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PREPARATION AND CHARACTERIZATION OF GELS OF SiO$_2$–Al$_2$O$_3$ COMPOSITION

MICHEL A. AEGERTER AND DOROTÉIA F. BOZANO

INTRODUCTION

Al$_2$O$_3$ and SiO$_2$ have widespread technical and industrial applications because of their refractoriness and chemical stability. SiO$_2$ is a basic product for the glass industry while Al$_2$O$_3$ is an important material for the preparation of, for example, electronic substrates, spark plugs, tools, and lamp envelopes. It is not surprising that mixed compounds of SiO$_2$–Al$_2$O$_3$ also present interesting properties, for instance, for catalytic substrates and dental porcelain frits.

The composition 3Al$_2$O$_3 \cdot$ 2SiO$_2$, known as mullite, is of particular interest. It is the only stable product in a reaction between Al$_2$O$_3$ and SiO$_2$ at high temperature and is now an important structural engineering ceramic for high-temperature applications due to its excellent chemical and thermal stability, high strength and creep resistance, and low thermal expansion and dielectric constant. Advances in the manufacture of high-purity material and control of the microstructure have also revealed its potential for optical and electronic uses.

A large number of studies of mullite formation involve its preparation by a high-temperature reaction using powders. The solid-state reaction depends upon the particle size, their crystalline form, the Al–Si ratio, and impurity

effects. As the thermal diffusivities are low, it may result in incomplete reactions, despite the high firing temperature, if Al$_2$O$_3$ and SiO$_2$ are not mixed at a molecular level. Chemical routes such as the sol–gel process look attractive for preparation of submicrometer-scale particles, and low processing temperatures are common. These processes should a priori allow a good control of the homogeneity [1].

Approaches to sol–gel mullite processing can be divided into three categories: polymeric, colloidal, and hybrid.

1. The polymeric route allows molecular-scale mixing through hydrolysis and polycondensation of mixed aluminum and silica salts or alkoxides [2–4]. The amorphous gels known also as single-phase gels crystallize rapidly into mullite with or without Si–Al spinel at around 980°C; the materials transform into pure, homogeneous mullite at $\approx$ 1150°C, but complete sintering is only obtained at very high temperature ($T \approx 1600$°C). As the diffusion path length is minimized (polymeric structure), the kinetics of mullite formation are not governed by a diffusion-controlled process but by a nucleation mechanism; the growth process is hindered by the particle boundary of the gel. The mullite formation activation energy was found to be 293–362 kJ/mol [5, 6].

2. The colloidal route [2, 7, 8] usually involves mixing of crystalline alumina phase [as, e.g., boehmite (γ-AlOOH) or γ-alumina] together with an amorphous colloidal or fumed silica phase. The resulting gel is known as a diphasic gel. Heterocoagulation results in homogeneous mixing of particles. Because of the size of the colloidal particles, the onset of crystallization is delayed to a higher temperature ($\approx$ 1250°C). Combined approaches where one colloidal component is mixed with the salt or the alkoxide of the other have also been used [2, 9, 10]. The kinetics of mullite formation at about 1200°C follows an Avrami-type, diffusion-controlled growth mechanism with the nucleation process essentially completed before substantial growth takes place. This formation has a high activation energy of 10^3 kJ/mol. The colloidal route allows the preparation of sintered mullite ceramics of high densities at relatively low temperatures ($T \approx 1400$°C).

3. The hybrid route is a relatively new process that consists of the preparation of a gel from a mixture of polymerically and colloidally derived sols [11, 12]. This process allows in situ mullite seed development by crystallization of the polymeric species within the colloidal gel. Mullite nucleates homoepitactically from the viscously densified colloidal gel. Transformation temperatures are not dramatically lowered by seeding, but the reduction of the grain size does result in improvement in the intergranular homogeneity of the sintered gels. High sintered densities and full microstructural homogeneity should be attained.

