

DEVITRIFICATION BEHAVIOUR OF A GLASS OBTAINED FROM PORPHYRIC SANDS WITH ADDITION OF TiO₂ (4%) AND MgO (8%)

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ABSTRACT

The non-isothermal devitrification of a glass obtained from porphyric sands with addition of TiO₂ (4%) and MgO (8%) has been studied. Scanning electron micrography observations suggest that the glass demixes on quenching. After prolonged heat treatment at temperatures in the glass transformation range an evolution of the glass texture is observed, with formation of non-spherical particles of a separated phase. This does not seem to influence greatly the crystal growth activation energy, which has been evaluated as being $E = 105 \pm 5 \text{ kcal mol}^{-1}$. The maximum nucleation rate temperature has been estimated to be $T = 710^\circ \text{C}$. Evidence has been found that the glass–glass interfaces produced by demixing provide alternative sites of nuclei formation.

INTRODUCTION

This paper is part of a more general work about the possibility of obtaining glass ceramics from a porphyry of composition: SiO₂ = 72.40%, Al₂O₃ = 13.85%, K₂O = 4.60%, Na₂O = 3.00%, Fe₂O₃ = 2.15%, CaO = 1.30%, MgO = 0.84%, TiO₂ = 0.20%, with loss on calcination = 2.06%.

In the present study, a glass was obtained by adding MgO and TiO₂ in wt. percentages 8% and 4%, respectively. The devitrification behaviour of this glass was investigated and the kinetic parameters evaluated by means of thermoanalytical techniques and scanning electron micrograph (SEM).

EXPERIMENTAL

A glass of composition SiO₂ = 65.23%, Al₂O₃ = 12.50%, MgO = 8.09%, TiO₂ = 4.26%, K₂O = 4.16%, Na₂O = 2.71%, Fe₂O₃ = 1.94%, CaO = 1.17%

was prepared by adding appropriate amounts of MgCO_3 and TiO_2 to porphyric sands of the composition reported above. The mixture was melted for 5 h at 1450°C in a platinum crucible in an electric oven. The melt was cooled rapidly to $T = 500^\circ\text{C}$ and then slowly to room temperature.

The glass quenched in this way was then crushed in an agate mortar and sieved in order to obtain fine (-325 mesh) and coarse ($+50-35$ mesh) particles.

Differential thermal analysis (DTA) of ≈ 90 mg of the glass was carried out in air at various heating rates ($1-20^\circ\text{C min}^{-1}$). A Netzsch differential thermal analyser Model 404M was used with Al_2O_3 powder as reference material.

X-ray diffraction analysis was performed using a Rigaku D/max IIIB diffractometer equipped with a graphite curved crystal monochromator in the diffracted beam. Each sample was analysed in the range $2\theta = 15-65$ with a step of 0.02 deg and a speed of 1 deg min^{-1} , using the $\text{Cu K}\alpha$ radiation. The data-processing was performed using a Casio 6000 computer; a search-match program supported by JCPDS cards [1] was used to identify the crystalline phases.

SEM observations were made using a Cambridge Stereoscan-200 apparatus after 2 min of etching with 5% HF solution.

RESULTS AND DISCUSSION

Differential thermal analysis and X-ray diffraction results

Figure 1 shows the DTA curve for a fine powder sample recorded at heating rate $20^\circ\text{C min}^{-1}$. After the slope change in the glass transformation range, there appears an exothermic peak representing devitrification. The successive slope change is due to softening of the remaining glassy matrix and consequent wetting of the sample holder walls, which alters the heat transfer coefficient. The DTA curve for a sample melted in the holder recorded at the same heating rate is also given in this figure. The softening effect just described can be avoided by this means, and the melting behaviour observed. The glass transformation temperature $T_g = 737^\circ\text{C}$ can be evaluated from the reported curves. It is worth noting that no melting effects are observed at temperatures above $T = 1326^\circ\text{C}$.

Figure 2 shows the X-ray diffraction patterns of one sample which had been quenched in the manner described above and one which had been subjected to a DTA cycle at $20^\circ\text{C min}^{-1}$ stopped just after the devitrification peak. As can be seen, the devitrification product is a mixture of enstatite (JCPDS Card 22/714) and clinoenstatite (JCPDS Card 19/769) and, as a minor component, titanium dioxide in the rutile form (JCPDS Card 21/1276).

