JOURNAL OF MATERIALS SCIENCE 23 (1988) 1895–1900

Formation of mullite and other alumina-based ceramics via hydrolytic polycondensation of alkoxides and resultant ultra- and micro-structural effects

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This manuscript discusses the formation of alumina-based ceramic materials from alkoxide starting materials. Particular attention is given to Al_2O_3–SiO_2 systems, especially mullite. When the oxide network of these materials is formed via chemical polymerization of alkoxides, the ultrastructure of the resultant condensates is fundamentally affected by the nature and kinetics of the condensation reactions. Crystallization of mullite from an amorphous $Al_6Si_2O_{13}$ at ~ 980° C appears to be related to the intimacy and homogeneity of the aluminium–silicon bonding in the precursor networks. Network inhomogeneities due to the different hydrolysis rates of mixed alkoxides diminish by reduction of the chemical encounter rates with water during the hydrolytic polycondensation. Mullite produced from homogeneous and stoichiometric condensate shows a large spontaneous densification at ~ 980° C. The microstructure of this material shows no indication of a liquid phase at the grain boundaries.

1. Introduction

In the last decade, as advancing technologies have required unprecedented material functions and unprecedented capabilities, the need for new materials and new forming methods has become increasingly clear. One of the emerging processes in the ceramic field is the non-thermal formation of ceramic substructures by chemical methods [1, 2]. The chemical polymerization method is often combined with colloidal-based methods in the so-called "sol–gel" process. There are fundamental differences between the two systems, not only in the gelation mechanisms, but in the material consequences of gelation [3].

The sol–gel process basically evolved from the use of colloids and metal-organic compounds as ceramic precursors to attain a higher degree of homogeneity and reactivity [4, 5]. Later, formation of monolithic glass and ceramic materials by non-thermal means was developed [2, 6]. Recently, the feasibility of modifying fundamental material properties by the modification of condensation reactions has been demonstrated [7, 8]. This last development may prove to be the most significant development in this field, and is clearly an aspect of the chemical polymerization process. The chemical polymerization process allows for the existence of stable non-equilibrium states, essentially by circumventing the high-temperature reactions usually required in the formation of ceramics. These non-equilibrium states, whether in molecular-network topology, in stoichiometry or in microstructure, then affect fundamental material properties. The properties of aluminium and other metal alkoxides have been extensively investigated [9–11].

In this paper, particular attention is given to materials preparation in the Al_2O_3–SiO_2 binary. Effects of the condensation reactions on the sintering, crystallization, and microstructure of mullite are presented.

2. Incorporation of other components into alumina

Condensation effects in the pure alumina system, along with preparation techniques for the solutions used in this investigation, are presented elsewhere [10]. Striking effects of hydrolytic polycondensation reactions on the microstructure of Al_2O_3 produced from such condensates are shown in Fig. 1.

Introduction of other elements into a sol–gel derived alumina matrix can be done by two general methods. The first method involves using soluble compounds of these elements which can later be thermally decomposed to oxides. These include metallic salts, acetates and hydroxides. A disadvantage of this method is that the amount of any constituent that can be incorporated into the alumina matrix is limited by its solubility. Where relatively small amounts of dopant are needed for structural stabilization and sintering purposes this method works extremely well. An example of such a case is the stabilization of transition alumina structures. Aluminas produced from the hydrolytic polycondensation of aluminium alkoxides undergo a structural transformation at around 1200° C. At this temperature the initially