In this chapter we review the SiO$_2$–Al$_2$O$_3$ sol–gel processing with particular emphasis on mullite and show how precursors and molecular manipulation affect the properties of the gels, their thermal processing, and final products.

PREPARATION AND CHARACTERIZATION OF POLYMERIC (SINGLE-PHASE) GELS

Polymeric gels obtained from hydrolysis and condensation of alkoxides have been widely studied for SiO_2 [1]. The information about multicomponent systems and in particular SiO_2–Al_2O_3 is still limited. The phenomena are more complicated as the kinetics of the hydrolysis–condensation of each component may differ widely. For the $SiO_2 \cdot Al_2O_3$ composition, the hydrolysis rate of silicon alkoxide is much slower than that of aluminum alkoxide, and consequently, if these reactions are not controlled, precipitation or autocondensation of Al–OH groups will occur, introducing heterogeneities in the molecular structure of the gels. These heterogeneities can be completely eliminated if water is added in a controlled way. Several methods have been tested.

Processes involving the mixture of silicon and aluminum alkoxides in which the water of hydrolysis is added very slowly, usually utilizing the humidity of the air, have been developed by Yoldas [13], Pouxviel et al. [14, 15] and Bozano et al. [4].

Pouxviel et al. [14, 15] studied various precursors in order to reduce the discrepancies between the hydrolysis kinetics and obtain an intimate mixing of the Al and Si atoms by connecting them by bridging oxygens. The following reaction involves an alcoholic solution of tetraethoxysilane (TEOS) and $Al(OBu)_3$ with equal molar quantities maintained in an open container in an atmosphere of 50% relative humidity saturated in butanol. This sol is therefore slowly hydrolyzed and leads, in about 12 days, to an optically clear amorphous and monolithic gel.

The evolution of the polymerization was followed by ^{27}Al nuclear magnetic resonance (NMR), clearly showing that —Al—O—Si— bonds are effectively realized through the probable reaction

$$Al(OBu)_3 + Si(OR')_4 \xrightarrow{\text{H}_2\text{O}} \text{—Al—O—Si} \rightarrow \text{powder, gel} \qquad (16.1)$$
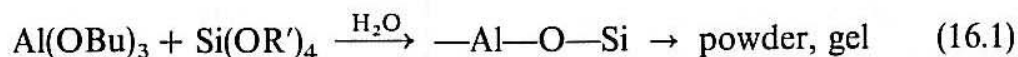
At $t/t_g = 0.5$ almost all silicate species have reacted with the Al(OH) groups so that each Si atom is connected to at least one Al atom through a bridging oxygen. The slow hydrolysis (SH) method is therefore effective to reduce the discrepancy between the reactivity of Al and Si alkoxides. The evolution of these gels under heat treatment and their transformation into a ceramic material have not been studied.

More recently Bozano et al. [4] followed a similar route for preparing stoichiometric mullite ($3Al_2O_3 \cdot 2SiO_2$). The sol was prepared by mixing vigorously isopropanol, TEOS, aluminum *sec*-butoxide, and acetylacetone at room temperature. The sol (pH 11) was maintained in an open container in an atmosphere saturated with isopropanol at a relative humidity of 74–80%. Clear amorphous and monolithic gels can be obtained in about 55 hr for molar ratios R = acetylacetone/Al alkoxide ≈ 5 and r = isopropanol/Al and Si alkoxides

≈ 0.25. Drying of the gels at 60°C reduces their volume by at least 90%. These gels have a Brunauer–Emmett–Teller (BET) surface area of about 575 m^2/g and a matrix density of about 2.8 g/cm^3. The pore size distribution is narrow with a mean radius of 20 Å. Scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM–EDX) indicates good homogeneity of Si and Al.

