

Sintering and crystallization of mullite in diphasic gels

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Diphasic monolithic mullite gel of stoichiometric composition shows a multiple aggregation of colloidal SiO_2 (~ 12 nm) and AlOOH (~ 10 nm) particles. The identity of the colloidal particles is retained up to the crystallization of mullite at a temperature of 1240°C in unpressed or 1220°C in gels cold-isostatically pressed at 1.5 GPa. Intensive sintering is closely followed by crystallization of mullite. Both sintering and crystallization are apparently related with the formation of a silica continuum. Nucleation of mullite appears to occur at points of contact (interface) of $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ particles.

1. Introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is a potential ceramic material for high-temperature structural applications principally because it retains, for the most part, its room-temperature strength to 1500°C and displays very high creep and thermal-shock resistance [1]. The recent resurgence in sol-gel chemistry has renewed interest in this ceramic material as well.

The ceramic, which is the final product of the sol-gel process, is a polycrystalline material. The sol-gel precursor is mostly, however, amorphous or semi-crystalline and the crystallization or recrystallization process is therefore the key-point in achieving very good mechanical properties [2]. The crystallization of mullite at high temperature depends upon the arrangement of both SiO_2 and Al_2O_3 components in the system. Mullitization of monophasic gels (atomic-scale arrangement of Al–O–Si groupings) occurs at $\sim 980^\circ\text{C}$ [3–7] due to a very intimate mixing of aluminium and silicon. There is a general agreement that the crystallization of mullite occurs by a nucleation-controlled process [8, 9]. On the other hand, the crystallization of mullite in diphasic gels is not yet fully understood and there are some differences in the interpretation of the experimental results [3, 10–13]. The main problem is represented by two different points of view as follows.

1. According to Wei and Halloran [11, 12], nucleation of mullite in diphasic gels occurs at the $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ interface and mullite is formed by direct solid-state reaction between amorphous silica and $\delta\text{-Al}_2\text{O}_3$. Such nucleation can be regarded as heterogeneous. The transformation is preceded by a temperature-dependent incubation period. Following this period, nucleation occurs in a very short time, producing about 1.8×10^{11} nuclei/cm³. New nucleation

sites are not formed, only the original ones are saturated. Therefore, nucleation density remains constant throughout the rest of the transformation. Wei and Halloran [11, 12] concluded that this transformation is probably controlled by a near-interface diffusion process or by the interfacial reaction itself.

2. On the other hand, Sundaresan and Aksay [3] concluded that the constant nucleation density is a result of the homogeneous nucleation of mullite in the forming of alumino-silicate phase. The alumina particles dissolve into the amorphous silica. When the concentration of alumina exceeds the critical nucleation concentration, mullite nuclei form. This concentration is exceeded only once, therefore the nucleation density remains constant in the system. The growth rate of mullite grains is controlled by the dissolution of $\delta\text{-Al}_2\text{O}_3$ into the amorphous matrix.

The aim of this work was to investigate mullite nucleation in diphasic gels, based on correlation of sintering and crystallization of monolithic mullite gels, using unpressed and cold-isostatically pressed samples.

2. Experimental procedure

Monolithic diphasic gels with the mullite stoichiometry $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ were prepared from commercial boehmite (Condea, ~ 10 nm particle size) and silica sol (Tosil, 30 wt % SiO_2 , pH ≈ 9 , particle size ~ 12 nm, stabilized by NH_3). An aqueous boehmite dispersion (18 wt %) was peptized by mixing it with HNO_3 (pH ≈ 2), at 55°C . The boehmite sol was intensively mixed as the silica sol was slowly added. The mixed sol was gelled within 1 h in a pan on a hot plate at about 80°C . The nearly transparent mullite gels were extruded to rods ($d \approx 0.5$ cm, $l \approx 5$ cm). The

monolithic gel rods were allowed to dry in air in a vertical position in order to retain their circular cross-section and shape. Dried gel rods were thermally treated at 150, 550 and 850 °C and then each gel rod ($d \approx 0.35$ cm, $l \approx 4$ cm) was separately encapsulated and cold-isostatically pressed at 1.5 GPa. The gels, both unpressed and pressed, were isothermally sintered at temperatures up to 1500 °C using a heating rate of 10 °C min⁻¹.

