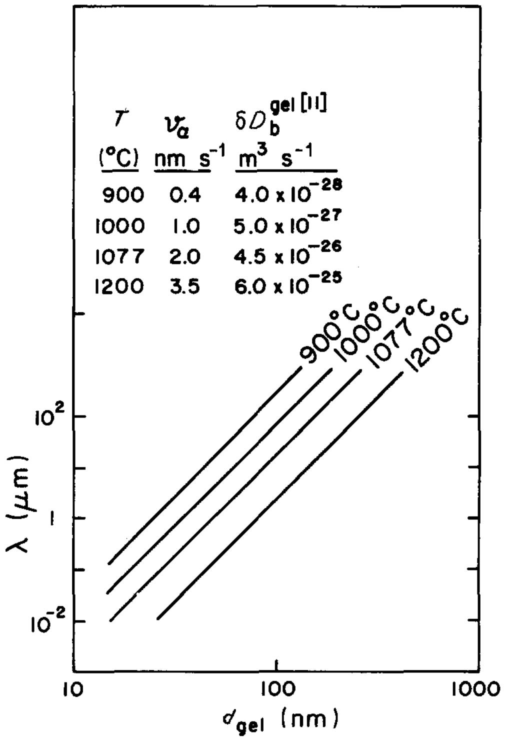

Figure 12 Dendrite spacing, λ, as a function of grain size of transitional alumina in the gel: $\lambda \propto d_{\text{gel}}^4$ (Equation 8).

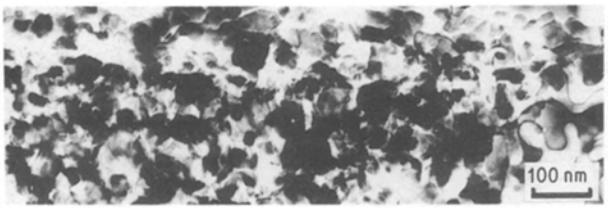

Figure 13 TEM micrograph of the ultrafine grain boehmite gel consisting of transitional phases of alumina (unseeded gel held at 1000 °C for 20 min).

3.5. Dendrite spacing in seeded gels

Experiments with seeded gels have been performed with bulk as well as with thin film specimens. The results of the bulk specimens are described first.

In seeded gels, α-alumina begins to grow at much lower temperatures. Therefore the gel grain size is very small and λ, the size of the α-dendrites, is finer than that in the unseeded gels. At 1077 °C, for example, the gel grain size is approximately 50 nm and λ is approximately 0.1 μm, which is in reasonable agreement with the theoretical estimate (the size of wavy α-crystallites in seeded specimens that have transformed to α but not yet sintered, as shown in Fig. 4, is about 0.1 μm).

The fine dendrites in the seeded crystals coarsen rapidly because their small scale produces a large driving force for Oswald ripening. As a result, they tend to change quickly into wavy and eventually equiaxed grains. We believe that the dendritic morphology was the precursor to the wavy grain morphology shown in Fig. 4.

In thin film (0.1–1 μm) specimens of seeded gels, α grows as whiskers. Most likely, the poor coordination of the dendrites in two-dimensional growth retards the coarsening of dendrites, allowing the chance of growing single crystal whiskers of α-alumina from the boehmite gels. At 1000 °C, the whisker width was 30 nm [5]; the whisker spacing is estimated as 80–100 nm from the micrographs. If we assume that $\lambda = 80$ nm, then Equation 8 predicts $d_{\text{gel}} = 25$ nm, which is in agreement with the measurements from the micrograph in Fig. 13.

The model is in qualitative agreement with the result presented in Fig. 7 that the whisker diameter increases with crystallization temperature in seeded films. According to Equation 8, the whisker diameter increases as the fourth power of the gel grain size. Thus the larger whisker diameter at higher temperature is explained by the coarser gel grain size as the temperature is increased.

4. Conclusions

1. The dendritic mechanism of crystal growth of the α-phase in boehmite gels can explain the vermicular structure of the unseeded gels and the wavy grain structure of the seeded gels. It is also the likely mechanism for the growth of whiskers in the gel films reported earlier [5].
2. The dendritic morphology is explained by the following argument. The growth of large α-alumina crystals, in a gel that consists of superfine grains of transitional phases, constrains the sintering of the gel. Therefore the α-crystal growth occurs under conditions where the external volume of the gel remains essentially constant. The dendritic growth of α allows a mechanism for the redistribution of the porosity in the gel, so that the volume of the dendrites plus the interdendritic volume of the empty space is equal to the total volume of the gel.
3. The model for dendrite growth suggests that the dendrite spacing is proportional to the fourth power of the grain size of the transitional aluminas in the gel. Thus the dendrites which form early, when the gel grain size is small, will be more finely spaced. Therefore the α-alumina dendrites in seeded gels, which transform quickly to α-alumina, are expected to be smaller than those in unseeded gels.
4. As the majority of the external shrinkage in the gel occurs after the formation of α-alumina, the initial size of the α-dendrites and the coarsening of these dendrites has a significant effect on the shrinkage rate. The ability of the seeded gels to reach full density is attributed to the fine and uniform spacing of the α-dendrites.

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