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Effect of Pressure on α-Alumina Nucleation in Boehmite Gel

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Abstract

The intensity of α-Al_2O_3 nucleation, in seeded as well as unseeded monolithic boehmite-derived alumina gel, increases after isostatic cold pressing at 1000 and 1500 MPa. In unseeded gels, a general increase in particle coordination induced by the pressure results in a rise in the number of potential nucleation sites. In seeded gels, a heterogeneous nucleation of α-Al_2O_3, which takes place on the contact surface of the (γ, δ, θ)-Al_2O_3 particles with a seed, is a function of the number of these contacts and the pressure applied.

In aus Böhmit erhaltenen monolithischen Al_2O_3-Gelen wird durch kaltisostatisches Pressen (1000–1500 MPa) die Nukleationsgeschwindigkeit erhöht, sowohl in geimpften als auch ungeimpften Proben. In ungeimpften Gelen wird die Anzahl der potentiellen Keimbildungszentren in Folge der durch den Druck verursachten Erhöhung der Koordinationszahl vermehrt. In geimpften Gelen beginnt die Transformation mit einer heterogenen Nukleation von α-Al_2O_3 an den Berührungsstellen der (γ, δ, θ)-Al_2O_3 Partikel mit der Oberfläche des Impfmittels.

L'intensité de la nucléation de α-Al_2O_3 dans les gels compacts dérivès de la boehmite avec et sans germe de Al_2O_3 augmente aprés une compression isostatique à froid de 1000–1500 MPa. Dans les gels sans germe, le nombre potentiel de sites de nucléation s'accroit avec l'augmentation de l'indice de coordination des particules sous l'effet de la pression. Dans les gels avec germes, une nucléation hétérogène d'α-Al_2O_3, qui se produit au niveau de la surface de contact entre les particules d'(γ, δ, θ)-Al_2O_3 et un germe, est fonction du nombre de ces contacts et de la pression appliquée.

1 Introduction

Crystallization of gels is an important step in the preparation of ceramics by the sol–gel method. Characteristic ceramic properties result from the crystallization of gels.[1–4] Sometimes crystallization is a secondary process of calcination of powdered or bulk gels.

The crystallization of colloidal gels depends to a larger extent on processes that take place in solution, where a microstructure of gels begins to form, than on those in the solid phase. The dried gel microstructure is then the dominant factor, which has significant influence on all solid state processes.[5]

If only a monolithic gel is considered, its microstructure potentially could be changed at least by processes already in the colloidal solution, by heat treatment of gel and by pressing–forced reorganization of colloidal particles. The first two possibilities are very difficult to perform and probably not well enough known for effective control.

For processes in solution there are the important interactions of colloidal particles, the effective hydrodynamic radius of colloidal particles and the ability of particles to rearrange.[6–8] All these processes are difficult to control.

In the boehmite gel studied, various heat treatments did not develop such changes of microstructure, that would lead to an alteration of the crystallization of α-Al_2O_3.[9,10]

The objective of the present investigation was to show the influence of cold isostatic pressing (1500 MPa) of unseeded and seeded[2,11–13] monolithic boehmite gels on the microstructure and so on the crystallization of α-Al_2O_3 (transformation of (γ, δ, θ)-$Al_2O_3 \rightarrow$ α-Al_2O_3).

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To avoid the influence of gel aggregates on solid state processes, the authors intentionally did not use pressed powdered gels, as is otherwise common.[3,14] The microstructure of the monolithic gel used (extruded stick) can then be described by the size of boehmite particles and their coordination.

2 Experimental Procedure

The boehmite gel used in this work was prepared from a commercial boehmite (Condea, 350 $m^2 g^{-1}$, $\approx$10 nm particle size) by the commonly used procedure.[2,10-13] Water-boehmite dispersion (18 wt%) was peptized by mixing it with HNO_3, (pH $\approx$ 2), at 55°C. The seeded gel was prepared by using α-Al_2O_3 crystals smaller than 0·5 μm. The α-Al_2O_3 seed crystals were dispersed with HNO_3 prior to their addition to boehmite hydrosol. The two sols were mixed thoroughly until the diphasic sol gelled. The gels obtained (unseeded, seeded) were further slowly mixed at ~55°C, thickened (~26% of boehmite) and extruded to sticks ($d \approx 0{\cdot}5$ cm, $l \approx 5$ cm).

Dried gels were thermally treated at 150, 550 and 850°C for 1 h and stored in a desiccator. Each xerogel stick ($d \approx 0{\cdot}35$ cm, $l \approx 4$ cm) was separately encapsulated and isostatically pressed at 500, 1000 or 1500 MPa. The prepared gel sticks can be regarded as monoliths without the agglomerates typical of pressed powdered gels.