Shrinkage of gel rods was measured during sintering using a Netzsch 402-E dilatometer at a heating rate of 10 °C min⁻¹. The crystallization of mullite was detected by X-ray phase analysis (Dron 2.0, CuK_α radiation) and by differential thermal analysis (DTA) using a Netzsch 404 apparatus. Bulk density was determined according to Archimedes' method. The samples were hydrophobized with melted paraffin before measurement of the volume. For calculation of relative densities, the ρ/ρ_0 , of gels, the theoretical density of stoichiometric amorphous mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) = 3.08 g cm⁻³ was used. It was calculated based on the density of $\delta\text{-Al}_2\text{O}_3$ (3.65 g cm⁻³) [14] and SiO₂ glass (2.20 g cm⁻³). The microstructure of sintered samples was examined by SEM (JSM 840, Jeol). Some sample surfaces before SEM observation were chemically etched with 24% HF (5 min polished or 20 s fractured). The size and the number of mullite crystals were evaluated semiquantitatively by counting on the fracture surfaces after sintering. The specific surface area and the pore size were determined by BET adsorption using Carlo Erba (Sorpomatic 1900) equipment.

3. Results

3.1. Phase composition

An unpressed monolithic diphasic mullite gel showed a DTA exothermic crystallization peak of mullite at 1325 ± 5 °C in agreement with previous studies [10,15]. This peak is shifted to lower temperature (1300 ± 5 °C) in the pressed gel specimens (1.5 GPa). By isothermal annealing, as expected, mullite crystallization was detected by X-ray diffraction (XRD) at lower temperatures than by the dynamic heating of DTA. Narrow mullite crystallization temperature ranges of 1220–1240 °C for unpressed and 1180–1220 °C for pressed gels were found by XRD after 4 h annealing at these temperatures. Mullite was not detected by XRD after annealing at 1220 and 1180 °C of unpressed and pressed samples, respectively. However, the well-known topotactic transformations of boehmite to δ and $\theta\text{-Al}_2\text{O}_3$ [14, 16] were found by XRD. Formation of mullite was clearly evident after annealing at 1240 and 1220 °C in unpressed and pressed gels, respectively (Table I).

Isothermal heat treatment for 4 h of unpressed and pressed gels up to 1220 and 1180 °C, respectively, had no effect on studied properties such as the temperature of the DTA peak and number and size of mullite grains after sintering at 1500 °C. Under the experimental conditions used, nucleation of mullite seems to be improbable below temperatures of 1220 and 1180 °C for unpressed and pressed samples, respectively.

3.2. Sintering and microstructure

Sintering of gels observed by dilatometry shows significant changes at very narrow temperature ranges of 1220–1240 °C for unpressed (Fig. 1) and 1200–1220 °C for pressed gels (Fig. 2). The unpressed and pressed gels sinter intensively at 1240 and 1220 °C,

TABLE I Bulk density, ρ , relative density, ρ/ρ_0 ($\rho_0 = 3.08$ g cm⁻³)^a and phase-composition ($\delta, \theta\text{-Al}_2\text{O}_3, \text{M}$ - mullite) dependence on time, τ , and temperature, t , of annealing for unpressed and pressed (1.5 GPa) mullite gels

t (°C)	τ (min)	P (GPa)	ρ (g cm ⁻³)	ρ/ρ_0 (%)	Phase
1220	300D ^b	–	2.95	95.8	δ, θ
1240	30D	–	3.05	99.0	M (δ, θ)
1280	240	–	3.07	~ 100.0	M
1180	300D	1.5	2.93	95.1	δ, θ
1200	250D	1.5	3.05	99.0	δ, θ (M)
1220	60D	1.5	3.09	~ 100.0	M

^a $\rho_0 = 3.08$ g cm⁻³ is based on $\delta\text{-Al}_2\text{O}_3$ (3.65) + SiO₂ (2.20) (see text).

^b D, after dilatometric measurements.