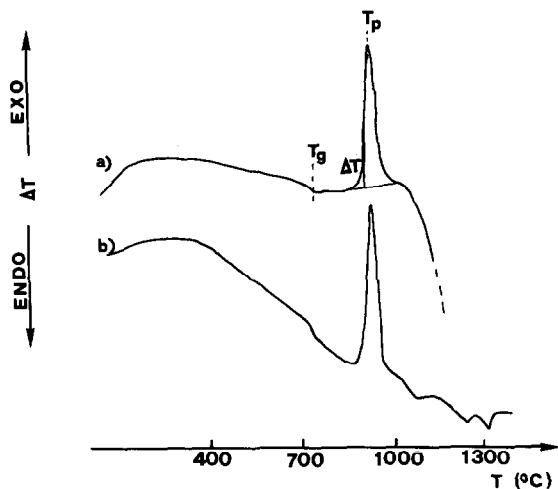


Fig. 1. DTA curves recorded at heating rate $20^{\circ}\text{C min}^{-1}$ for (a) a fine powder sample, and (b) a bulk sample melted in the sample holder.

A quantitative estimate of the crystallized percentage was obtained by evaluating the parameter [2,3]

$$C\% = \left(1 - \frac{\theta'_{am}}{\theta_{am}}\right) \times 100$$

where θ'_{am} is the integrated intensity of the spectrum of the sample treated at

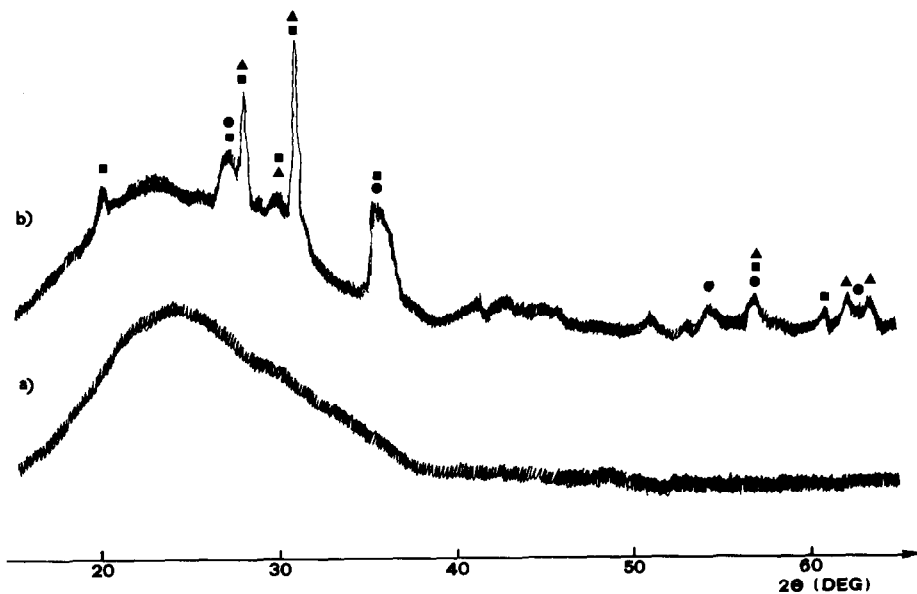


Fig. 2. X-ray diffraction patterns of (a) a quenched sample, and (b) a sample after a DTA cycle at heating rate $20^{\circ}\text{C min}^{-1}$ stopped just after the devitrification peak: ▲, enstatite; ■, clinoenstatite; ●, rutile.

700°C, which is completely amorphous, and θ_{am} is the analogous quantity relative to the amorphous halo of the other samples. In the case of the sample subjected to a DTA cycle at 20°C min⁻¹ stopped just after the devitrification peak, an estimated crystallinity percentage of 20 ± 2% was obtained. It is worth noting that samples heat treated for 1 and 2 h at 950°C, i.e. in the devitrification peak temperature range of Fig 1, gave the same X-ray diffraction pattern as that shown for sample (b) in Fig. 2, so the same crystallinity percentage, $C\% = 22 \pm 2$, was found.

Non-isothermal devitrification results

The non-isothermal devitrification of glasses is described well by the equation [4,5]

$$-\ln(1 - \alpha) = \frac{AN}{\beta^m} \exp\left(-\frac{mE}{RT}\right) \quad (1)$$

where α is the degree of crystallization, β is the heating rate, A is a constant, E is the crystal growth activation energy, and m is a parameter whose value depends on the devitrification mechanism and growth morphology. When devitrification is controlled by the crystal-glass interface reaction, it ranges from $m = 1$ for one-dimensional crystal growth (or growth from the surface) to $m = 3$ for three-dimensional crystal growth. In the case of diffusion-controlled crystal growth, the corresponding variations are $m = 0.5-1.5$.