These gels have been heat treated in air up to 1550°C. Thermogravimetric and differential thermal analysis (DTA) show that a large reduction of weight occurs up to 500°C due to elimination of water (≈ 150°C) and organic products (300–500°C). The narrow and sharp exotherm at 980°C (Fig. 16.1) is typical of the polymeric nature of these gels [13]. X-ray diffraction data indicate that this narrow DTA exotherm corresponds to an amorphous–crystalline phase transformation. A careful analysis of the results show that the initial crystalline phase is a mixture of mullite and cubic Al–Si spinel. This last phase disappears at a slightly higher temperature such that at 1150°C the diffraction spectrum is already typical of an orthorhombic mullite. At higher temperatures the material progresses toward a better organized mullite and becomes fully organized and highly homogeneous for $T \geqslant 1450$°C.

Mullite has been sintered up to 1550°C; it was prepared from room temperature uniaxial or isostatic pressing of powders obtained by milling calcined gels. These materials do not have good thermal and mechanical properties and present large macroscopic pores, although their microscopic
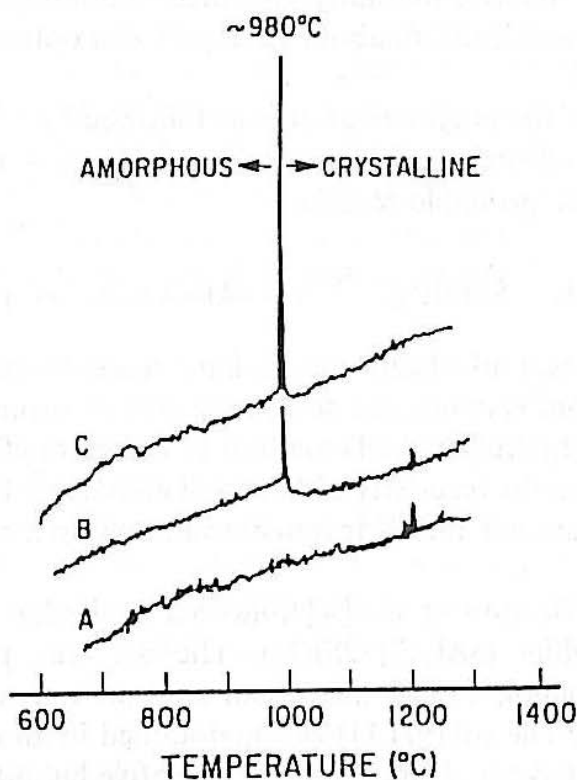

Figure 16.1. The DTA curves for single-phase (slow (C) and medium (B) hydrolysis) and diphasic gels (A) [3].

aspect is formed by small and homogeneously distributed grains of 0.15 μm mean diameter.

Transmission infrared measurements corroborate these results. The structural evolution is compatible with the model proposed recently by Low and McPherson [16].

Another method initially proposed by Yoldas [3] but also tested by Pouxviel et al. [14, 15] is to prehydrolyze a TEOS–ethanol mixture with 1 mol water/mol silicon in acid conditions (pH $\approx$ 2). When all the water has been consumed, aluminum butoxide is added, giving the following reaction:

$$Al(OBu)_3 + (OH)Si(OR)_3 \rightarrow -Al-O-Si- \rightarrow powder, gel \qquad (16.2)$$
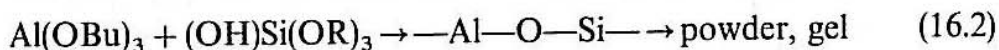
When the Al alkoxide is introduced, a white precipitate forms but this condensate dissolves rapidly at 60°C.

The NMR analyses show, however, that the TEOS prehydrolysis is not homogeneous and reveal the presence of monomers with zero, one, or two OH groups and that, in the final sol, silanols have condensed with [other silanol and $Al(OR)_3$ groups, leading to Si—O—Si— and Si—O—Al— bonding. The condensation ratio of the silicate species is however less than in a pure alcoholic TEOS–H_2O sol, indicating that the water liberated during the condensation has been preferentially consumed by the Al precursor and demonstrating that the $\equiv SiOH + Al(OR)_3$ reaction is possible but with a low yield.