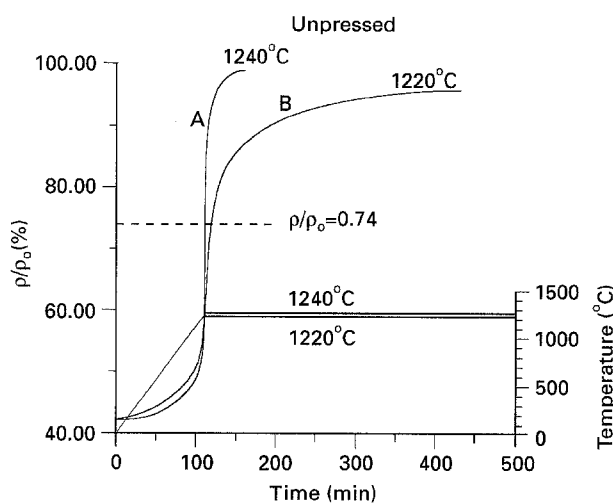


Figure 1 Plots of relative density, measured by dilatometry, and bulk density versus time of isothermal annealing for calcined and unpressed mullite gels.

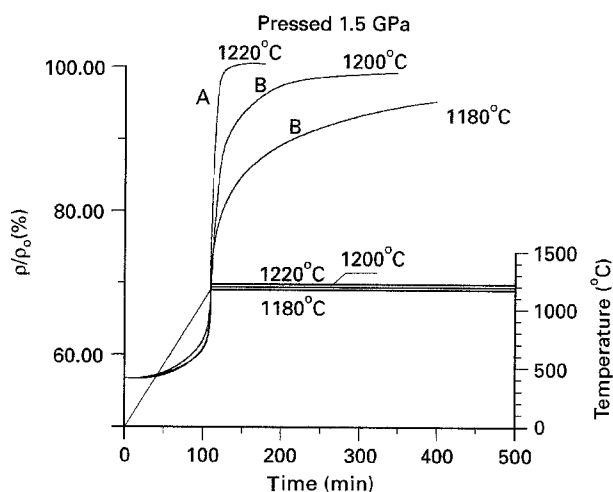


Figure 2 Plots of relative density, measured by dilatometry, and bulk density versus time of isothermal annealing for calcined mullite gels pressed at 1.5 GPa.

respectively, resulting in nearly full density in a few minutes. Their sintering curves are steep and in Figs 1 and 2 these are labelled type "A". For later discussion it is very important to note that crystalline mullite is always present in samples having sintering curves "A" (Table I, Figs 1 and 2). Unlike curves "A", curves labelled "B" show much slower sintering of gels, i.e. even after sintering for 7 h at 1220 °C. These "B" samples do not show any mullite (Table I). The unpressed sample (Fig. 1) shows a relative density of only about 96%.

Initial bulk densities of pressed gels are higher (Table II, Figs 1 and 2) than those of unpressed ones and densities increase with calcination temperatures of pressed gels (Table II). The density of dried (150 °C) gels is probably more influenced (is lower) by water-vapour adsorption during the preparation of samples than those calcined at higher temperatures of 550 or 800 °C.

The aim of the microstructure observation of samples sintered at about the temperature of transformation of gel to mullite was to judge the process of nucleation. The scanning electron micrographs

TABLE II Effect of calcination temperature, t_c , of mullite gels on density after cold-isostatically pressing at 1.5 GPa

t_c (°C)	ρ (g cm ⁻³)	ρ/ρ_0 (%)
^a	1.30	42.2
150	1.56	50.6
550	1.74	56.5
800	1.75	56.8

^a Unpressed sample.

(Fig. 3) show the development of the mullite phase from the stage before crystallization of mullite (Fig. 3a, b), through primary crystallization (Fig. 3c) to the stage of relatively large mullite grains (Fig. 3d). Before crystallization at 1220 °C, there are distinguishable individual primary colloidal particles (Fig. 3a). There is also visible multiple aggregation of colloidal particles (denoted by arrows) as described by Zarzycki [17].

The first-order aggregates (the size of 50–150 nm) are observable without doubt. The second-order aggregates of ~500 nm size are more or less clear. One of them is marked (Fig. 3a, see arrows). The individual colloidal particles are more visible after etching (20 s) of the surface with 24% HF (Fig. 3b). Outlines of the first-order aggregates can also be distinguished on this micrograph. Fig. 3c shows the cut, polished and etched (5 min, 24% HF) surface of fully crystallized sample at low temperature (4 h, 1280 °C). The size of the mullite crystals (Fig. 3c) is not very different from the original size of silica (~12 nm) and alumina (~10 nm) particles. Therefore, it appears that a large number of small mullite crystals were formed. Each point of contact of silica and alumina particles can be a potential site for mullite nucleation. Fig. 3c suggests a high mullite nucleation density compared to Fig. 3d which shows a calculated mullite crystal number density of 4.6×10^{11} cm⁻³ after 2 h sintering at 1500 °C. These numbers were calculated from the SEM observation of the surface (Fig. 3d).