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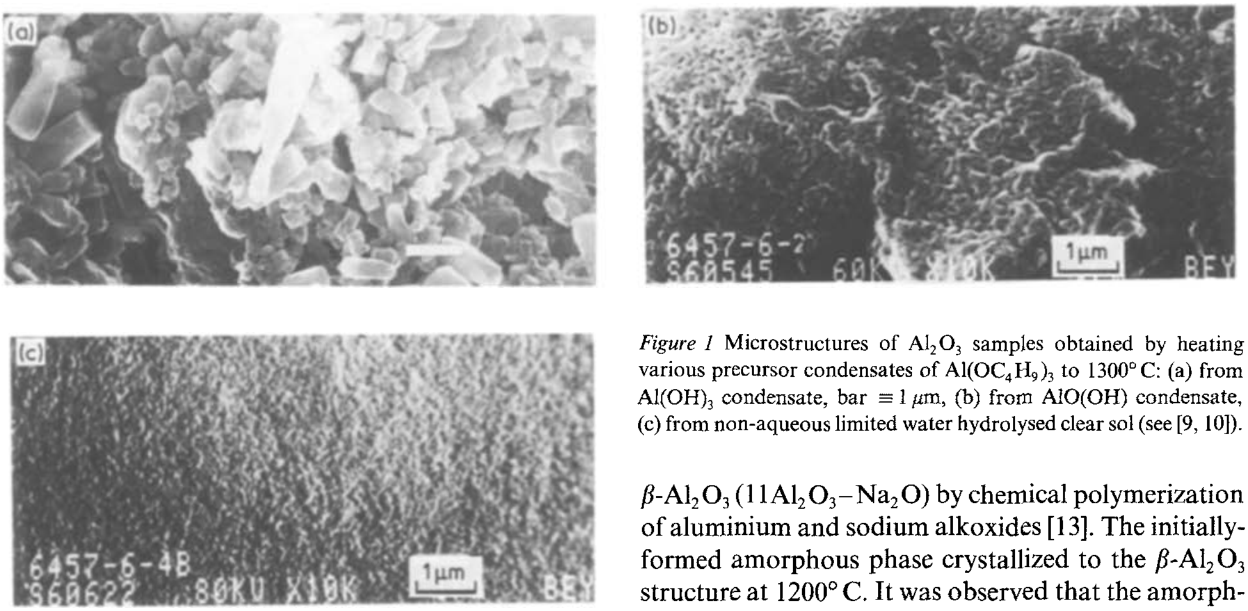

Figure 1 Microstructures of Al_2O_3 samples obtained by heating various precursor condensates of $Al(OC_4H_9)_3$ to 1300° C: (a) from $Al(OH)_3$ condensate, bar ≡ 1 µm, (b) from AlO(OH) condensate, (c) from non-aqueous limited water hydrolysed clear sol (see [9, 10]).

formed oxides convert to α-Al_2O_3 with a change in the aluminium ion coordination [6, 7]. This transformation eliminates the high surface area and is reflected in a strong exothermic peak in differential thermal analysis (DTA). The high surface area transition phase can be stabilized by doping the alumina network with few per cent of thorium, zirconium or silicon. Incorporation of as little as 3% SiO_2 shifts the α-Al_2O_3 transformation temperature by ~150° to approximately 1375° C [12]. Fig. 2 shows reaction DTA peaks occurring in the alumina system when 4% of various oxides are incorporated from their acetates into the precursor alumina sol.

The second method involves using metal alkoxides entirely to attain the desired composition. This method allows the preparation of a wider range of compositions. The principle behind this method has been discussed previously [1, 2]. Briefly, it involves the formation of inorganic networks by controlled hydrolysis and polymerization reactions of organometallic compounds. Since the oxide network is formed below the crystallization temperature, some unusual non-equilibrium materials can be formed. For example, we previously reported the formation of β-Al_2O_3 ($11Al_2O_3$–Na_2O) by chemical polymerization of aluminium and sodium alkoxides [13]. The initially-formed amorphous phase crystallized to the β-Al_2O_3 structure at 1200° C. It was observed that the amorphous precursor phase was also a sodium ion conductor. The significance of this is that the amorphous phase is formed at low temperatures, e.g. 500° C, and its optimum conductivity may occur at a different Na/Al ratio, and may be higher than the value observed for the crystalline phase. This has not been investigated.