Isostatic pressure was generated by multiplying the pressure in a universal hydraulic press. A high-pressure steel vessel capable of withstanding pressures up to 2000 MPa was used. The samples were then sintered at 1350°C in static air for 30 min or 3 h in a furnace equipped with Kanthal-super heating elements. The heating rate was 10°C min^{-1}.

The crystallization of α-Al_2O_3 in xerogels was studied by the DTA method using a Netzsch 404 apparatus and by X-ray phase analysis (Dron 2·0, Cu-K_α radiation).

Bulk density was measured according to Archimedes' law. The samples were hydrophobized with melted paraffin before measurement. The microstructure of sintered samples was examined by SEM (BS 300, Tesla). The size and number of α-Al_2O_3 crystals present on fracture surfaces after sintering were evaluated semiquantitatively by counting. The specific surface area of gels was determined by BET adsorption using Carlo Erba (Sorptomatic 1800) equipment.

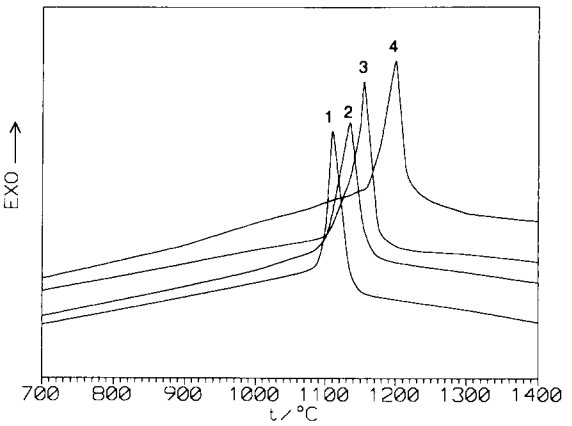

Fig. 1. DTA of unseeded boehmite gels isostatically pressed at a pressure of 1500 MPa in dependence on thermal treatment prior to pressing (150, 500 and 850°C); 1, calcined at 850°C; 2, calcined at 500°C; 3, dried at 150°C; 4, without pressure treatment.

3 Results

3.1 Processing path I: (150, 550, 850°C → 25°C 1500 MPa → 1350°C)

Gels dried at 150°C for 1 h lost only physically bound water. Boehmite was transformed to γ-Al_2O_3 by the calcination of the gels at 550 and 850°C for 1 h. The specific surface area, ~350 m^2/g, and the mean pore size, ~2 nm, were unchanged during this heat treatment. The isostatic pressing at 1500 MPa increased the bulk density of unseeded and seeded gels depending on the heat treatment prior to pressing (Table 1).

The DTA curves of the gels and the temperature of α-Al_2O_3 crystallization exothermic peaks (t_{max}), are in response to these influences. Depending on the degree of gel densification the temperature t_{max} shifts towards lower values (Figs 1 and 2). In unseeded samples a maximum drop in t_{max} of 90°C (in seeded

Table 1. Densification ($\Delta V/V_0$, ρ = bulk density) of gels by cold pressing at 1500 MPa depending on a temperature of drying and calcination ($t_{d.c}$) prior to pressing, and corresponding temperatures t_{max}, $\Delta t = t^*_{max} - t_{max}$, as obtained by DTA

$t_{d.c}$ (°C)	*Unseeded gel*				*Seeded gel*			
	$\Delta V/V_0$ (%)	ρ (Mgm^{-3})	t_{max} (°C)	Δt (°C)	$\Delta V/V_0$ (%)	ρ (Mgm^{-3})	t_{max} (°C)	Δt (°C)
150[a]	0	1·86	1 200	0	0	1·91	1 110	0
150	10·2	2·07	1 160	40	8·8	2·09	1 100	10
550	35·1	2·43	1 140	60	34·9	2·42	1 080	20
850	38·3	2·56	1 110	90	37·0	2·50	1 060	40

[a] Unpressed dried sample.