Drying and calcination of this condensate having the mullite composition presents the characteristic strong exothermic peak at around 980°C related to the formation of crystalline mullite [3].

The preparation of polymeric gel using more economic precursors such as silicon alkoxide and aluminum nitrate has been tested by different authors [2, 5, 6, 17, 18, 19]. The sols are usually prepared by mixing TEOS and aluminum nitrate nonhydrate dissolved in absolute ethanol for 3 hr. The sol is allowed to gel very slowly in an oven at 60°C. Some authors also used $Al(NO_3)_3 \cdot 9H_2O$ using the water liberated from the dissolution for the hydrolysis reaction. Gelation is usually obtained in about two weeks; the products are transparent.

Usually acid solutions of aluminum salts maintained at this temperature precipitate with the formation of amorphous aluminum hydroxide. However, in the case of Al nitrate, the NO_3^{-1} ions have been shown to act as a peptizing agent for the precipitate such that a true aluminum sol can be made [20]. Therefore, a polymeric network can be formed between the aluminum and the silicon polymeric species. These gels crystallize at 980°C into mullite with a strong exothermic peak. The kinetics of the transformation of these single-phase gels have been studied by Li and Thomson [5, 6]. Isothermal X-ray measurements performed at 940 and 1160°C show that the average grain size of mullite stays constant (10 and 20 nm, respectively) although the conversion increases with time (Fig. 16.2). This is explained by a growth limitation of the boundary of the single-phase gel particles. Each particle is assumed to be a single crystal and the
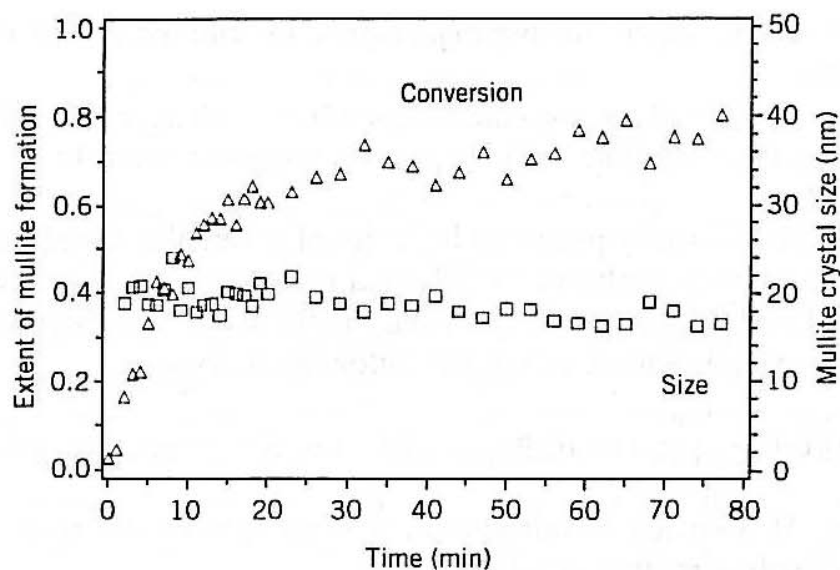
Figure 16.2. Average particle size and conversion of mullite in the single-phase gel (polymeric route) vs. time at 1160°C [5].

transformation is controlled by a nucleation process. The activation energy at the initial temperature is low (293–362 kJ/mol).