3. Formation of materials in the Al_2O_3–SiO_2 binary

Preparation of these materials in the Al_2O_3–SiO_2 binary system by various sol–gel methods, as well as structural investigations, have been reported [14–18]. Since the hydrolytic polycondensation rates of aluminium and silicon alkoxides are substantially different, a homogeneous aluminosilicate cannot readily be formed by the hydrolysis of the alkoxide mixtures. One way to resolve this problem would be to use aluminosiloxanes, rather than separate alkoxides. Such compounds have been synthesized [19, 20] and were demonstrated to form aluminosilicate gels [21]. In the present work, only preparation methods using aluminium and silicon alkoxides are discussed.

When separate alkoxides are used, two methods come to mind to produce bridging oxygen bonds between silicon and aluminium. The first method is to create aluminium hydroxyl bonds without significant

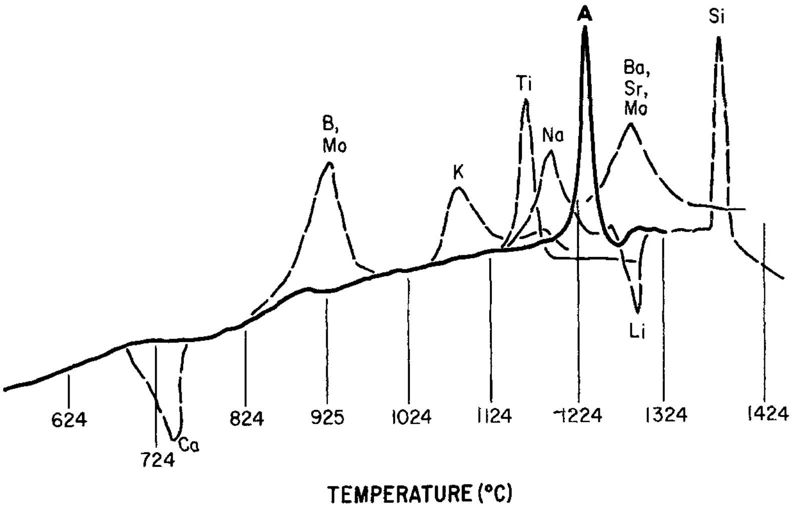

Figure 2 DTA curves when 4% of various dopants are introduced into an alumina network from their acetates. SiO_2 is introduced from $Si(OC_2H_5)_4$; Peak A is due to α-Al_2O_3 transformation of undoped alumina.

self-condensation and react these bonds with the alkoxy bonds of silicon:

$$=\mathrm{Al-OH} + \mathrm{RO-Si}\equiv \;\rightarrow\; =\mathrm{Al-O-Si}\equiv + \mathrm{ROH} \qquad (1)$$

In the aqueous alumina sol [10], the pendant bonds of the alumina colloids are hydroxy bonds and react with silicon alkoxides. When this aqueous AlO(OH) sol is used to form aluminosilicates, the immiscibility of $Si(OR)_4$ in the aqueous medium must first be overcome by the addition of alcohol. The microstructures of aluminosilicates produced by this method have been described [17].

The second method involves the partial hydrolysis of $Si(OR)_4$ followed by addition of unhydrolyzed aluminium alkoxide:

$$\begin{aligned}&\mathrm{(RO)_3Si{-}OH} + \mathrm{RO{-}Al(OR)_2}\\ &\rightarrow \mathrm{(RO)_3Si{-}O{-}Al(OR)_2} + \mathrm{ROH} \qquad (2)\end{aligned}$$

These two methods produce different levels of homogeneity, and their suitability depends on the compositional regime under study.