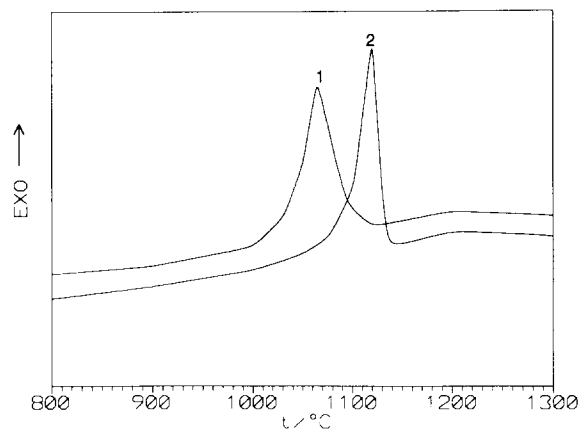

Fig. 2. DTA of seeded (1% α-Al_2O_3, particle size below 0·5 μm) boehmite gels; 1, gel calcinated at 850 C and isostatically pressed at 1500 MPa; 2, without pressure treatment.

samples a drop of 40°C) was observed (Δt, Tables 1 and 2).

The observed decrease in t_{max} depending on the densification of the gels was due to an increase in the number of α-Al_2O_3 nuclei.[10,15,16]

The effect which influences the drop in α-Al_2O_3 crystallization temperature t_{max} was not due to the temperature of drying or calcination before pressure treatment, but to the degree of densification of the material. Pressure treatment alters the gel microstructure and the arrangement of individual boehmite or alumina particles (size ≈ 10 nm). A specific forced arrangement of particles occurs, leading to an increase in their coordination numbers.

3.2 Processing path II: (850°C → 25°C, 500 or 1000 MPa → 1350°C)

The highest degree of densification of gels was found after calcination at 850°C and isostatic pressing at 1500 MPa. For this reason the calcination temperature of 850°C was kept constant and the pressing experiments were made also at 500 and 1000 MPa. The results obtained (Table 2) correlate with t_{max} and $\Delta V/V_0$ values found for xerogels pressed at 1500 MPa.

3.3 The microstructure of samples sintered at 1350°C

The microstructure of sintered boehmite-derived alumina gels is a result of (γ, δ, θ)-Al_2O_3 defect-phase sintering, α-Al_2O_3 nucleation, and growth and sintering of α-Al_2O_3. As can be seen from the SEM fractograms, the microstructure of sintered seeded samples differs considerably from that of the unseeded ones (Figs 3 and 4). This is a consequence of a different mechanism of α-Al_2O_3 crystallization.[10] In the seeded gel the growth of α-Al_2O_3 can occur on added nuclei, while in the unseeded gel at first the new α-Al_2O_3 nuclei must be homogeneously formed.

The characteristic difference between the microstructure of sintered seeded and unseeded gel is that the relative number (N/N_0) of α-Al_2O_3 crystals after 3 h sintering at 1350°C rises with the increase in density of unseeded gel, while in seeded gel the ratio N/N_0 decreases (Figs 3 and 4, Table 3).

The number of crystals was estimated under the

Table 2. Densification of calcined (850 C, 1 h) gels depending on pressure

P	*Unseeded gel*				*Seeded gel*			
(*MPa*)	$\Delta V/V_0$ (%)	ρ (Mgm^{-3})	t_{max} (°C)	Δt (°C)	$\Delta V/V_0$ (%)	ρ (Mgm^{-3})	t_{max} (°C)	Δt (°C)
0[a]	0	1·58	1 200	0	0[a]	1·59	1 110	0
500	3·8	1·64	1 185	15	3·6	1·65	1 100	5
1 000	12·2	1·80	1 150	50	11·81	1·80	1 090	20
1 500	38·3	2·56	1 110	90	37·0	2·50	1 070	40

[a] Unpressed calcined sample.

Table 3. A relative number (N/N_0) of α-Al_2O_3 crystals per area unit (Figs 3 and 4) in pressed (1500 MPa) gels, sintered at 1350 C for 3 h and bulk density after sintering, depending on heat treatment prior to pressing ($t_{d.c}$)

$t_{d.c}$ (°C)	*Unseeded gel*				*Seeded gel*			
	$\Delta V/V_0$ (%)	ρ (Mgm^{-3})	N/N_0	*Figure*	$\Delta V/V_0$ (%)	ρ (Mgm^{-3})	N/N_0	*Figure*
150[a]	0	3·18	1	3(g)	0[a]	3·96	6·4	4(a)
150	10·2	3·33	2	3(a), (d)	8·8	3·96	3·1	4(b)
550	35·1	3·47	23	3(b), (e)	34·9	3·97	1·4	4(c)
850	38·3	3·58	31	3(c), (f), (h)	37·0	3·98	1·0	4(d), (f)
850		—		—	37·0[b]	3·82	100	4(e)

[a] Unpressed dried sample.
[b] Sintered at 1350 C for 30 min.