If the nuclei number is not dependent on the heating rate, then taking into account that at the peak temperature T_p the crystallized fraction is not dependent on the heating rate [6] and the deflection from the baseline ΔT is proportional to the devitrification rate [7], the following equations can be derived

$$\ln \beta = -\frac{E}{RT_p} + \text{const.} \quad (2)$$

$$\ln \Delta T = \frac{mE}{RT} + \text{const.} \quad (3)$$

Fine and coarse powder samples of the quenched glass were subjected to DTA at various heating rates (1–20°C min⁻¹). A third series of coarse powder samples which had previously been subjected to a DTA cycle at 1°C min⁻¹ until the onset of the devitrification peak was also examined. The data are plotted in Figs. 3 and 4. The kinetic parameters evaluated by means of eqns. (2) and (3) are given in Table 1. As can be seen, specific surface changes of the samples do not affect the peak temperature or the values of the devitrification kinetic parameters. Variations are, however, observed for the series of preheated samples. The sample surface provides sites of preferential nuclei-formation. It is for this reason that specific surface

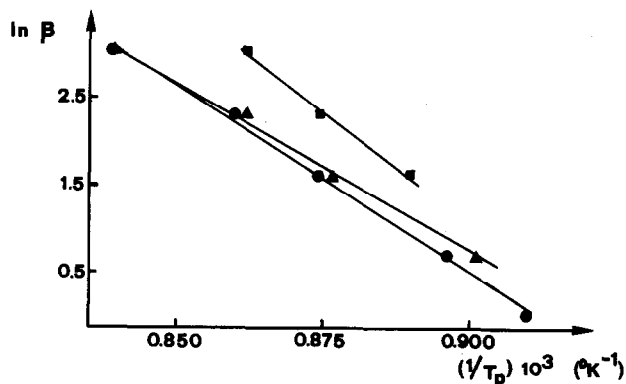


Fig. 3. Plot of $\ln \beta$ vs. $1/T_p$: \blacktriangle , fine powder sample; \bullet , coarse powder sample; \blacksquare , coarse powder sample after a DTA cycle at 1°C min^{-1} stopped at the onset of the devitrification peak.

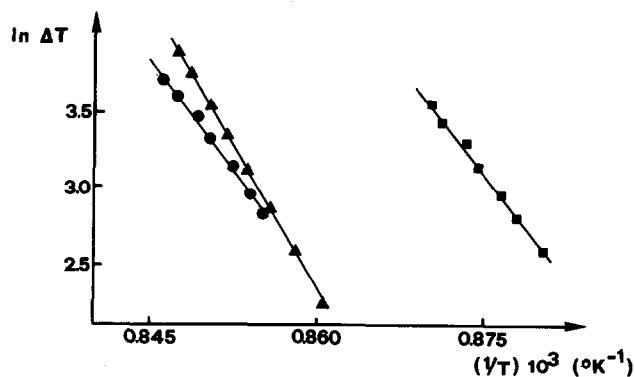


Fig. 4. Plot of $\ln \Delta T$ vs. $1/T$ from DTA curves recorded at $20^\circ\text{C min}^{-1}$: \blacktriangle , fine powder sample; \bullet , coarse powder sample; \blacksquare , coarse powder sample after a DTA run at 1°C min^{-1} stopped at the onset of the devitrification peak.

increases usually result in the peak being shifted towards lower temperatures, and bring about a decrease in the value of the Avrami parameter m [8–11]. It is known, however, that although titanium oxide is soluble in a

TABLE 1

Kinetic parameters E , mE and peak temperature T_p , from DTA at $20^\circ\text{C min}^{-1}$

Sample	T_p ($^\circ\text{C}$)	E (kcal mol^{-1})	mE (kcal mol^{-1})
Fine powder, quenched	918	76	246
Coarse powder, quenched	918	86	194
Coarse powder, after DTA at 1°C min^{-1} until 786°C	887	100	188
Coarse powder, 2 h at 700°C	887	100	218
Coarse powder, 14 h at 705°C	878	112	153

TABLE 2

Peak temperature T_p and product mE , from DTA at $20^\circ\text{C min}^{-1}$ on coarse powder samples

Heat treatment	T_p ($^\circ\text{C}$)	mE (kcal mol^{-1})
2 h at 582°C	926	206
2 h at 621°C	925	224
2 h at 663°C	916	180
2 h at 685°C	900	182
2 h at 700°C	887	218
2 h at 721°C	887	184
2 h at 746°C	892	194
2 h at 777°C	904	254

wide range of molten glass compositions, on cooling or subsequent reheating phase separation usually takes place, in the form of submicroscopic particles rich in TiO_2 [12]. So the result reported above could be due to the expected demixing, which could provide zones of preferred nucleation [12]. In order to discuss the results the fact must also be taken into account that, in the absence of a nucleation pretreatment, when bulk nuclei (which form in a number inversely proportional to the heating rate) are dominant, the peak shift would not depend solely on the E values, as predicted by eqn. (2). Given that DTA at heating rates of $5\text{--}20^\circ\text{C min}^{-1}$ after the described pretreatment at 1°C min^{-1} increases by no more than 20% the time spent at temperatures lower than the devitrification onset, eqn. (2) should be correctly applied in this last case.