4. Formation of mullite

Mullite, $Al_6Si_2O_{13}$, is the most stable compound in the Al_2O_3–SiO_2 binary, occurring in almost all compositions within this binary. Due to its well-known technological significance, this material has been extensively studied [22–25]. Among the many combinations of polymerization reactions which may be used to form mullite are those that involve either aqueous or alcohol-based alumina sols with unhydrolysed or partially hydrolysed alkoxy silanes. Alternatively, aluminium alkoxides may be reacted with partially hydrolysed alkoxy silanes, or mixtures of alkoxides and aluminosiloxanes may be cohydrolysed. Each of these methods is expected to lead to a different level of homogeneity and ultrastructure.

The preparation of materials using $Si(OR)_4$ and aqueous colloidal AlO(OH) solutions presents several difficulties. The immiscibility may be dealt with by the introduction of alcohol as a mutual solvant. To reduce the amount of alcohol required the alumina sol can be initially concentrated. The sols most amenable to concentration are those formed with 0.07 moles of acid per mole of AlO(OH), which can be concentrated to 15 to 20 wt % equivalent Al_2O_3 [26]. This significantly reduces the amount of alcohol required to facilitate the miscibility. Secondly, mixing of these two components leads to gelling within a short period of time, the exact time depending upon solution concentration. The mixture must therefore be rapidly homogenized before the system solidifies. In the process, the hydroxy groups of the AlO(OH) colloids react with $Si(OR)_4$, creating chemically-bonded silica around and between the alumina colloids:

$$\begin{aligned}&\equiv\mathrm{Si-OR} + \mathrm{HO{-}[AlO(OH)_{(n-1)/n}]_n}\\ &\rightarrow \;\equiv\mathrm{Si-O{-}[AlO(OH)_{(n-1)/n}]_n} + \mathrm{ROH} \qquad (3)\end{aligned}$$

Drying and heat treating of the resultant gel yields large transparent granules having the mullite composition. Although chemical bond formation occurs between aluminium and silicon, the homogeneity is limited by the size of the alumina colloids, which are in the 10 to 30 nm range. In this case, the molecular grain boundaries are rich in silica.

To attain a higher degree in homogeneity, another preparation method was devised. This method is based on the fact that polyorganoaluminium condensates formed by 0.5 to 1.0 mole of water per mole of aluminium alkoxide dissolve in alcohols to form clear polymer solutions [10]. In this method, stoichiometric quantities of the aluminium and silicon alkoxides are first mixed and then hydrolysed with 0.5 to 1.0 mole of water per mole of total alkoxides in an alcohol medium. In a preferred variation of this theme, a stoichiometric amount of silicon alkoxide is first introduced into the water–alcohol liquor and given up to 10 min to react before the aluminium is introduced, since the hydrolysis and self-condensation rate of $Si(OR)_4$ is much slower than that of $Al(OR)_3$. When the aluminium alkoxide is introduced into the liquor, a white precipitate forms, but this condensate dissolves, forming a water-clear solution within hours at 60° C. The total equivalent oxide concentration should be kept below 10 wt % in the liquor. After the solution clears, it may be hydrolysed further by excess water, which causes either immediate gelation or fine powder formation, depending on variations in the hydrolysis conditions such as pH. The precursor solution may also be used for coating and deposition of thin films, where the final hydrolysis is done in the solid state.

Drying and calcination of this condensate yields material having the stoichiometric mullite composition. Upon further heating, the amorphous phase converts to crystalline mullite with an extremely strong exothermic peak at approximately 980° C, often imparting the appearance of fusion to the material. The occurrence of this exothermic peak and its relationship to mullite formation in the Al_2O_3–SiO_2 binary has been reported previously [21, 27–29]. There have been some questions as to the exact nature