4. Discussion

The enhanced densification of diphasic mullite gels to almost theoretical density before crystallization is

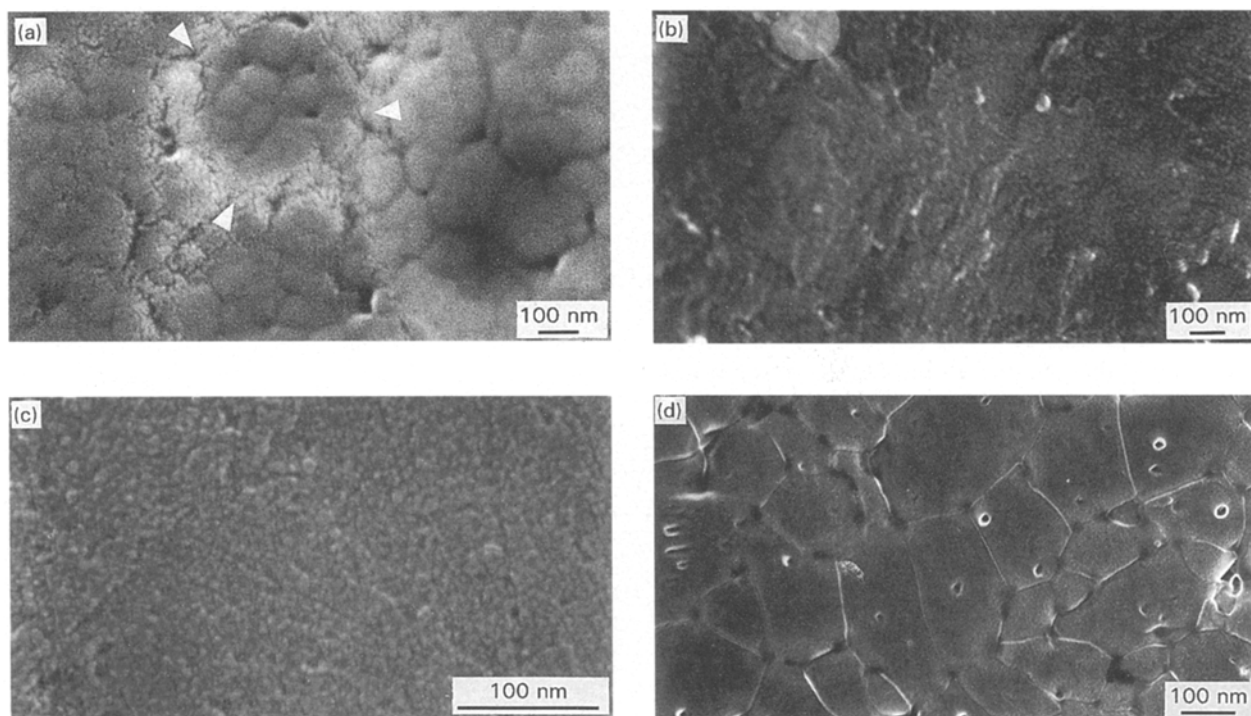


Figure 3 Scanning electron micrographs of diphasic calcined and unpressed mullite gels (a, b) before and (c, d) after crystallization of mullite: (a) fracture surfaces annealed for 4 h at 1220 °C (mullite was not detected); (b) the same sample as in (a) but after etching for 20 s with 24% HF; (c) cut and polished surface of sample after 4 h treatment at 1280 °C (sample mullitized) and etching for 20 s with 24% HF; (d) cut and polished surface of sample after 2 h treatment at 1500 °C and etching for 5 min with 24% HF.