A series of coarse powder samples was heat treated for the same period of time (2 h) at various temperatures in the glass transformation range, and thereafter subjected to DTA at $20^\circ\text{C min}^{-1}$. The results are reported in Table 2. As can be seen, all the mE values but one fall within $mE = 200 \pm 20$ (kcal mol^{-1}). Rather, it is the peak temperature which is sensitive to the temperature of heat treatment. These variations can be ascribed to differential nuclei formation. The following equation, obtained from eqn. (1), allows us to draw a nucleation rate-temperature curve [13]

$$\ln N = \frac{mE}{R} \frac{1}{T_p} + \text{const.} \quad (4)$$

A plot of $1/T_p$ vs. the heat treatment temperature T_n is shown in Fig. 5. The maximum nucleation rate temperature $T = 710^\circ\text{C}$ was determined in this way.

Two series of coarse powder samples were therefore heat treated for 2 and 14 h at 700°C and then subjected to DTA at heating rates of $2\text{--}20^\circ\text{C min}^{-1}$. Plots of $\ln \beta$ vs. $1/T_p$ and $\ln \Delta T$ vs. $1/T$ are shown in Figs. 6 and 7. The values of E and mE obtained by means of eqns. (2) and (3) are

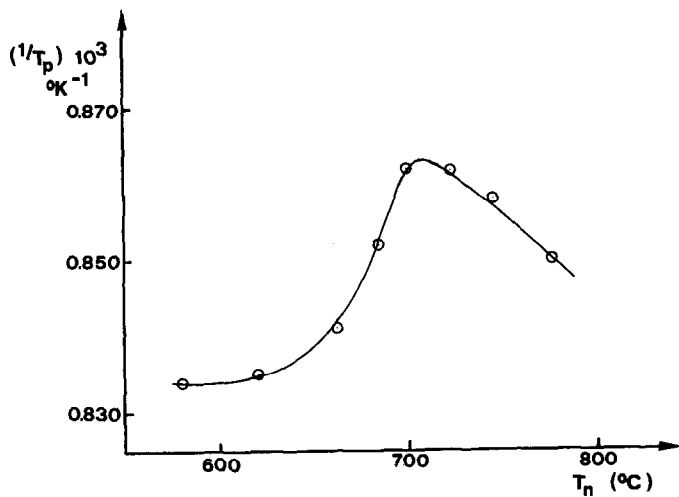


Fig. 5. Nucleation rate-temperature curve.

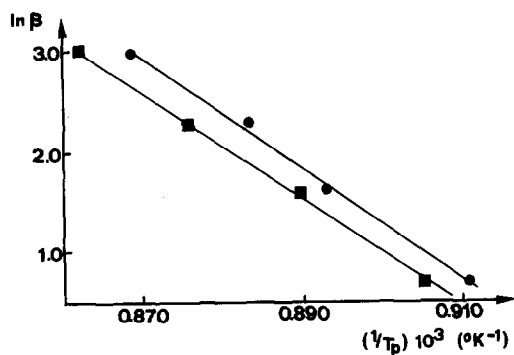


Fig. 6. Plot of $\ln \beta$ vs. $1/T_p$ for a coarse powder sample preheated for 2 h (■) and 14 h (●) at 700 $^{\circ}\text{C}$.

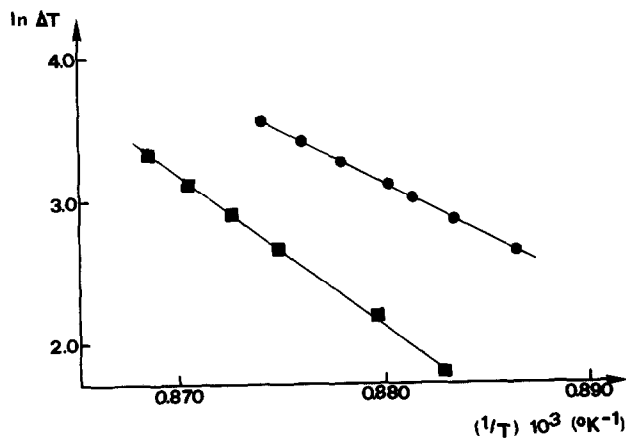


Fig. 7. Plot of $\ln \Delta T$ vs. $1/T$ from DTA curves recorded at 20 $^{\circ}\text{C min}^{-1}$ for coarse powder samples preheated for 2 h (■) and 14 h (●) at 700 $^{\circ}\text{C}$.

reported in Table 1. The E values are very close to those obtained previously. Therefore, we estimate a value for E of 105 ± 5 kcal mol⁻¹. A decrease of the product mE is observed in the case of heat treatment for 14 h: some change in the devitrification mechanism must take place when the heat treatment is as prolonged as this.