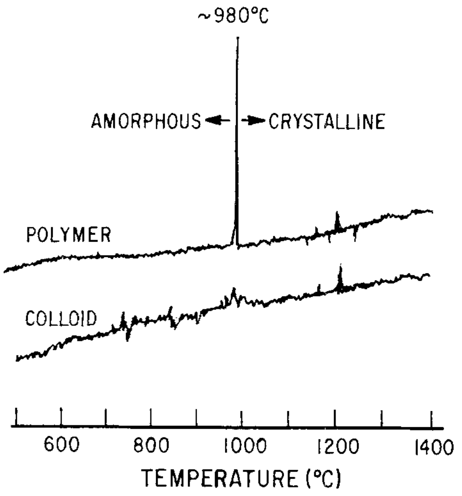

Figure 3 When $Al_6Si_2O_{13}$ composition is formed by a polymeric method, it shows a strong exothermic DTA peak at approximately 980° C and is crystallized to mullite. When the same composition is formed by colloidal precursors, this exothermic peak does not occur.

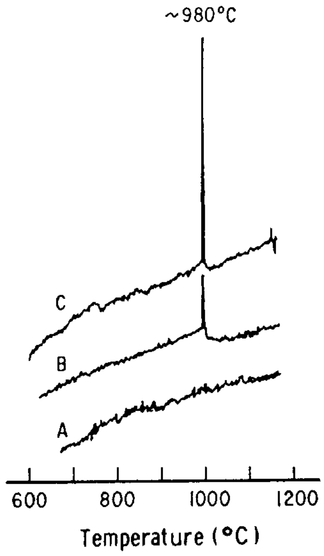

Figure 4 The occurrence and intensity of the ~980° C DTA peak of $Al_6Si_2O_{13}$ condensates is a function of the rate of hydrolysis of the base solution prepared from a stoichiometric mixture of $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$ in alcohol. (A) The solution is hydrolysed vigorously with excess water; (B) the solution is thinly poured over a tray and hydrolysed in humid air within hours; (C) the solution is hydrolysed in humid air over 90 days while mixing.

of the peak, e.g. crystallization or liberation of the free SiO_2. In our experiments the occurrence of this exothermic peak was directly associated with the conversion of the amorphous phase to mullite (Fig. 3). Secondly, and perhaps more importantly, its occurrence and intensity appear to be closely related to the intimacy and homogeneity of the aluminium–silicon bonding in the network. For example, mullite prepared from colloidal aqueous sols shows a very small or no exothermic peak at 980° C when similarly treated (see Fig. 3). Thus, the 980° C exothermic peak might be used for monitoring the nature of the precursor ultrastructure.

Polycondensation of a physical mixture of $Al(OR)_3$, $Si(OR)_4$ and H_2O gives gross inhomogeneities in the oxide networks due to large differences in the reaction rates:

$$\equiv\text{Si}-\text{OR} + \text{HO}-\begin{pmatrix}\text{H}\\ \text{Al}=\\ \text{Si}\equiv\end{pmatrix}$$

$$\rightarrow\ \equiv\text{Si}-\text{O}-\begin{pmatrix}\text{H}\\ \text{Al}=\\ \text{Si}\equiv\end{pmatrix} + \text{ROH} \qquad (4)$$

$$=\text{Al}-\text{OR} + \text{HO}-\begin{pmatrix}\text{H}\\ \text{Al}=\\ \text{Si}\equiv\end{pmatrix}$$

$$\rightarrow\ =\text{Al}-\text{O}-\begin{pmatrix}\text{H}\\ \text{Al}=\\ \text{Si}\equiv\end{pmatrix} + \text{ROH} \qquad (5)$$

where the reaction rate (5) $\gg$ (4). This condition leads to self-condensation of alumina first and polymerization with silica later, a condition similar to the one depicted by Equation 3.

However, the alkoxide mixtures form a more homogeneous oxide network when the chemical encounter rates with water are reduced significantly. The chemical encounter rates in the condensation reaction can be reduced greatly by first diluting the alkoxides in a non-aqueous solvent, then introducing water in very small quantities.

$$x\ \text{Al(OR)}_3,\ y\ \text{Si(OR)}_4,\ z\ \text{SLV} + w\ \text{H}_2\text{O}$$

$$\rightarrow\ =\text{Al}-\text{O}-\text{Si}\equiv\ + \text{ROH},\ z\ \text{SLV} \qquad (6)$$

where $w \ll x, y \ll z$ and SLV is a solvent. This principle is applicable to other systems and can be further manipulated by the type of solvent and reaction temperature.