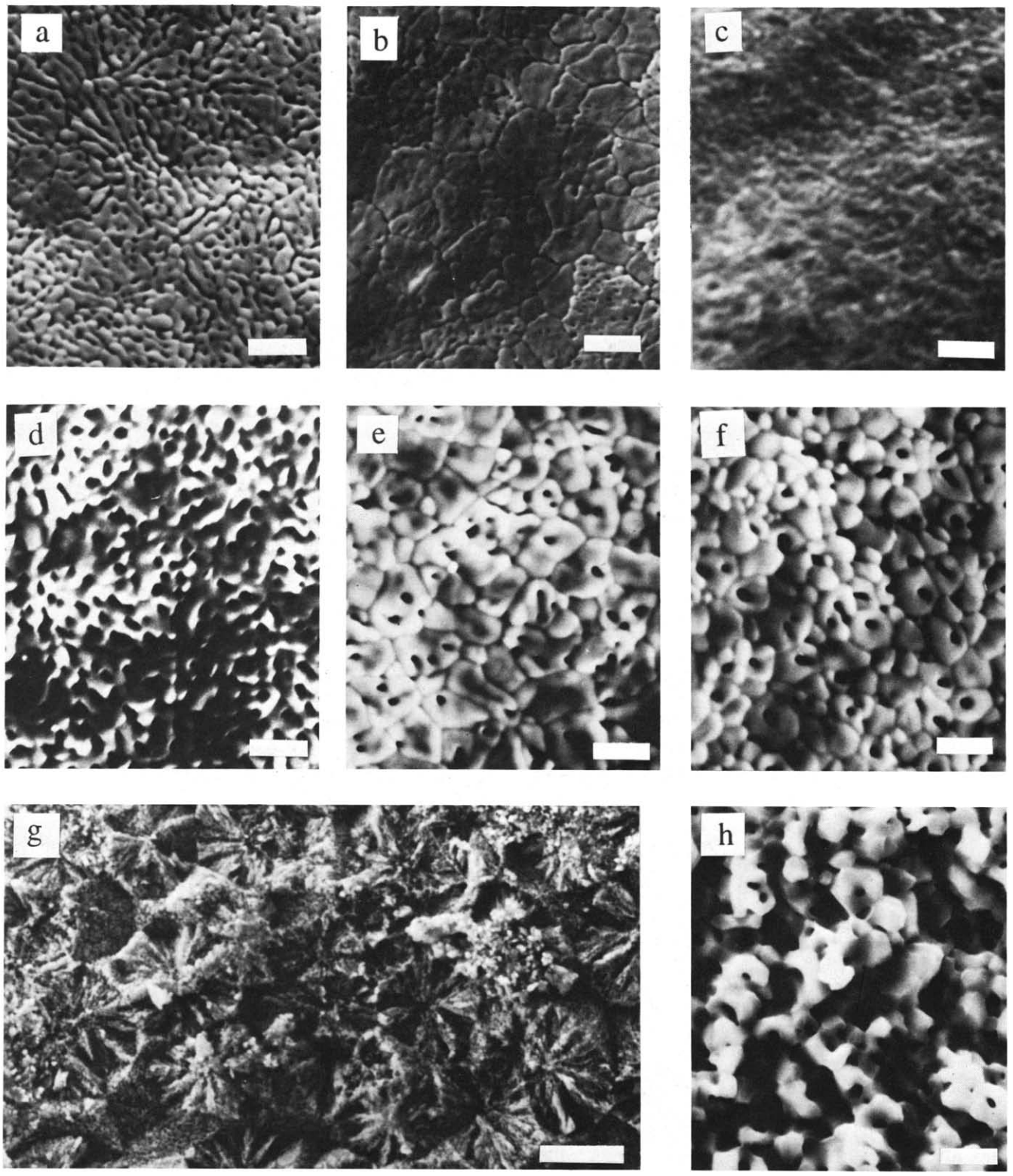

Fig. 3. SEM fractograms of unseeded gels isostatically pressed at 1500 MPa, sintered for 30 min or 3 h at 1350°C (bar = 5 μm). Pressure densification: (g) $\Delta V/V_0 = 0$ (without pressure treatment); (a), (d) $\Delta V/V_0 = 10{\cdot}2\%$; (b), (e) $\Delta V/V_0 = 35{\cdot}2\%$; (c), (f), (h) $\Delta V/V_0 = 38{\cdot}3\%$. Sintering time: (a)–(c) 30 min; (d)–(h) 3 h. Fracture surface created: (a)–(f) prior to sintering; (g), (h) after sintering (fresh fracture).

same conditions (area, size, magnification). The number of crystals in the sample untreated by pressure was obtained from the fresh fracture surface after sintering.

