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Metastable immiscibility and microstructural development during sintering of a SiO_2-Al_2O_3 plasma prepared powder

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The sintering characteristics of SiO_2–36.6 wt % Al_2O_3 powder, prepared by condensation from high frequency plasma, have been studied and microstructural changes occurring during sintering followed by transmission electron microscopy The as-prepared amorphous powder showed evidence of spinodal decomposition into an Al_2O_3-rich and SiO_2-rich glass consistent with the position of a previously reported metastable miscibility gap in the SiO_2–Al_2O_3 system. Mullite crystallized on an extremely fine scale at 1000° C and gradually coarsened at higher temperatures. Sintering occurred above 1100° C by a viscous flow mechanism with activation energy 87 kcal mol^{-1} which corresponds to the activation energy for viscous flow of SiO_2–Al_2O_3 glass containing approximately 17 wt % Al_2O_3.

1. Introduction

Cationic field theories of liquid immiscibility in silicate systems suggest that there should be a large miscibility gap in the SiO_2–Al_2O_3 system; the fact that this is not observed has been attributed to the tendency for Al ions to remain in four-fold coordination [1, 2]. The low slope of the mullite liquidus does, however, suggest that there is a tendency for liquid phase separation and a metastable miscibility gap, between 20 and 40 wt% Al_2O_3, was first proposed in 1964 by Galakhov and Konovalova on the basis of optical studies of the structure of heat treated glasses [3].

McDowell and Beall [4] studied the microstructure of SiO_2–Al_2O_3 glasses using electron microscopy and observed that rapidly quenched specimens containing 30 to 60wt % Al_2O_3 showed evidence of co-connective phase separation on a scale of approximately 20 nm. They accepted this as evidence of spinodal decomposition of homogenous glass during cooling and proposed a metastable miscibility gap with consolute point at approximately 40 wt% Al_2O_3 and at least 100° C below the liquidus temperature. Takamori and Roy [5], although observing very fine (< 10 nm) inhomogeneities in the structure of rapidly cooled SiO_2–Al_2O_3 glasses in the same composition range, concluded that there was insufficient evidence for a miscibility gap in the system. They estimated that the quenching rate necessary to prevent phase separation was 10^5 to 10^7 ° C sec^{-1}, comparable to the cooling rates used in their flame spraying and splat cooling experiments, and suggested that the structure observed was a result of "a significant non-uniformity in the stable liquid structure above the liquidus". Takamori and Roy also questioned the interpretation, by McDowell and Beall, of the morphology of the crystalline phase in terms of phase separation, because many of the heat treatments used were above the temperature at which mullite rapidly crystallizes.

More recently Risbud and Pask [6] have proposed, on the basis of thermodynamic calculations, that a metastable miscibility gap exists in the SiO_2–Al_2O_3 system with a consolute point of approximately 50 wt% Al_2O_3 and 1540° C; the spinodal extending from 35 to 65 wt% Al_2O_3 at 1200° C.

The presence of a miscibility gap suggests that ceramics consisting of an extremely fine distribu-

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tion of mullite in silica could be prepared by sintering amorphous powders with composition near the consolute point. Such powders, with particle sizes of the order of 0.1 μm, can be prepared by co-condensation from an oxygen, high-frequency plasma into which the appropriate halides have been introduced [7]. The subject of the present paper is a study of the sintering characteristics of these powders and the accompanying microstructural development.

2. Experimental

The preparation and properties of the powder used have been described in detail previously [7]. It contained 36.6 wt% Al_2O_3 and consisted of spherical particles, with mean diameter of 0.22 μm, which were completely amorphous to X-ray diffraction. Rapid crystallization of mullite occurred on heating to 1000° C and cristobalite was formed at temperatures greater than approximately 1450° C.

Cylindrical compacts, approximately 10 mm in diameter and 50 mm long, were prepared by isostatic pressing of the powder in rubber envelopes at a pressure of 69 MPa. The compacts were sintered at a constant heating rate of 4.4° C min^{-1} in a differential dilatometer which employed an LVDT to monitor continuously the specimen shrinkage. Specimens were heated to various maximum temperatures, up to 1440° C, after which they were rapidly cooled to room temperature by removal of the surrounding furnace. The phases present after cooling were determined by X-ray diffraction and the microstructure examined by transmission electron microscopy of specimens prepared by ion beam thinning.