The importance of the rate of hydrolysis on the molecular-structural makeup and on the mullite crystallization is demonstrated by the experimental results shown in Fig. 4. Here a stoichiometric mixture of $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$ corresponding to the mullite composition was prepared in dry ethyl alcohol at a concentration of 5 wt% equivalent oxide. This solution was divided into three portions and hydrolysed at three different rates. The first portion (A) was mixed directly with excess water, the second portion (B) was spread thinly over a tray and allowed to hydrolyse and dry in humid air, and the last portion (C) was put in an open flask and stirred for three months, providing a very slow and methodical hydrolysis with humid air. The DTA peaks of these three materials during the heat treatment through 980° C are shown in Fig. 4. This experiment shows that the vastly different rates of hydrolysis between aluminium and silicon alkoxides can be largely compensated by using a slow, restricted hydrolysis.

5. Effect of condensation reactions on the sintering, crystallization and microstructure

The condensation reactions affect the material's sintering and microstructure [30]. Differences in the sintering rates of various condensates may be partly due to the size effect. The tendency to coalesce is also

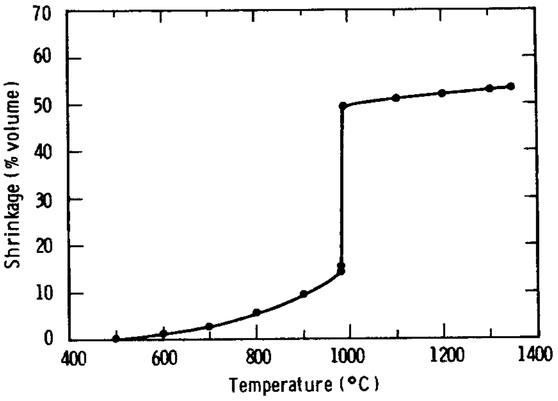

Figure 5 Monolithic amorphous $Al_6Si_2O_{13}$ gels produced by intimate polymerization of aluminium and silicon shows a spontaneous shrinkage (approximately 35%) at the mullite crystallization temperature.

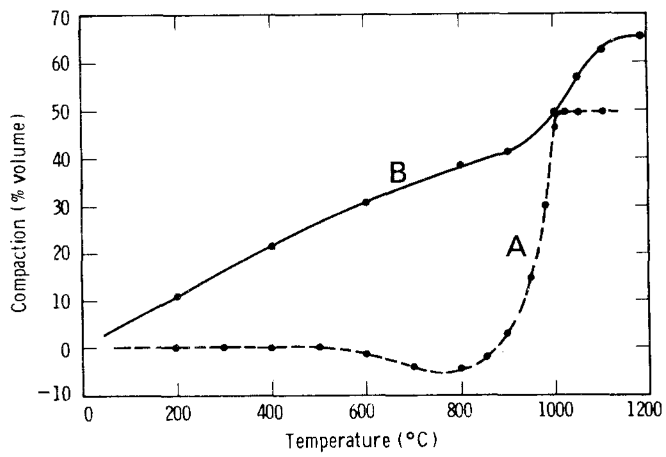

Figure 6 The sintering behaviour of $Al_6Si_2O_{13}$ powder condensate around 980° C also reflects the intimacy of the aluminium and silicon polymerization in the network. (A) Powder produced by slow hydrolysis of a stoichiometric alkoxide mixture in alcohol using humid air; (B) powder produced from a precursor solution where $Si(OC_2H_5)_4$ was initially hydrolysed. Powders hot-pressed at 4000 p.s.i. (27.6 MPa).

affected by the hydrolysis conditions (see Fig. 7 in Yoldas [7]). The effect of agglomeration on mullite sintering behaviour is well known [31]. However, the large variations exhibited in these chemically polymerized systems cannot be entirely attributed to particle size and agglomeration effects. The surface activity, the nature of the terminal bonds, the stoichiometry, and the morphology of the network structure all appear to play very significant roles. All of these parameters are affected by the condensation conditions.