Although sintering time at a temperature of 1350°C affects the size and distribution of pores (Fig. 3(a)–(f)) the identity of crystals is basically retained. The identity of α-Al_2O_3 crystals is evident after sintering for 30 min and 3 h from Fig. 3(b) (30 min) and Fig. 3(e) (3 h). That means the number of nuclei equals the number of crystals. The size of crystals is similar, but the size of pores increases with time. Within the sintering time used, processes inside the crystals are dominant and not those between the crystals.

As is obvious from Fig. 3(a)–(c), pore size

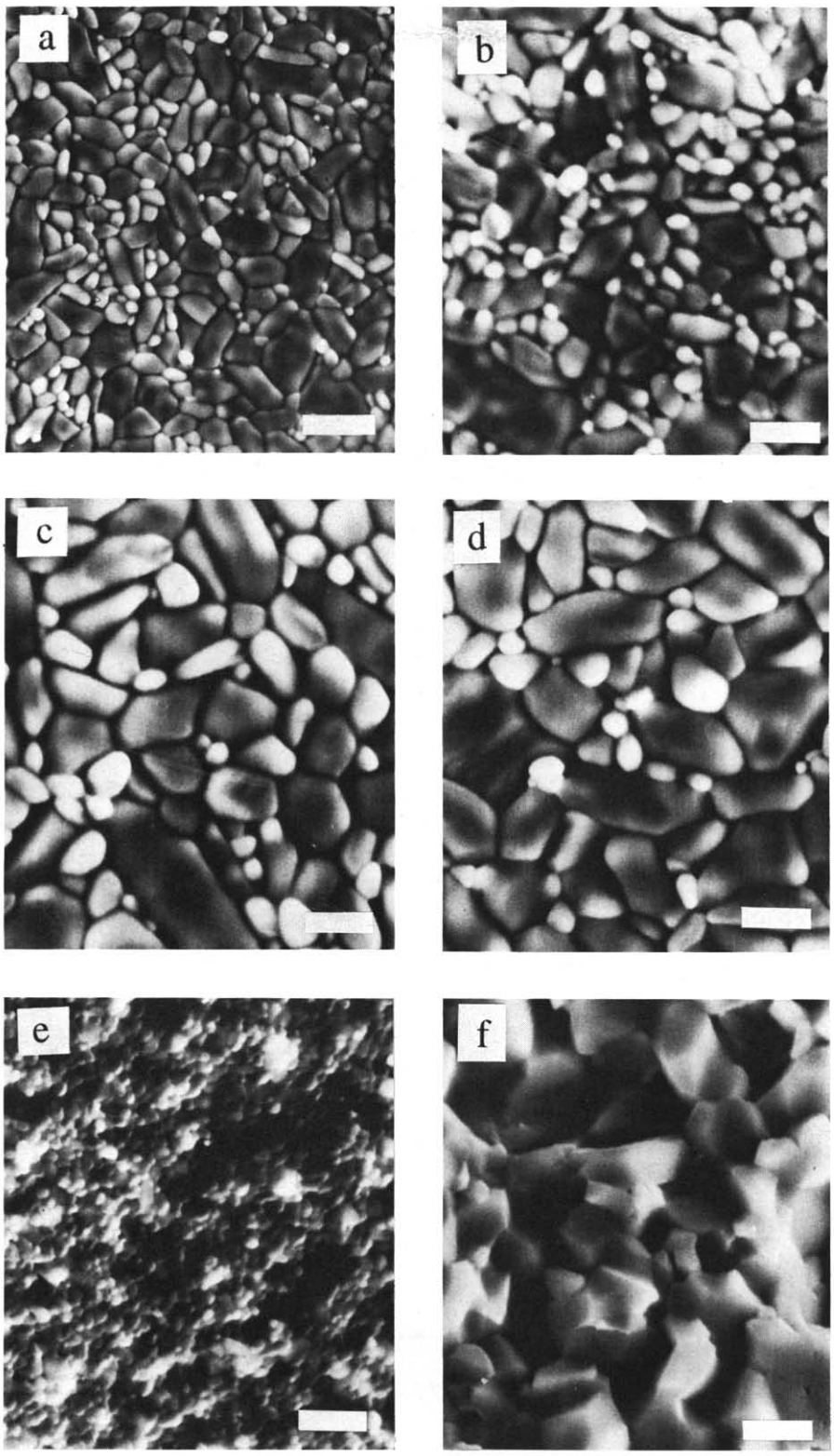

Fig. 4. SEM fractograms of seeded gels isostatically pressed at 1500 MPa and sintered for 30 min or 3 h at 1500°C, (bar = 5 μm). Pressure densification: (a) $\Delta V/V_0 = 0$ (without pressure treatment; (b) $\Delta V/V_0 = 8{\cdot}8\%$; (c) $\Delta V/V_0 = 34{\cdot}9\%$; (d)–(f) $\Delta V/V_0 = 37{\cdot}0\%$. Sintering time: (e) 30 min; (a)–(d), (f) 3 h. Fracture surfaces created: (a)–(e) prior to sintering; (f) after sintering.