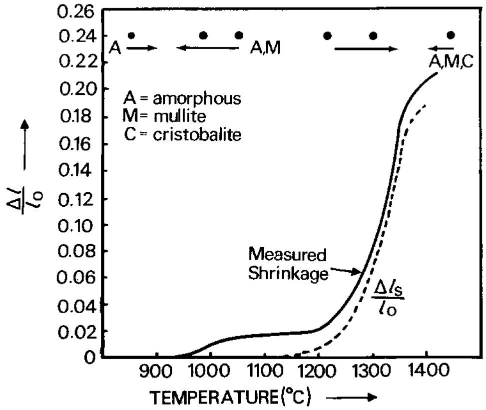

Figure 1 Shrinkage ($\Delta l_s/l_0$) as a function of temperature at constant heating rate of 4.4° C min^{-1}. The shrinkage due to sintering, after allowing for the volume change accompanying crystallization of mullite ($\Delta l_s/l_0$), is shown dashed.

The apparent specific gravity (S_a) and bulk density (D_a) of the compacts were also measured at various stages during sintering. The apparent specific gravity was determined by the water displacement method ($S_1 = W_d/W_d - W_s$), where W_d = dry weights of specimen, W_s = weight suspended in water with the pores saturated). The bulk density was determined from the weight and the volume, measured using a mercury displacement volumeter. The open porosity (P_0) was derived from the relationship $P_0 = 1 - D_a/S_a$. The pore size distribution was also determined using a mercury intrusion porosimeter [8].

3. Results

The shrinkage at constant heating rate is shown as a function of temperature in Fig. 1. The shrinkage at $\simeq$950° C corresponds to the change in volume accompanying crystallization of mullite as shown by X-ray diffraction. The variation of apparent specific gravity and porosity with temperature are shown in Fig. 2, and the pore size distribution in Fig. 3. The latter were plotted as cumulative pore volume (penerated mercury volume) per mass against pore size and show a narrow, normal distribution in all cases up to the intrusion pressure of 104 MPa corresponding to a pore diameter of 15 nm. Satisfactory results could not be obtained for the specimen sintered to 1440° C because of the low porosity.

These results indicate that considerable sintering occurred over the temperature range between 1200 and 1400° C, the specimens approaching zero open porosity with an extremely small pore size. As shown by the continuous increase in apparent specific gravity, the amount of mullite formed increased up to approximately 1300° C after initial crystallization at 1000° C.

The microstructures of compacts heated to various maximum temperatures at 4.4° C min^{-1} are illustrated in Figs. 4a to d. Inhomogeneities of structure were observed in the as-prepared powder (Fig. 4a) which was confirmed by selected area diffraction to be completely amorphous. The scale of the inhomogeneities varied somewhat from particle to particle, with a mean value of approximately 5 nm. This structure persisted without change up to 985° C, however the

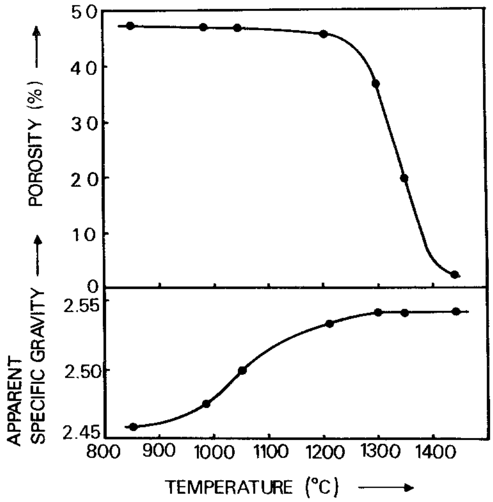

Figure 2 Porosity (P_0) and apparent specific gravity (S_a) as a function of temperature at constant heating rate of 4.4° C min^{-1}.

contrast between the two phases increased after heating to 1050° C (Fig. 4b) with perhaps a slight increase in the scale of the structure. Selected area diffraction revealed the presence of small crystallites of mullite in glass (inset to Fig. 4b). With further heating above 1050° C the size of the mullite crystals gradually increased to approximately 10 nm at 1300° C (Fig. 4c). The crystals increased sharply in size above this temperature, reaching approximately 70 nm at 1440° C (Fig. 4d).

Cristobalite was detected by X-ray diffraction in specimens sintered to 1440° C although some amorphous phase remained. These specimens fractured on a very fine scale after rapid cooling, presumably because of internal stresses resulting from the large density change accompanying the α–β cristobalite transformation.