The crystallization of mullite from the amorphous $Al_6Si_2O_{13}$ polymer at 980° C is associated with approximately 35% linear shrinkage in monolithic gels (Fig. 5). When hot-pressed, the powders produced from the same solution also exhibit similar accelerated sintering in this temperature regime (Curve A in Fig. 6). In comparison, a sample produced from the reaction of hydrolysed $Si(OC_2H_5)_4$ with $Al(OC_4H_9)$ powders shows a completely different sintering behaviour (Curve B in Fig. 6). In the latter case, the initial hydrolysis of $Si(OC_2H_5)_4$ clearly leads to the formation of free SiO_2, which is reflected in the sintering curve.

As the rate of hydrolysis can be slowed, it can also be increased. For example, the use of hydrogen peroxide instead of water causes a significantly more vigorous hydrolysis. This has consequences in the microstructure. Fig. 7 shows a comparison of the $Al_6Si_2O_{13}$ condensate produced from the same base solution by water and by hydrogen peroxide hydrolysis. In this experiment, a stoichiometric mixture of $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$ in dry ethanol was first partially hydrolysed in humid air by stirring the solution in an open beaker for 24 h. Then, using this base solution, secondary hydrolysis by mixing with water and hydrogen peroxide was performed. The fluffy texture of the condensate formed under the vigorous action of the hydrogen peroxide (Fig. 7b) contrasts with the relatively dense texture of the condensates formed under the less vigorous action of water (Fig. 7a). The condensation rates and the textures can also be modified by changes in the catalyst and pH of solution. For example, condensation in the presence of NH_4OH yields a significantly different texture to condensation in the presence of HNO_3.

The microstructures of mullites produced by the polymeric and colloidal condensation techniques discussed here have been investigated [32]. Those investigations showed that there were significant differences in grain geometry, orientation and porosity between mullite samples prepared by the two different methods (Fig. 8). Mullite produced from the reaction of colloidal AlO(OH) sol with $Si(OC_2H_5)_4$ tends to show elongated crystals with considerable intergranular void space, e.g. 15%, and the presence of a liquid phase.

The mullite produced from the alcohol-based polymer solutions, on the other hand, has a dense microstructure with equiaxed grains with no indication of