considerably decreases with the increase in value of $\Delta V/V_0$ (degree of pressure densification) of a gel sintered for a short time (30 min). Prolongation of sintering time results in the movement of pores into a crystal (Fig. 3(e) and (f)). Pores are observably linked in unpressed gels ($\Delta V/V_0 = 0$, Fig. 3(g)) and in partially densified ($\Delta V/V_0 \approx 10\%$) ones (Fig. 3(a) and (d)). Gels densified by about 35% show from one to several isolated pores per crystal (Fig. 3(e)). The most densified gels ($\sim 38\%$) mostly contain only a single pore (Fig. 3(f)). Size of the pores is $-0{\cdot}5\,\mu$m. Individual pores are easily observable, even on surfaces formed after sintering (Fig. 3(h)).

The increase in the number of α-Al_2O_3 crystals,

depending on the densification of gels, correlates with the decrease in t_{max} of the α-Al_2O_3 crystallization DTA peak.

The number of crystals in seeded gels drops with a rise in densification (paradoxically in comparison to the unseeded gel), as can be seen from fractograms of gels sintered for 3 h at 1350°C (Fig. 4(a) and (d)). The number of crystals does not correlate with the temperature t_{max} of α-Al_2O_3 crystallization DTA peaks. However, a comparison of fractograms obtained for sintering time of 30 min (Fig. 4(e)) and 3 h (Fig. 4(d)) evidently shows that in a stage of the evolution of α-Al_2O_3 crystallization heat, there is approximately a hundred times more crystals in the system (e.g. 30 min at 1350°C) than after a 3 h sintering at 1350°C. The finding leads to the conclusion that t_{max} can be correlated with a number of crystals only in the case of short-term sintering. Thus, within a sintering time of 30 min–3 h, in seeded gels, the identity of α-Al_2O_3 crystals is not retained, in contrast to what was observed in unseeded gels.

4 Discussion

4.1 Unseeded gels

As a consequence of high pressure densification of boehmite gels prior to sintering, and their subsequent thermal treatment at 1350°C, some interesting phenomena have been found:

(1) The identity of α-Al_2O_3 crystals is retained during sintering (up to 3 h) at a temperature of 1350°C (Fig. 3(b), (e) and (f)).

(2) In a short-term sintering (30 min, 1350°C) pore size decreases with the rise in values $\Delta V/V_0$ of gels (Fig. 3(a)–(c)).

(3) In a long sintering time (3 h at 1350°C) and at the highest pressure densification, porosity is located (shifted) at the centre of crystal, where a spherical pore with diameter of about $\sim 0{\cdot}5\,\mu m$ is formed (Fig. 3(f)).

All individual α-Al_2O_3 crystals were grown from one homogeneously formed α-Al_2O_3 nucleus somewhere in the middle of the crystal (e.g. Fig. 3(d)–(h)), where the coordination of (γ, δ, θ)-Al_2O_3 particles is highest[10] (potential nucleation site). These large porous α-Al_2O_3 crystals are known as single-crystal colonies.[10,17–19] Easily observable single-crystal colonies can be seen in the fractogram (Fig. 3(g)).

The size of single-crystal colonies depends on the degree of pressure densification (Fig. 3(g), (e) and (f)). There is a higher number of potential nucleation sites (a higher coordination of particles) at a higher densification degree and therefore the area belonging to α-Al_2O_3 nucleus (Fig. 5) is smaller and hence the space surrounding this site (nucleus) has a higher

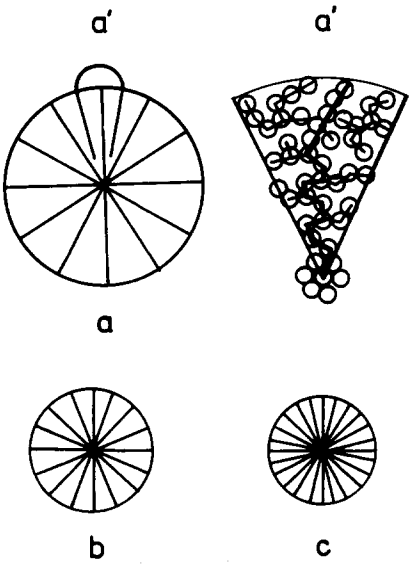

Fig. 5. Scheme of (γ,δ,θ)-Al_2O_3 particles cross-linked around homogeneously formed α-Al_2O_3 nucleus in dependence on increasing pressure densification ($a < b < c$).

average coordination number of alumina particles. The area with a higher coordination number can be regarded as cross-linking of alumina particles at a higher degree, and simultaneously as a higher amount of direct contacts of nuclei with the margin.