Scanning electron micrography results

SEM results are reported in Figs. 8 and 9. In the case of the quenched sample, high magnifications allow it to be seen that demixtion is already present on a very fine scale (Fig. 8a). As can be seen in the picture 8b, prolonged heat treatment in the temperature range between the temperatures of glass transformation and devitrification peak onset has marked effects on the glass texture. Non-spherical particles of separated phase can be seen to have formed. An analogous result has been obtained in the case of a 10 h heat treatment of 700 °C (picture not shown). After heating at 1 °C min⁻¹ until the onset of the devitrification peak a very low density of this kind of particle has also been obtained (picture not shown). This kind of pretreatment has a very marked effect on the ceramized samples (Fig. 9: a, b, c). As has already been suggested by the non-isothermal devitrification results, the heat treatment described induces nuclei formation, giving rise to a finer grained glass ceramic than the one obtained by simply heating at the higher temperature. The devitrification mechanism seems to be different in the case of a sample preheated for a long time at 700 or 785 °C (Fig. 9: d, e, f). Evidence of devitrification starting from the glass-glass interface is found, in this case, by the SEM technique. Given that devitrification from surface nuclei occurs with the lower values of the Avrami parameter m , the observed decrease of the mE product in this kind of sample is as would be expected.

The phase nature and crystallinity percentage developed in the samples which had been preheated for a long period were checked. No differences were found, with respect to the results reported above, compared to the samples which had not been preheated.

CONCLUSIONS

The experimental results suggest the following conclusions.

- (1) The glass is, on quenching, already demixed on a very fine scale.
- (2) The crystal growth activation energy is $E = 105 \pm 5$ kcal mol⁻¹.
- (3) The maximum nucleation rate temperature is $T = 710$ °C.
- (4) An evolution of the glass texture is observed during heat treatment at temperatures in the glass transformation range, with formation of non-spherical particles of a separated phase. The glass-glass interfaces produced in this way seem to provide alternative sites of nuclei formation.