4. Discussion

The electron microscope observations of the structure of the as-prepared powder show that glass–glass phase separation has occurred during cooling of the particles from the liquid state in the plasma flame. The extremely fine scale and co-connective structure further suggest that phase separation has occurred by spinodal decomposition. As discussed elsewhere [7], the conditions of particle size, cooling rate and nucleation rate are such that cystallization of mullite is suppressed in these particles as they cool in the plasma flame. It is apparent from the present results however that the cooling rate has not been sufficiently rapid to suppress metastable phase separation below the liquidus temperature.

The maximum rate of spinodal decomposition occurs at an undercooling of approximately $0.1\,T_s$ where T_s is the spinodal temperature (K). Cahn and Charles [9] have estimated that the time constant (t_c) at this temperature is given by $t_c \simeq 10^{-17}/D$, where D is the diffusion coefficient (m^2 sec^{-1}). A later paper by Cahn [10] gives a value an order of magnitude higher, but this seems

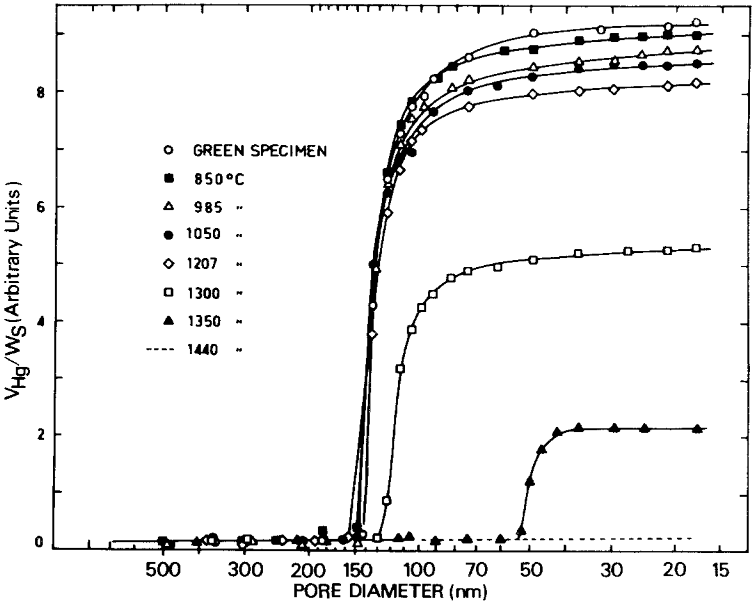

Figure 3 Pore size distribution as a function of temperature at constant heating rate of 4.4° C min^{-1}.