Consider a newly formed nucleus of α-Al_2O_3 and an area of $(\gamma, \delta\,\theta)$-Al_2O_3 particles around it (Fig. 5). The α-Al_2O_3 nucleus-crystal grows centrifugally in every direction in the form of single-crystal colonies (Fig. 3(g), (e) and (f)). Sintering of the material continues simultaneously, but in front of the crystallization zone is faster (defect Al_2O_3 phases) than after the zone (stable phase, α-Al_2O_3, even single crystal). The crystallization zone spreads until it comes in collision with similar crystallization zones of neighbouring α-Al_2O_3 nuclei. Crystallization is finished when all crystallization zones are in contact. In that moment the density gradient must exist between the margin (higher density) and centre (lower density) of the crystal. Further sintering leads to the coalescence of pores in direction of lower density, in this case (at the highest pressure densification of gel) in the centre of the crystal (Fig. 3(f)). Pores are not really entrapped, but they are pushed by the density gradient into the centre of the crystal. This observed coalescence of pores has some new features.

According to the recent understanding of pore coalescence (growth) only those pores can grow which are appreciably greater (up to one order of magnitude) than the diameter of primary particles.[20] In the present case this condition is not fulfilled (original pore size ~ 2 nm, particles ~ 10 nm).

4.2 Seeded gels

Nucleation of α-Al_2O_3 in seeded gel cannot be quantitatively evaluated from SEM fractograms

(Fig. 4), because the growth of crystals is rapid. When sintering time at 1350°C increased from 30 min (Fig. 4(e)) to 3 h (Fig. 4(d) and (f)) the number of crystals decreased ~100 times (Table 3). So, the identity of the nucleus-crystal is not preserved in contrast to what was observed in unseeded gels. Correlation of the DTA results (Table 2, decrease of t_{max} means an increase in the number of nuclei) with the microstructures (Fig. 4(a)–(d) and (f)) of sintered gels follows the logical tendency, that a larger number of nuclei leads to a smaller number of crystals, if the crystals growth is fast (Fig. 4(a) unpressed, and (d)–(f) pressed).

From the DTA of gels (Table 1, Fig. 2) it follows explicitly that α-Al_2O_3 nucleation in pressed gels is more intensive than in unpressed ones. These results support the concept that the transformation of (γ, δ, θ)-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ is not an ordinary growth of α-Al_2O_3 seeds, but it is enhanced by epitaxial nucleation[19] or multiple nucleation[2] of α-Al_2O_3 on the surface of seeds. Multiple nucleation in fact means that the number of the nuclei formed is much larger than the number of introduced α-Al_2O_3 seed crystals.

Multiple nucleation is a kind of heterogeneous nucleation of α-Al_2O_3 at the contact of (γ, δ, θ)-Al_2O_3 particles with the surface of the seed crystal. It is logical to assume that in pressed gels, the number of these contacts (Fig. 6) is larger and therefore nucleation is more intensive than in unpressed gels.

A newly developing crystal of α-Al_2O_3 acts as the new site of further heterogeneous nucleation. The probability of a new crystal continuing to grow or of another crystal forming on its surface depends on the character and on the orientation of the contact.

5 Conclusions

The intensity of α-Al_2O_3 nucleation, in seeded as well as unseeded monolithic boehmite-derived alumina gels, increased depending on pressure densification (1000, 1500 MPa) applied prior to sintering.

Different mechanisms of α-Al_2O_3 nucleation lead in unseeded gel to highly porous and in seeded gel to highly dense sintered material. Pores in gel-derived materials are inside the α-Al_2O_3 crystals (single-crystal colonies). At the highest pressure densification of gels used, pores are coalesced in a single pore (~0·5 mm) located in the centre of the crystal, which presents an unusual microstructural feature.

Nucleation of α-Al_2O_3 in seeded gels is heterogeneous and takes place on the contact surface of the (γ, δ, θ)-Al_2O_3 particles with an α-Al_2O_3 seed.