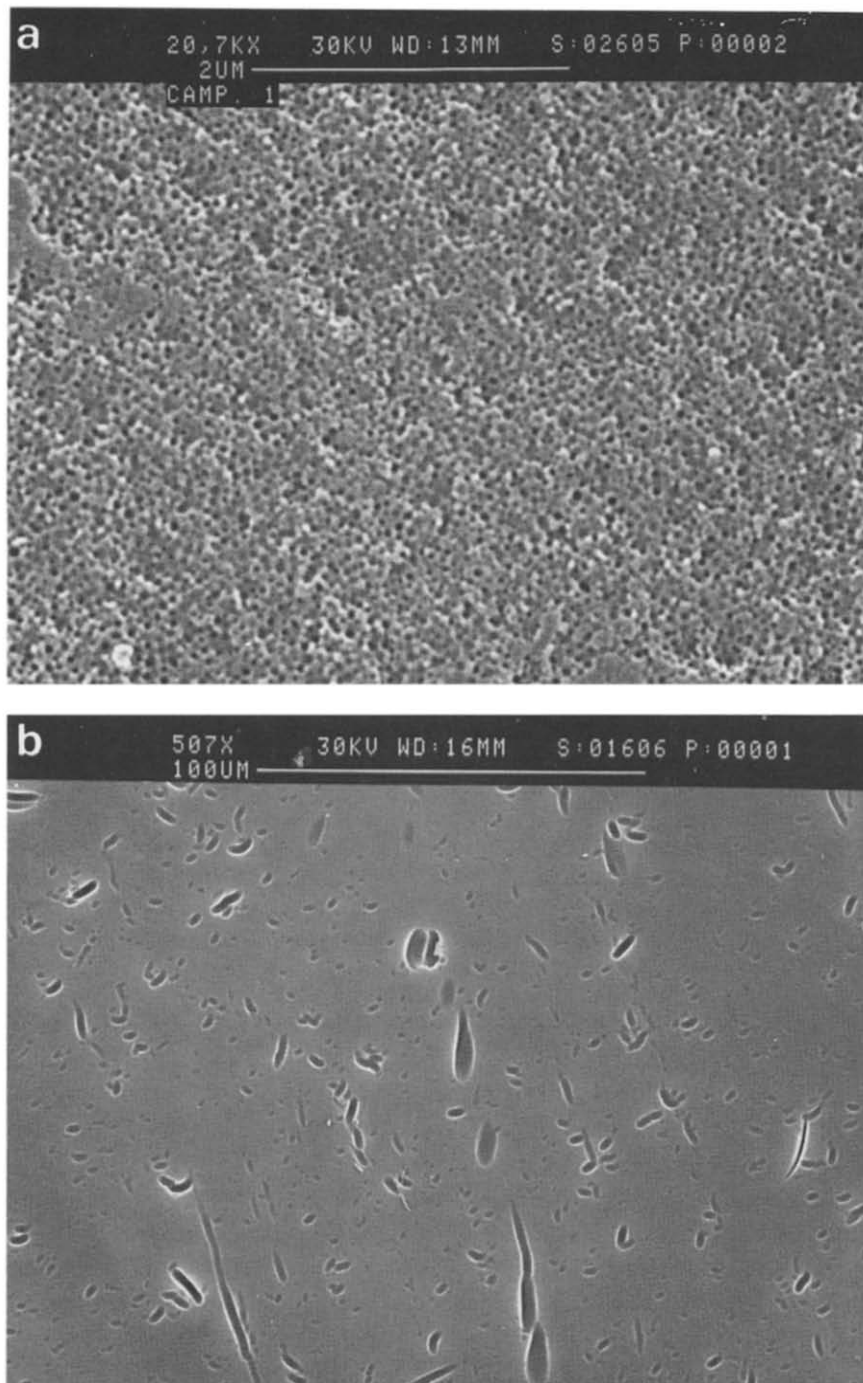


Fig. 8. SEM pictures of samples: a, quenched (20000X); b, after heating at $1^{\circ}\text{C min}^{-1}$ until 780°C and then for 12 h at this temperature (500X).