Pouxviel et al. [14, 15] have also tried the polymerization of a double alkoxide (OBu)$_2$Al—O—Si(OEt)$_3$. This silicon–aluminum ester was diluted in propanol before addition of a water–propanol mixture with HCl or NH$_3$ as catalyst. The preparation, kept in a sealed glass container, led to monolithic and optically clear gels in about 1 day:

$$(OR)_2Al-O-Si(OR')_3 \xrightarrow{H_2O} \text{Powder, gel} \qquad (16.3)$$
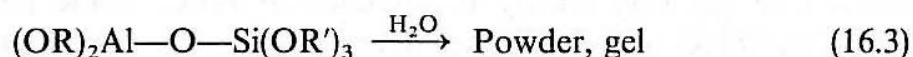
The polymerization was traced by ^{28}Si and ^{27}Al NMR and small-angle X-ray scattering (SAXS). It shows a progressive polymerization through Al—O—Al linkages with partial conversion of 4-coordinated Al to 6-coordinated Al and with the formation of a mass-fractal structure. The reactivity of —Si(OR)$_3$ was very weak compared to the Si(OR)$_4$ group; near the gel point only a few percent of the Si(OR)$_3$ groups had undergone hydrolysis and condensation. The inorganic polymerization results mainly from the formation of Al—O—Al bonds. This is probably due to the rapid hydrolysis of —Al(OR)$_2$ groups, which make water less available, and to the amphoteric nature of Al—OH, which maintains the pH of the sol at about 7, where hydrolysis of Si—OR is known to be slow. Increasing the water content or modifying the catalytic conditions should improve the process.

PREPARATION AND CHARACTERIZATION OF COLLOIDAL (DIPHASIC) GEL

Colloidal or diphasic xerogels are gels consisting of separate discrete silica (or silica-rich) and alumina (or alumina-rich) "phases," each of them noncrystalline [2]. Their preparation has been widely studied using different techniques and precursors.

One of the techniques was developed by Yoldas [3, 13] and consists of preparing a colloidal sol of alumina from alkoxide (Fig. 16.3). When aluminum alkoxides $Al(OR)_3$ are mixed with water, they react vigorously, forming condensates that are crystalline above 80°C and amorphous below 80°C [2]:

$$Al(OR)_3 + 2H_2O \rightarrow AlO(OH) + 3ROH \qquad (16.4)$$
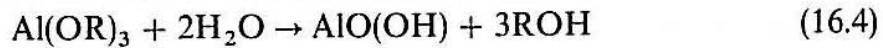
The crystalline phase (boehmite) is unaffected by aging. The amorphous phase is unstable and can be converted into a crystalline boehmite when heated above 80°C or into bayerite, $Al(OH)_3$, if kept below 80°C with water, with the formation of large triangular and rectangular crystals [21]. Both crystalline and amorphous forms of aluminum monohydroxide $AlO(OH)$ can be peptized to obtain clear aqueous alumina sols. The choice of the acid to be added to the slurry is critical as well as its temperature, which should be kept higher than 80°C. The acids must be noncomplexing, such as HCl or HNO_3, but organic acids such as acetic acid can also be used. The size and the shape of the final
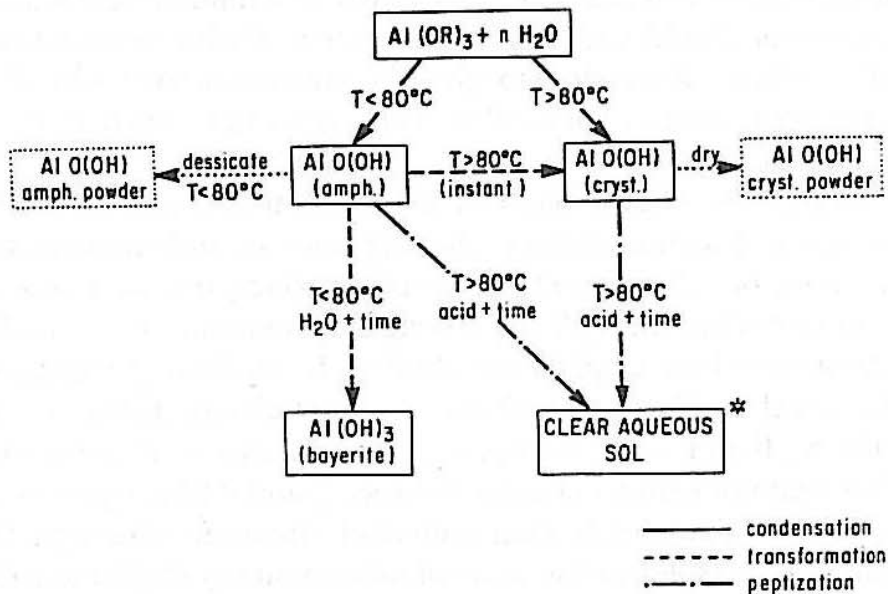
Figure 16.3. Schematic representation of the various structural transformations and peptization conditions for the condensates in the $Al(OR)_3-H_2O$ system [13].