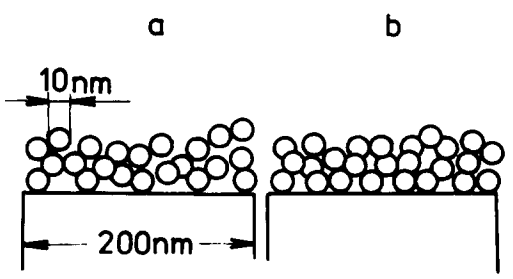

Fig. 6. Scheme of contact of a seed (200 nm) with defect (γ, δ, θ)-Al_2O_3 particles (10 nm); a, gel densified to a lower degree; b, gel densified to a higher degree.

References

1. Roy, R., Ceramics by the solution–sol–gel route. *Science*, **238** (1987) 1644–69.
2. Shelleman, A., Messing, G. L. & Kumagai, M., Alpha-alumina transformation in seeded boehmite gels. *J. Non-Cryst. Solids*, **82**(7) (1986) 277–85.
3. Colomban, Ph., Gel technology in ceramics, glass–ceramics and ceramic–ceramic composites. *Ceramics Int.*, **15** (1989) 23–50.
4. Lim, B. C. & Jang, H. M., Crystallization kinetics and phase transformation characteristics in seeded monophasic cordierite gel. *J. Mater. Res.*, **6** (1991) 2427–33.
5. Brinker, C. J. & Scherer, G. W., *Sol–Gel Science*. Academic Press, Inc., Boston, 1990, Chapter 11, pp. 730–42.
6. Aksay, I. A. Shih, W. Y. & Sarikaya, M., In *Ultrastructure Processing of Ceramics, Glasses and Composites. Proc. 3rd Int. Conf.*, ed. J. D. MacKenzie & D. R. Ulrich. John Wiley & Son, NY, 1988, pp. 393–406.
7. Agrawal, D. C., Raj, R. & Cohen, C., Nucleation of flocs in dilute colloidal suspensions. *J. Am. Ceram. Soc.*, **72**(11) (1989) 2148–53.
8. Hench, L. L. & West, J. K., The sol–gel process. *Chem. Rev.*, **90** (1990) 33–72.
9. Pach, L., Svetík, Š. & Kozánková, J., The sintering of boehmite gel. *Silikáty*, **33**(3) (1989) 193–202.
10. Pach, L., Roy, R. & Komarneni, S., Nucleation of alpha-alumina in boehmite gel. *J. Mat. Res.*, **5**(2) (1990) 278–85.
11. Roy, R., Suwa, Y. & Komarneni, S., Nucleation and epitaxial growth in diphasic (crystalline + amorphous) gels. In *Science of Ceramic Chemical Processing*, ed. L. L. Hench & D. R. Ulrich. J. Wiley, NY, 1986, Chapter 27, pp. 247–58.
12. Kumagai, M. & Messing, G. L., Enhanced densification of boehmite sol–gels by alpha-alumina seeding. *J. Am. Ceram. Soc.*, **67** (1984) C230–C231.
13. Suwa, Y., Komarneni, S. & Roy, R., Solid-state epitaxy demonstrated by thermal reactions of structurally diphasic xerogels: the system Al_2O_3. *J. Mat. Sci. Lett.*, **5** (1986) 21–4.
14. Dislich, H., Darstellung von Mehrkomponentgläsern ohne Durchlaufen der Schmelzphase. *Glastechn. Ber.*, **44**(1) (1971) 1–8.
15. Marotta, A., Buri, A. & Branda, F., Nucleation in glass and differential thermal analysis. *J. Mater. Sci.*, **16** (1981) 341–4.
16. Weinberg, M. C., Interpretation of DTA experiments used for crystal nucleation role determinations. *J. Am. Ceram. Soc.*, **74**(8) (1991) 1905–9.
17. Dynys, F. W. & Halloran, J. W., Alpha-alumina formation in alum-derived gamma-alumina. *J. Am. Ceram. Soc.*, **65** (1982) 442–8.
18. Dynys, F. W. & Halloran, J. W., In *Ultrastructure Processing in Ceramics, Glasses and Composites*, ed. L. L. Hench & D. R. Ulrich. J. Wiley, NY, 1984, Chapter 11, pp. 142–51.
19. Yarbrough, W. A. & Roy, R., Microstructural evolution in sintering of AlOOH gels. *J. Mater. Res.*, **2** (1987) 494–515.
20. Zheng, J. & Reed, J. S., The different roles of forming and sintering on densification of powder compacts. *Am. Ceram. Soc. Bull.*, **71** (1992) 1410–16.