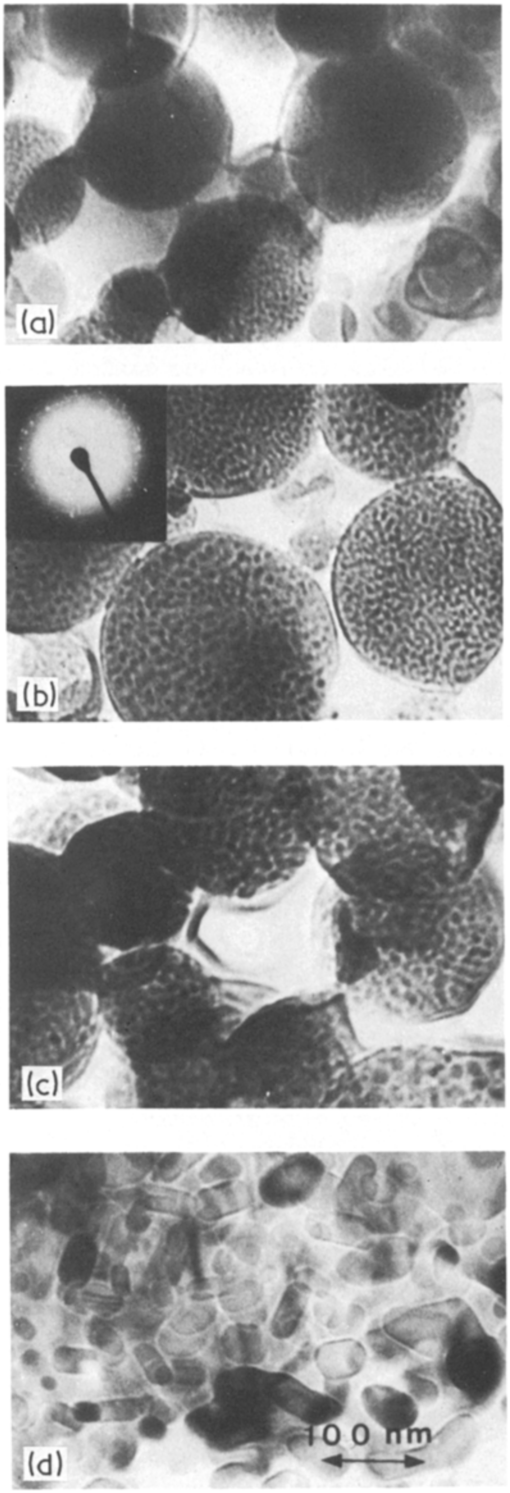

Figure 4 Transmission electron micrographs of ion-thinned compacts after heating to various maximum temperatures. (a) As-prepared powder, (b) 1050° C SAD inset, (3) 1300° C, (d) 1440° C. All micrographs at the same magnification.

to be the result of neglecting a factor of $2\pi^2$ in the derivation. Using the estimate of Cahn and Charles [9] for t_c together with their assumption that the critical cooling rate for spinodal decomposition corresponds to that at which t_c is equal to the time required to cool from T_s to $0.9\,T_s$, and taking the cooling rate of the plasma prepared particles to be $10^4\,\mathrm{C\,sec^{-1}}$ [7] suggests that a value of D greater than $10^{-15}\,\mathrm{m^2\,sec^{-1}}$ would be required at $0.9\,T_s$ for spinodal separation to occur in the present case.

Diffusion coefficients were estimated for the Al_2O_3 system from published viscosity data [11, 12] using the Stokes–Einstein relationship. The viscosity data were extrapolated to lower temperatures using the Fulcher equation [13]: $\log \eta = A + B/(T - T_0)$, where η is the viscosity and A, B and T_0 are constants. T_0 was assumed to correspond to the glass transition temperature, at which $\eta = 10^{13}$ poise; values for T_0 determined by differential thermal analysis were used [7]. The temperature at which $D = 10^{-15}\,\mathrm{m^2\,sec^{-1}}$ was thus estimated to be 1250° C, giving a minimum spinodal temperature of $\simeq 1420°$ C. This value is consistent with the spinodal suggested by McDowell and Beall [4] ($\simeq 1600°$ C at 37 wt% SiO_2 but higher than that proposed by Risbud and Pask [6] ($\simeq 1300°$ C at 37 wt% SiO_2).

There seems little doubt that the as-prepared powder has undergone phase separation into an Al_2O_3-rich and SiO_2-rich glass during cooling, confirming the presence of a metastable miscibility gap in the SiO_2–Al_2O_3 system. The observation that there is little change in microstructure on heating to temperatures below 1000° C is to be expected since the diffusion coefficient is so high at these temperatures that extremely long times would be required for appreciable coarsening to occur. Electron microscopy shows that mullite forms on heating to approximately 1000° C, by crystallization of the Al_2O_3-rich glass, giving a microstructure consisting of crystallites of mullite, approximately 10 nm in diameter, in a matrix of SiO_2-rich glass. The increase in size of the mullite crystals on heating to higher temperatures is consistent with coarsening by a classical Ostwald ripening process.

The increase in apparent specific gravity with increasing temperature (Fig. 2) indicates that the amount of mullite increases with temperature after initial rapid crystallization at approximately 1000° C by diffusion of Al_2O_3 from the SiO_2-rich glass. Assuming that the densities of the mullite and glass phases are the same as equilibrium mullite and SiO_2 glass, the glass composition after heating to 1200° C is about 12 wt% Al_2O_3, calculated from the apparent specific gravity. This may be compared with the measured glass phase composition in 42 wt% Al_2O_3–SiO_2 glass quenched from 2090° C and reheated to 1725° C [14]; although the quenching rate used was not sufficiently rapid to prevent mullite crystallization, the structure consisted of extremely fine crystals of mullite in silica-rich glass with a microstructure resembling that to be expected from spinodal decomposition. The structure coarsened on heating at 1725° C, allowing measurement of the composition of the phases by microprobe; this showed that the glass phase remained at approximately 16 wt% SiO_2 independent of treatment time.