generally known [3, 11, 12, 15, 18, 19]. The fact that sinterability, crystallization, and microstructure are significantly changed in a narrow temperature range is, however, not emphasized in the literature. Figs 1 and 2 show that only 20 °C difference in temperature of isothermal annealing (1220/1240 °C) causes a change in the character of the dilatometric curves (A to B) in both pressed and unpressed gels. Besides temperature, the cold densification of gels is known to influence their sintering behaviour. Because the initial bulk densities of pressed gels are higher than those of the unpressed ones, the densification and crystallization processes take place at about 20–30 °C lower in the former. Sintering is quite intensive even before reaching isothermal annealing temperatures of 1180–1240 °C and gels quickly achieve density corresponding to the theoretical arrangement of spherical particles (a model situation $\rho/\rho_0 \approx 0.74$, Fig. 1). Up to the dashed line, a rearrangement of particles is a probable control mechanism of sintering, because pores are not entrapped, as is evident from final density (Table I) and microstructure (Fig. 3a–c). Further sintering of gels (above the dashed lines in Figs 1 and 2) is only possible by a viscous sintering mechanism when interfaces of $\text{SiO}_2/\text{Al}_2\text{O}_3$ increase at the expense of interfaces of SiO_2/gas and $\text{Al}_2\text{O}_3/\text{gas}$. Initial pores in gels (2 nm, as determined by BET) are smaller than the particles (10–12 nm) and they can neither grow [20] nor remain in the system, but they must be eliminated along the interfaces. From this consideration it follows that sintering even above the dashed line (Fig. 1) does not lead immediately to the formation of a continuum of silica phase (pores should be entrapped) but the initial identity of colloidal particles has been preserved. Viscous flow occurs within individual silica particles when only the shape is changing, as dictated by the energy of the $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ interface.

The interface of $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ increases (gas is squeezed out) as its energy decreases due to the elimination of the sum of both SiO_2/gas and $\delta\text{-Al}_2\text{O}_3/\text{gas}$ interface energies. The simultaneous process (both intensive sintering and crystallization) is enabled by increased mobility of ions in the $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ interface. The mobility of ions occurs along the interface (concentration gradient), where it causes a further decrease in Gibbs energy of the system by crystallization of mullite.

It is known that silica colloidal particles (e.g. Ludox) are precisely spherical [21, 22] and alumina particles are rather rod-like. In the temperature range used (1180–1240 °C), a viscous flow can be assumed only inside the silica particles, but not in alumina. Silica particles adapt their shape to the surrounding alumina particles, as is shown schematically and ideally in Fig. 4.

Gels having sintering curves labelled “B” (Figs 1 and 2) reflect the schematic model microstructure shown in Fig. 4b. The unpressed gel achieves only 96% theoretical density even after sintering for 7 h at 1220 °C, while at a 20 °C higher temperature, i.e. 1240 °C, nearly theoretical density is achieved in a few minutes (model of microstructure in Fig. 4c). This intensive sintering is simultaneously taking place with

the crystallization of mullite and also with loss of the identity of the original colloidal SiO_2 particles. The justification for using this model for sintering (Fig. 4) of mullite gels can be supported by our parallel study [23] on sintering of monosized (~ 390 nm) silica particles (Fig. 5). Originally, spherical particles (Fig. 5a) in coordination 6 (coordination of 4 in plane) are deformed to nearly a cubic shape (Fig. 5b) as a consequence of existing silica/silica (particles) interfaces. Sintering of a colloidal SiO_2 gel or compact does not lead immediately to the formation of a SiO_2 continuum (Si–O–Si bonds), but the identity of SiO_2 particles is preserved nearly up to the final sintering stage.

The present results support the thesis of Wei and Halloran [11, 12] and others [10–13, 18] that mullite nucleation occurs at the points of contact of $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ phases. Unlike the above mentioned authors [11, 12], we postulate that mullite nuclei are not formed exclusively by solid-state reaction but rather

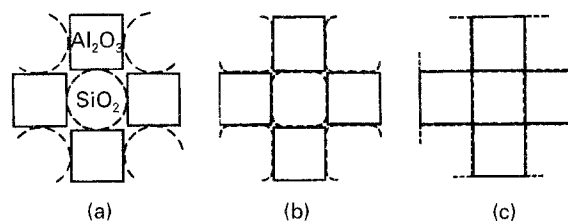


Figure 4 Model of the inside particle flow deformation of silica particles forced by the $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ (particles in the same plane) interface energy: (a) initial stage, (b) silica particle identity preserved during sintering, and (c) formation of silica continuum, the final stage of the pre-crystallization period.