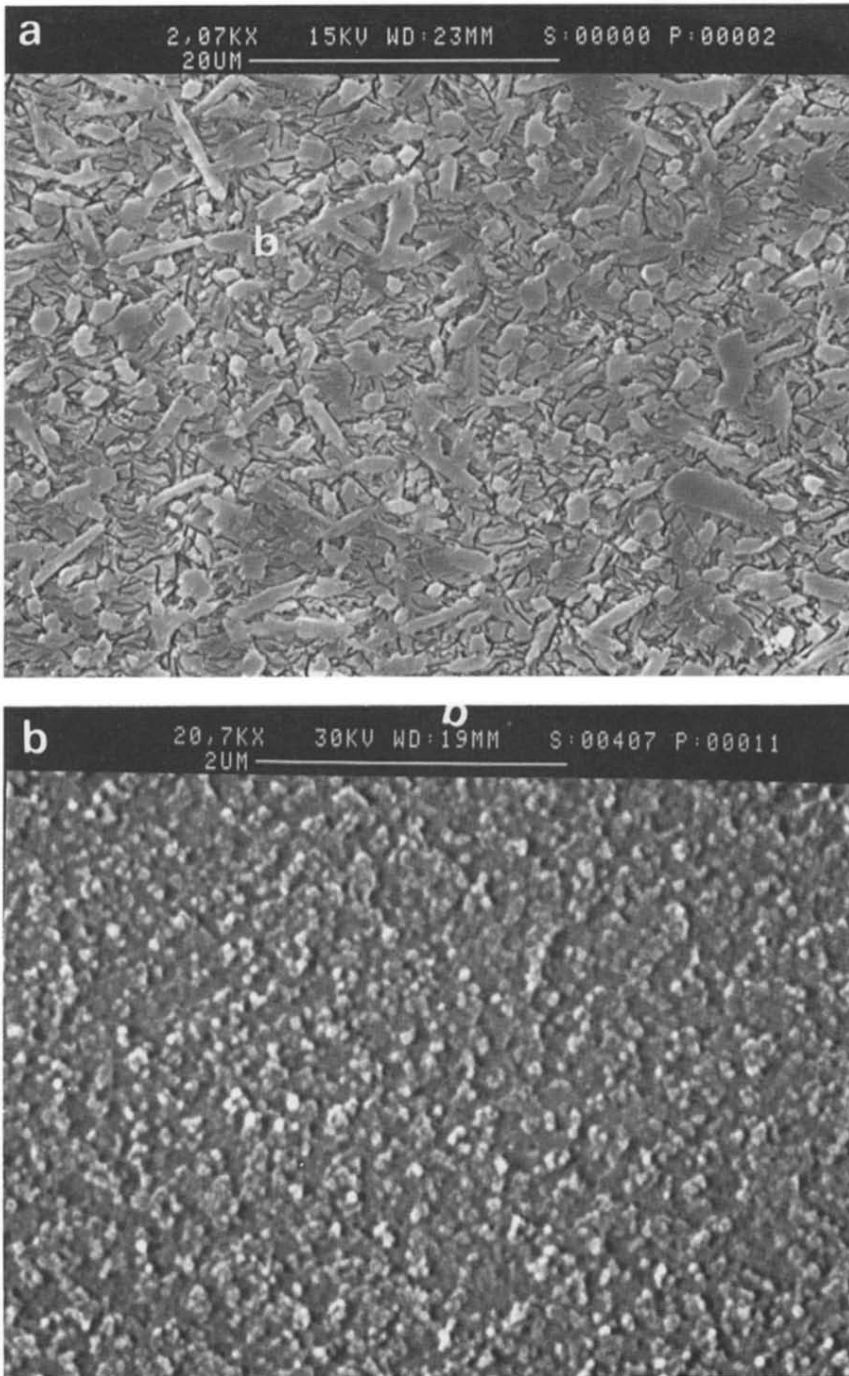


Fig. 9. SEM pictures of samples: a, after heating for 1 h at 950 °C (2000X); b, after heating at 1 °C min⁻¹ until 780 °C followed by a DTA cycle stopped just after the devitrification peak (20000X).

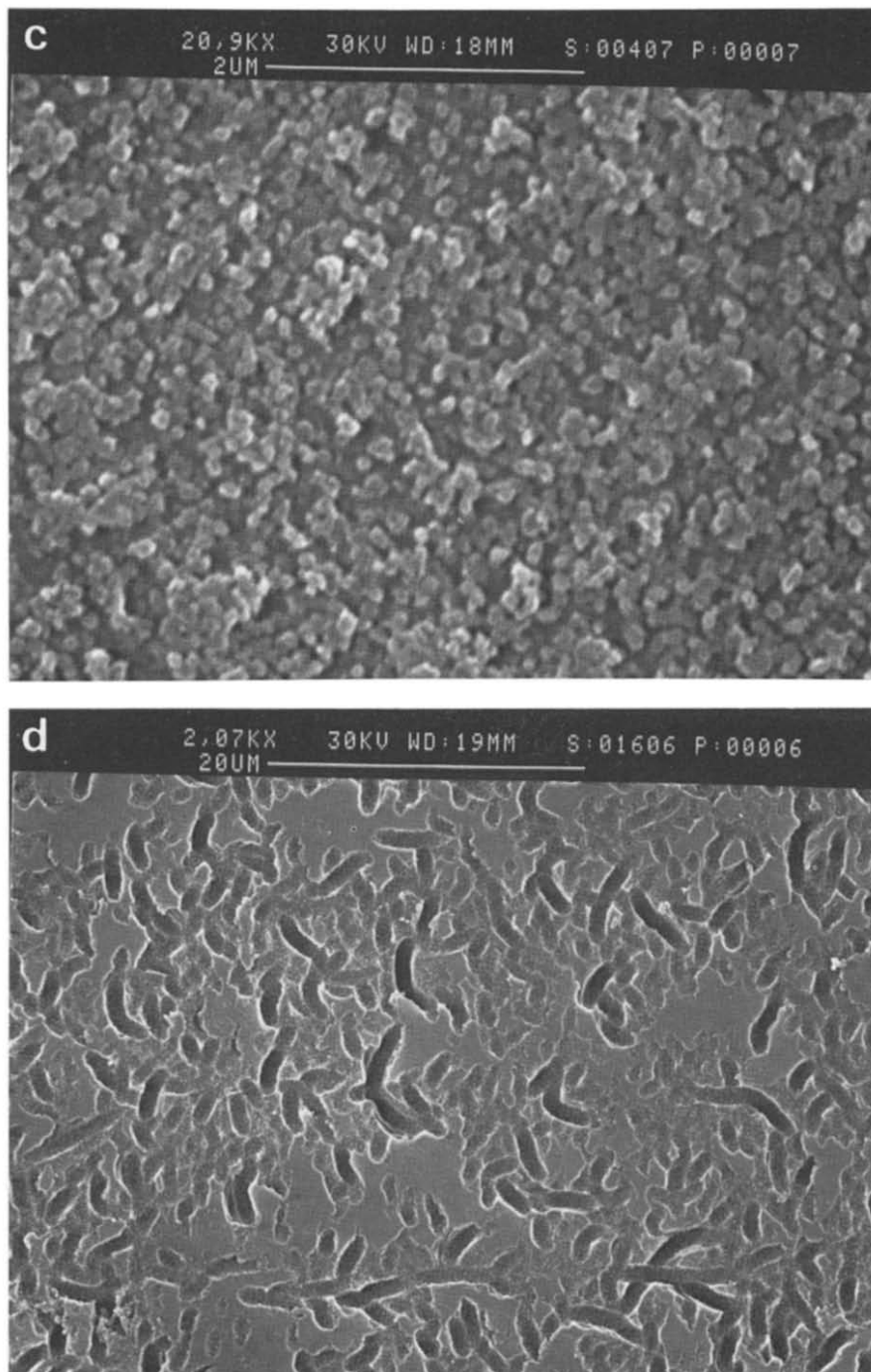


Fig. 9 continued. SEM pictures of samples: c, after heating at $1^{\circ}\text{C min}^{-1}$ until 780°C and then for 1 h at 950°C (20000X); d, heat treated as for the sample shown in picture (b) of Fig. 1 and then for 1 h at 950°C at magnification 2000X. (Continued over page).