Sintering of the powders used in the present study would be expected to occur by a viscous flow mechanism and this may be tested by application of the equation derived by Cutler [15] to describe the shrinkage for this case under constant heating rate conditions:

$$\frac{\Delta l}{l_0} = \frac{\gamma R T^2}{dCAQ} \exp\left(-Q/RT\right)$$

where Q is the activation energy for viscous flow and A is the pre-exponential term, γ is surface tension, d the particle diameter and C the heating rate. Some care is necessary in applying the equation to the present situation because the change in apparent specific gravity with temperature means that the shrinkage, particularly below 1200° C, arises partly from sintering and partly from crystallization of mullite. The contribution to shrinkage from phase transformation was therefore calculated from the specific gravity change and subtracted from the measured shrinkage to give the true sintering shrinkage $\Delta l_s/l_0$ (see Fig. 1). Plotting log $[\Delta l_s/l_0 T^2]$ against $1/T$, (Fig. 5) gives a straight line with slope equivalent to an activation energy of 87 kcal mol^{-1}. Comparison with published data for the activation energy of viscous flow of SiO_2–Al_2O_3 glasses [12] shows that this corresponds to a composition of 17 wt% Al_2O_3, similar to the composition of the glass phase determined by Risbud and Pask in 42 wt% SiO_2–Al_2O_3 [14] and in reasonable agreement with the composition determined from the specific gravity data.

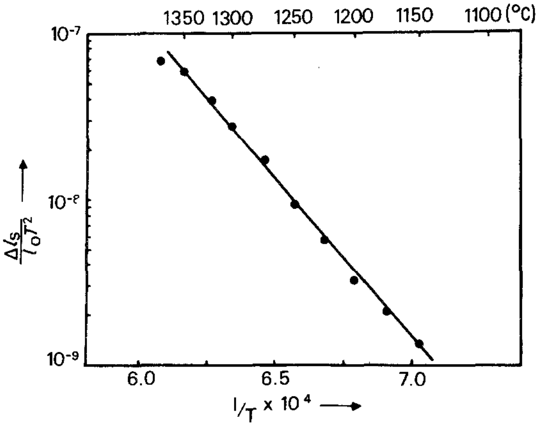

Figure 5 Plot of log $(\Delta l_s/l_0 T^2)$ versus $1/T$.

5. Conclusions

The structure of SiO_2–36.6wt% Al_2O_3 powders prepared by condensation from a plasma shows evidence of spinodal decomposition into a SiO_2-rich and Al_2O_3-rich glass during cooling from the liquid state. These observations are consistent with the position of the metastable miscibility gap proposed by McDowell and Beall.

During sintering of this powder, mullite crystallizes from the Al_2O_3-rich glass at $\simeq$1000° C and the mullite crystals coarsen at higher temperatures. The shrinkage during constant rate heating experiments is consistent with a viscous flow sintering mechanism with activation energy of 87 kcal mol^{-1} if allowance is made for the shrinkage arising from mullite crystallization.

It is possible to prepare low porosity ceramics consisting of extremely fine crystals of mullite in a SiO_2-rich glass or mullite and cristobalite, by sintering of sub-micron SiO_2–Al_2O_3 powder produced by plasma condensation.

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References

1. S. ARAMAKI and R. ROY, *J. Amer. Ceram. Soc.* 45 (1962) 229.
2. F. Ya. GALAKHOV and B. G. VARSHAL, "The Structure of Glass', Vol. 8 edited by F. A. Poroi-Koshits (Consultants Bureau, New York, 1973).
3. F. Ya. GALAKHOV and S. F. KONOVALOVA, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 8 (1964) 1373.
4. J. F. McDOWELL and G. H. BEALL, *J. Amer. Ceram. Soc.* 52 (1969) 17.

5. F. TAKAMORI and R. ROY, *ibid.* **56** (1973) 639.
6. S. H. RISBUD and J. A. PASK, *ibid.* **60** (1977) 418.
7. M. S. J. GANI and R. McPHERSON, *J. Mater. Sci.* **12** (1977) 999.
8. N. M. WINSLOW and J. J. SHAPIRO, *ASTM Bull.* **236** (1959).
9. J. W. CAHN and R. J. CHARLES, *Phys. Chem. Glasses* **6** (1965) 181.
10. J. W. CAHN, *Trans. Met. Soc. AIME* **242** (1967) 166.
11. V. P. ELYUTIN, V. I. KOSTIKOV, B. S. MITIN and Ya. A. NAGIBIN, *Zh. Fiz. Khim.* **43** (1969) 579.
12. R. ROSSIN, J. BERSAN and G. URBAIN, *Compt. Rend. Hebd. Seances Acad. Sci.* **258** (1964) 562.
13. G. S. FULCHER, *J. Amer. Ceram. Soc.* **8** (1925) 339.
14. J. H. RISBUD and J. A. PASK, *ibid* **61** (1978) 63.
15. I. B. CUTLER, *ibid.* **52** (1969) 14.

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