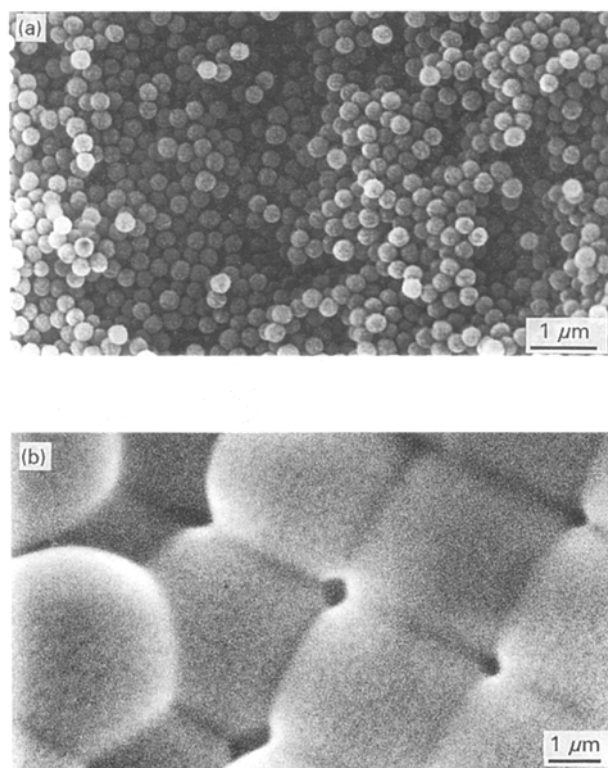


Figure 5 Scanning electron micrographs of colloidal SiO_2 particles (~ 390 nm): (a) dried at 40 °C, (b) the preserved identity of SiO_2 particles in co-ordination 6 (in plane with co-ordination of 4) after sintering for 4 h at 1100 °C.

by the reaction in which the mobility of ions plays a significant role at the $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ interface, which is consistent with the occurrence of SiO_2 continuum or an initial liquid phase. This statement agrees with observations of intensive sintering followed by crystallization (Figs 1 and 2, curves A), which cannot be caused by any other process than by the viscous flow of the formed silica continuum.

From the observed small size of the initially formed mullite crystals (Fig. 3c) one can postulate a very high nucleation density. If mullite crystals are formed epitaxially within colonies exhibiting single-crystalline nature rather than individually, as observed by Wei and Halloran [12], the nucleation density would be extremely low and may be approximately equal to the number of mullite grains obtained after sintering at 1500°C i.e. $4.6 \times 10^{11} \text{ cm}^{-3}$ (Fig. 3d). In this context it should be added that the gels used here consist of alumina and silica particles with a discrete size and shape unlike the materials used by Wei and Halloran [11, 12]. Their SiO_2 component, which is an acid-catalysed product of TEOS, is initially composed of linear or randomly branched species [24] which later transform into a continuum of an Si–O–Si network upon sintering. Such a diphasic gel can be regarded as a dispersion of $\delta\text{-Al}_2\text{O}_3$ particles in a porous SiO_2 continuum and in this case only one interface, i.e. $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$, exists between condensed phases. The diphasic system used in this study has an additional interface between individual silica particles ($\text{SiO}_2/\text{SiO}_2$).

The observed small size of mullite crystals and the apparent high nucleation density obtained either by individual nucleation or within single-crystal colonies, is different from that described by Sundaresan and Aksay [3]. Wang *et al.* [18] came to a similar conclusion studying the influence of water vapour on the reaction kinetics of mullite formation from sol–gel precursors.

5. Conclusion

Intensive sintering followed by crystallization of mullite (nearly theoretical density achieved in a few minutes) occurs in a narrow temperature range for diphasic gels. Both processes are dependent on losing the identity of SiO_2 particles and the formation of an SiO_2 continuum. These processes take place in unpressed gels at 1240°C and pressed (1.5 GPa) ones at 1220°C . If the annealing temperature of the gels is about 20°C lower, sintering and crystallization of mullite is significantly retarded and mullite crystals are not detectable even after 4 h annealing at 1220°C and

1180°C in the case of unpressed and pressed (1.5 GPa) gels, respectively.

Nucleation of mullite is postulated to occur at the points of contact of $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ particles and is initiated by the increased mobility of ions at this interface. The mullite nucleation density at temperatures of about 1280°C appears to be very high compared with the number of mullite grains ($\sim 5 \times 10^{11} \text{ cm}^{-3}$) after 2 h sintering at 1500°C .

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