colloidal particles depend on the type and amount of acid used for the peptization.

The preparation of a mullite sol is finally done by introducing a TEOS sol into the alumina colloidal sol prepared with a molar ratio of water–alkoxide of 100, at a hydrolysis temperature higher than 80°C and peptized with a molar ratio acid–monohydroxide of aluminum equal to 0.07. The homogenization of this mixture presents some difficulty. During the polymerization the hydroxyl groups of the AlO(OH) colloids react with Si(OR)$_4$, creating Si—O groups chemically bound to and between the particles:

$$\equiv\!Si\!-\!OR + HO\!-\!(AlO(OH)_{(n-1)/n})_n \longrightarrow$$

$$\equiv\!Si\!-\!O\!-\!(AlO(OH)_{(n-1)/n})_n + ROH \qquad (16.5)$$
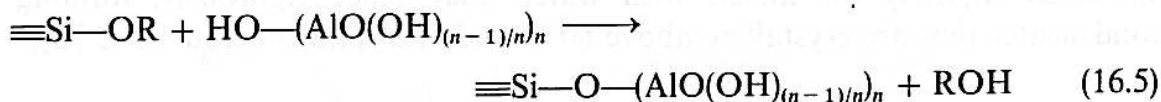
The gels obtained are transparent even after drying. Although the formation of chemical bonds occurs between Si and Al atoms, the homogeneity of the gels is limited because of the size of the colloidal particles (typically 10–30 nm) and by the fact that the boundary of the grains is rich in silica. Differential thermal analysis of these gels presents a totally different aspect (Fig. 16.1). The very sharp exothermic peak observed at 980°C for the polymeric gels is no longer present or is strongly reduced and is replaced by a broader and smaller structure around 1200–1400°C. The crystalline mullite produced by this process, by sintering at 1600°C, shows elongated crystals with considerable intergranular void spaces, in contrast to the case where the precursors are intimately mixed (polymeric route).

As the use of an aluminum alkoxide leads to the formation of boehmite particles, an alternative and cheaper technique is to begin with commercial γ-AlO(OH) dispersed powder. Li et al [5, 6] mixed, in a diluted HNO$_3$ solution, a suitable amount of TEOS with an equal volume of ethanol together with a commercial γ-AlOOH dispersion to give the stoichiometric ratio of mullite. Gelation takes place within 12 hr at 60°C. These gels can be dried at 60°C before being ground to powder for further experimentation.

The transformation of kaolinite (via metakaolinite) produces, at 980°C, a spinel phase with a structure similar to that of γ-alumina with an aluminosilicate chemical composition. This phase transforms completely into mullite at 1250°C. The synthesis of mullite through the mixing of γ-alumina and colloidal silica should therefore produce a spinel structure with the desired composition to promote the spinel–mullite composition. As the isoelectric point of γ-alumina and silica are ≈ 8.0 and ≈ 2.0, respectively, the particles of alumina and silica dispersed in a solution with a pH value between 2 and 9 have opposite charges and may heterocoagulate due to their mutual electrostatic attraction. Depending on the mixture, the solution has a semifluid consistency similar to a thick gel. Ghate et al. [22] slowly added a silica sol to a suspension of γ-alumina that was homogenized at pH ≈ 5. The sol pH was later increased to 6 to 7 by introducing NH$_4$OH in order to obtain a gel. The crystallization of these gels into mullite occurred around 1250°C, but higher temperatures (> 1400°C) and long heat treatments are necessary to obtain a complete transformation. It was suggested

that the mullite formation was due to diffusion and rearrangement of the structural spinel units.