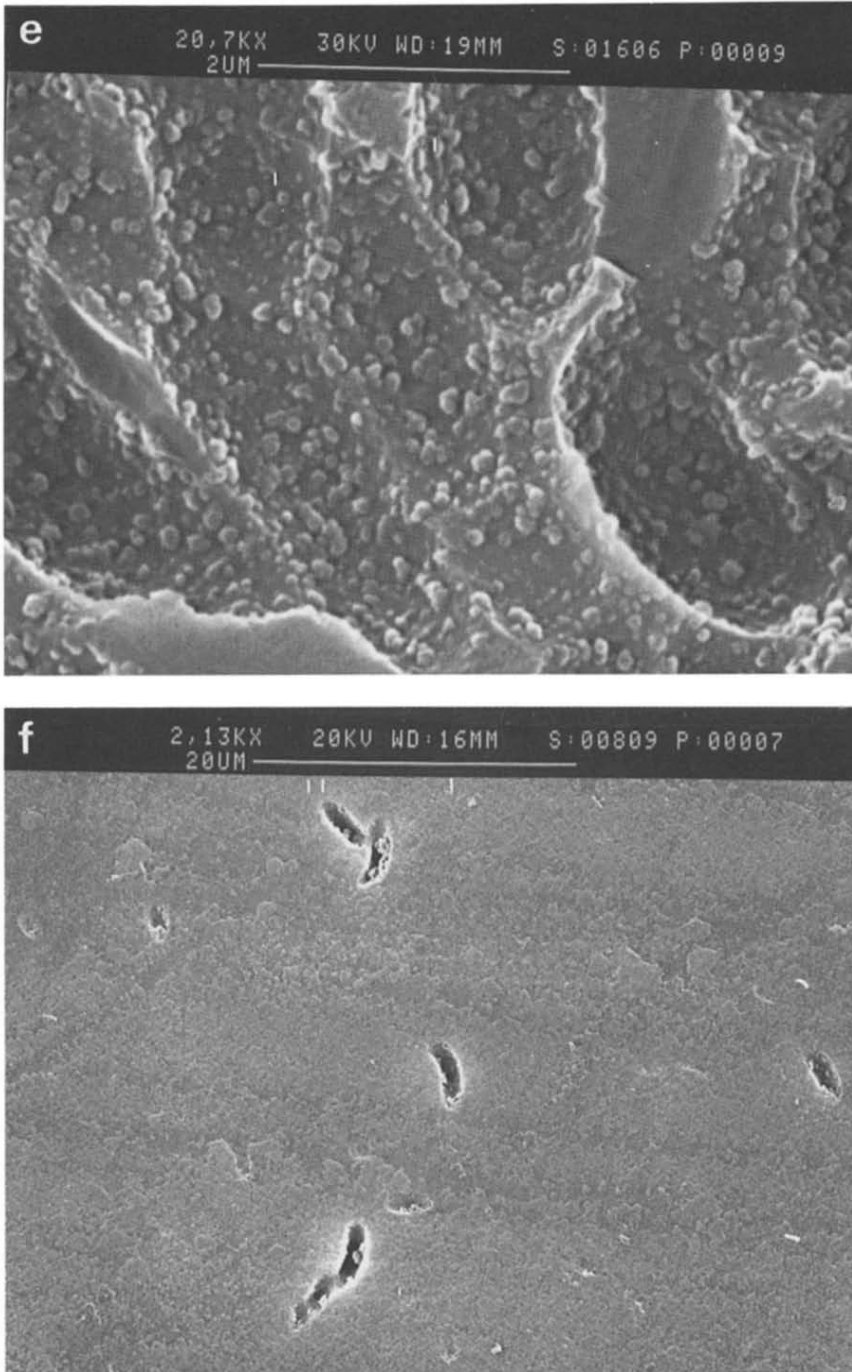


Fig. 9 continued. SEM pictures of samples: e, 20000X; f, after heating for 10 h at 700 °C followed by a DTA cycle at 20 °C min⁻¹ stopped just after the devitrification peak (2000X).

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