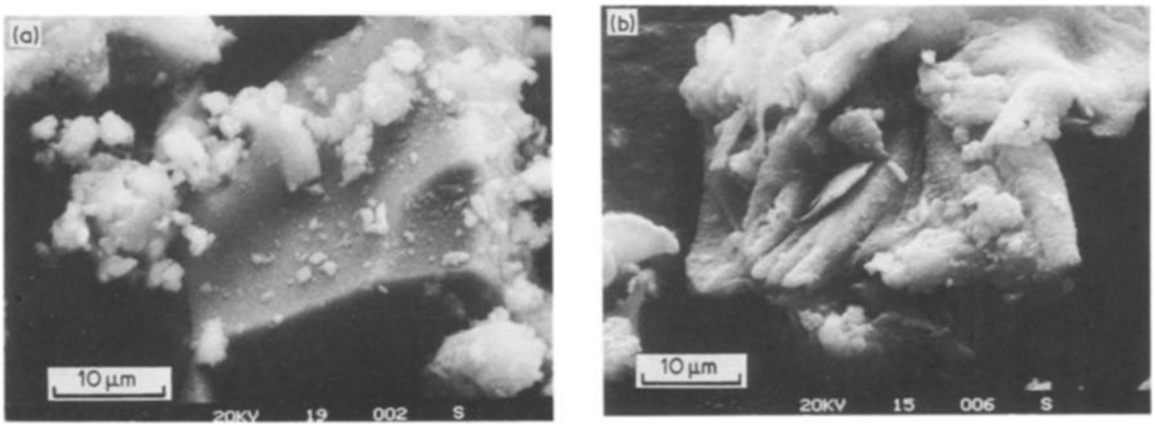

Figure 7 SEM of $Al_6Si_2O_{13}$ condensates produced by (a) water hydrolysis of a base solution and (b) hydrogen peroxide hydrolysis of the same solution.

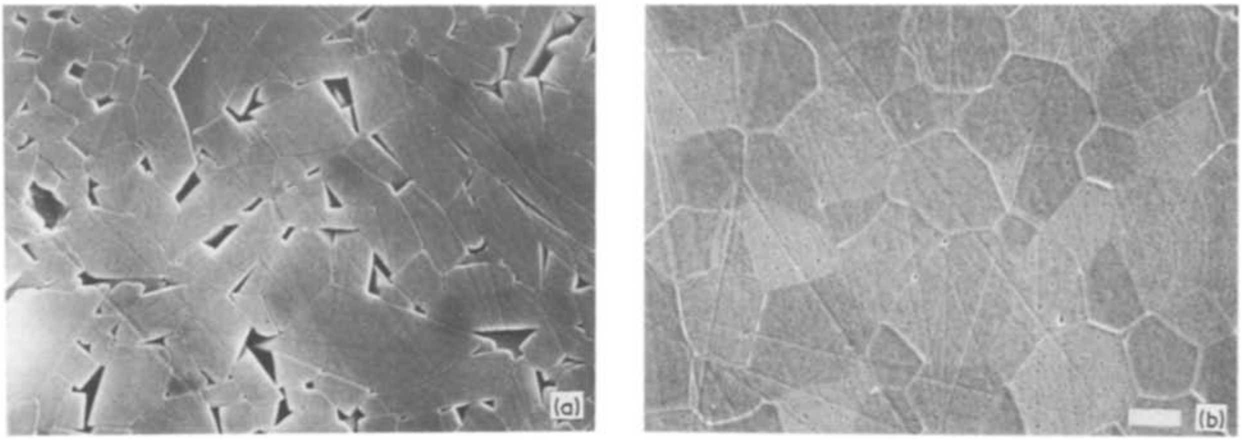

Figure 8 Microstructure of mullite upon heating at 1650° C as affected by the initial condensation process of the precursor: (a) the mullite precursor is produced from the colloidal aqueous alumina sol and $Si(OC_2H_9)_4$, bar $\equiv 2\,\mu m$, (b) the precursor is produced by intimate polymerization of silicon and aluminium from their alkoxides (from [32]).

liquid-phase presence [32]. The presence of the liquid phase is apparently related to silica-rich regions which exist as molecular boundaries in colloidal systems (see Equation 3).

6. Summary

Crystallization of mullite from the amorphous $Al_6Si_2O_{13}$ phase at ~980° C appears to be closely related to the intimacy and homogeneity of alumina–silica bonding in the ultrastructure. The occurrence of a peak at 980° C is also accompanied by a large spontaneous densification in this system. Mullite prepared from colloidal aqueous alumina shows a very small or no exothermic peak at ~980° C.

Inhomogeneities in the hydrolytic polycondensates of mixed alkoxides resulting from the different hydrolysis rates can largely be remedied by greatly reducing the chemical encounter rates with water. This can be done by first increasing the molecular separation by dilution with an inert solvent, and then introducing the water extremely slowly, e.g. from air humidity. These studies also indicate that considerable ultra- and micro-structural design can be performed in chemically condensed ceramic materials.

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*Received 4 February
and accepted 15 July 1987*