The mixing of aluminum salt–Si alkoxides is the more widely used technique for the preparation of colloidal gels of Al_2O_3–SiO_2 composition. Most of the preparations have been done with $Al(NO_3)_3 \cdot 9H_2O$, but sulfates and chlorides have also been used. The classical methods are described in the works of Hoffman et al. [2] and Okada et al. [17]. The diphasic gels are prepared by the rapid addition of NH_4OH to a solution of $Al(NO_3)_3 \cdot 9H_2O$, TEOS, and absolute ethanol at room temperature. It is well known that aluminum solution can be precipitated by the rapid introduction of a base at room temperature leading to the formation of a gelatinous solid. This material, when maintained in the solution at a pH $\approx$ 10, transforms into bayerite, $Al(OH)_3$ [23, 24]. Moreover, the hydrolysis of TEOS in basic conditions gives rise to the formation of small particles of $Si(OH)_4$ [20, 24] that can attain relatively large diameters. Therefore, this method of preparation, also known as the rapid hydrolysis method, leads to the formation of a colloidal sol. The gelation is promoted by the dehydration of the sol, which promotes the bonding Al—O—Si. The gels are white and can be dried. The formation of mullite occurs around 1100°C and grows rapidly to 1150°C and more gradually up to 1600°C. Unfortunately, no measurements have been done that test the engineering properties of these mullites.

The kinetics of transformation of the diphasic gel have been studied by Wei and Halloran [25] and Li and Thomson [5, 6]. The reaction mechanism is completely different from that of polymeric gel. Fig. 16.4 (compare with Fig. 16.2) shows the time behavior of the mullite conversion and the average size of the mullite crystals. In the case of diphasic gel, mullite formation follows an Avrami-type, diffusion-controlled growth mechanism with the nucleation pro-
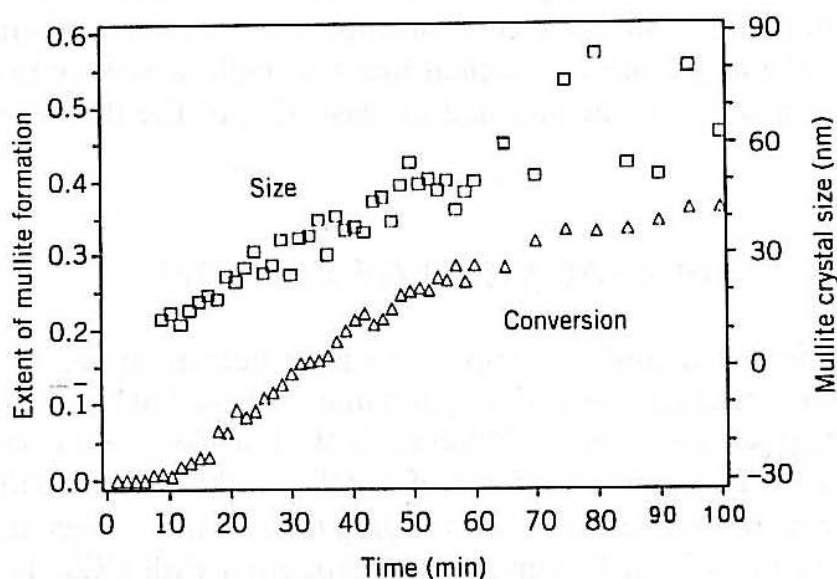

Figure 16.4. Average particle size and conversion of mullite in the diphasic gel (colloidal route) vs. sintering time at 1250°C [5].

cess essentially completed before substantial growth takes place. At the initial mullite formation, at about 1250°C, the activation energy is high (1028 kJ/mol).

PREPARATION AND CHARACTERIZATION OF HYBRID GEL

Hybrid gels are defined as gels obtained from mixtures of polymerically and colloidally derived sols. They offer many opportunities for crystalline microstructure development upon heating. Huling and Messing [11] prepared mullite gels by mixing a colloidal boehmite–silica sol with a polymeric aluminum nitrate–tetraethoxysilane derived sol. The polymeric gel crystallized in situ to form mullite, which acts as seed crystals for homoepitactic nucleation during the transformation of the colloidal gel. The introduction of polymeric gel increases the apparent nucleation frequency and leads to a sizable reduction in high-temperature (1550°C) grain size (1.4 down to 0.4 μm for a 30 wt% fraction). The microstructural homogeneity is improved, as shown by intragranular pore removal. This new technique allows more control of the process. Unfortunately, the physical properties of mullite were not reported.

An alternative method has been proposed by Mroz and Laughner [12]. They prepared mullite by firing colloidal aluminosilicate gels seeded with crystalline mullite. Pseudoboehmite and colloidal silica were peptized and gelled with dilute HNO$_3$. The mullite seeds were prepared from the same dried gel, milled in heptane, and then calcined for 2 h at 1600°C, yielding pure mullite. Powder was ball milled in acidic dispersion and then centrifuged to yield an agglomerate-free suspension of fine seed particles. The final sol was produced by introducing the seed suspension to a sample of precursor suspension before peptization and allowed to gel at room temperature. This procedure yields distinct changes in the final microstructure. At high seed concentration a dense equiaxial grain structure is obtained. A low seed concentration yields a bimodal distribution of grains where the large ones are acicular and the small ones equiaxed. All fired samples remained crack free and had at least 92% of the theoretical density (3.17 g/cm^3)

PREPARATION OF AEROGEL

Gels of stoichiometric mullite composition have been prepared by the rapid hydrolysis and gelation method of aluminum tri-*sec*-butoxide and TEOS, hydrolyzed with excess water (H$_2$O/butoxide 50:1) at 80°C and over, and then peptized by HCl. The required amount of TEOS was then added to the mixture. Gelation occurs in minutes. Instead of drying the gels in an oven, the authors, [26], removed the solvent by supercritical extraction with CO$_2$. This method prevents development of capillary stresses and avoids the large drying shrinkages observed with xerogels.

The aerogels had a very low density (<0.05 of theoretical density of mullite ρ_{th}) and experienced a shrinkage of up to 0.6 with a density of $\approx 0.5\,\rho_{th}$ after 1 hr sintering at 1350°C. However, mechanically compacted aerogels can be sintered to nearly theoretical density below 1200°C, a value higher than that obtained with similar gels dried conventionally. X-ray diffraction patterns were almost identical to mullite, but SEM–EDX analyses indicate two types of grain structure: elongated grains with an Al–Si atomic ratio of stoichiometric mullite surrounded by equiaxial grains with a lower Al–Si ratio.

CONCLUSIONS

We have reviewed the different sol–gel methods described in the literature to prepare gels of $Al_2O_3 \cdot SiO_2$ composition, giving special emphasis to the preparation of mullite, $3Al_2O_3 \cdot 2SiO_2$. This binary system is probably the only one where the many possibilities of the sol–gel route have been applied to improve the microstructure of the final products. At least four basic processes involving the preparation of aerogels, polymeric, colloidal, and hybrid xerogels, have been tested, each of them leading to different characteristics upon heating and different crystalline microstructures after complete sintering. Unfortunately, very few data exist on the engineering properties of these final products, and such important characterizations are definitely needed for future technologic applications.

ACKNOWLEDGMENTS

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