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Devitrification of a Glass Obtained from Porphyric Sands, MgO (15%) and TiO_2 (4%)

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Abstract

A glass of composition: SiO_2 = 59·84%; Al_2O_3 = 11·45%; MgO = 15·34%; TiO_2 = 4·23%; K_2O = 3·80%; Na_2O = 2·48%; CaO = 1·08%; Fe_2O_3 = 1·78%; was prepared from porphyric sands by addition of MgO and TiO_2. The quenched glass is demixed on a very fine scale. The non-isothermal devitrification has been studied. Three-dimensional crystal growth has been observed. The experimental data suggest a mechanism controlled by the crystal–glass interface reaction. The crystal growth activation energy $E_c = 467 \pm 20$ kJ/mole has been evaluated. The temperature of most efficient nucleation is approximately $T_N = 720°C$.

Unter Zugabe von $MgCO_3$ und TiO_2 zu einem porphyrischen Sand wurde ein Glas der Zusammensetzung SiO_2 = 59·84%; Al_2O_3 = 11·45%; MgO = 15·34%; TiO_2 = 4·23%; K_2O = 3·80%; Na_2O = 2·48%; CaO = 1·08%; Fe_2O_3 = 1·78% erschmolzen. Das schnell abgekühlte Glas weist im mikroskopischen Maßstab Entmischung auf. Das Kristallisationsverhalten wurde mit der differentiellen Thermoanalyse (DTA) untersucht. Es wurde ein dreidimensionales Kristallwachstum beobachtet. Die experimentellen Ergebnisse lassen vermuten, daß der Kristallisationsvorgang an der Grenzfläche Glas–Kristall kontrolliert wird. Die Aktivierungsenergie für das Kristallwachstum ergab sich zu $E_c = 467 \pm 20$ kJ/mol und die maximale Keimbildungsgeschwindigkeit liegt bei 720°C.

On a préparé un verre de composition: SiO_2 = 59·84%; Al_2O_3 = 11·45%; MgO = 15·34%; TiO_2 = 4·23%; K_2O = 3·80%; Na_2O = 2·48%; CaO = 1·08%; Fe_2O_3 = 1·78%; à partir de sables porphyriques, par addition de MgO et de TiO_2. Le verre trempé présente une démixtion à très petite échelle. On a étudié la dévitrification à l'aide de techniques d'analyse thermique différentielle (DTA). Les données expérimentales suggèrent que le mécanisme de la dévitrification est contrôlé par la réaction à l'interface cristal-verre. On a trouvé que l'énergie d'activation de la croissance cristalline a pour valeur $E_c = 467 \pm 20$ kJ/mole et que la vitesse de nucléation maximale est atteinte à la température $T_n = 720°C$.

1 Introduction

In a previous work[1] the isothermal devitrification behaviour of glasses obtained by melting mixtures of $MgCO_3$, TiO_2 and porphyric sands of composition: SiO_2 = 72·40%; Al_2O_3 = 13·85%; K_2O = 4·60%; Na_2O = 3·00%; Fe_2O_3 = 2·15%; CaO = 1·30%; MgO = 0·84%; TiO_2 = 0·20%; loss on calcination = 2·06%; at constant TiO_2 content (4%) and changing MgO content (8–15%) were compared. The non-isothermal devitrification study of the 8% MgO-containing glass has proved[2] that heat treatments at low temperatures in the glass transformation range can greatly affect the devitrification behaviour. In that case glass in glass demixing has been suggested

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to produce interfaces which provide alternative sites of nuclei formation. In this paper the non-isothermal devitrification study of the 4% TiO_2- and 15% MgO-containing glass is reported.

2 Experimental

A glass of composition $SiO_2 = 59{\cdot}84\%$; $Al_2O_3 = 11{\cdot}45\%$; $MgO = 15{\cdot}34\%$; $TiO_2 = 4{\cdot}23\%$; $R_2O = 3{\cdot}80\%$; $Na_2O = 2{\cdot}48\%$; $CaO = 1{\cdot}08\%$; $Fe_2O_3 = 1{\cdot}78\%$, was prepared adding appropriate amounts of $MgCO_3$ and TiO_2 to porphyric sands of the previously reported composition. The mixture was melted for 5 h at 1450°C. The melt was cooled rapidly to 500°C and then slowly to room temperature. The quenched glass was crushed and sieved in order to obtain fine (+230–325 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°C/min). A Netzsch differential thermal analyser Model 404 M has been 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 $2\nu = 15$–65 with a step of 0·02 degree and a speed of 1 degree/min, using the CuKα radiation. The data processing was performed using a Casio 6000 computer; a search–match program supported by JCPDS cards[3] was used to identify the crystalline phases.

SEM observations were performed using a Cambridge Stereoscan 200 apparatus after 3 min of etching with 5% HF solution.

3 Results and Discussion

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

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

where α is the devitrification degree, β is the heating rate, T is the temperature, E the crystal growth activation energy, m the Avrami parameter, A a constant and N the number of nuclei formed in the range of efficient nucleation before the onset of the DTA devitrification peak.

When the devitrification is controlled by the interface reaction, the Avrami parameter changes from $m = 1$ for one-dimensional crystal growth (or growth from surface nuclei) to $m = 3$ for three-dimensional growth from bulk nuclei. The corresponding values for diffusion-controlled devitrification are $m = 0{\cdot}5$–$1{\cdot}5$.

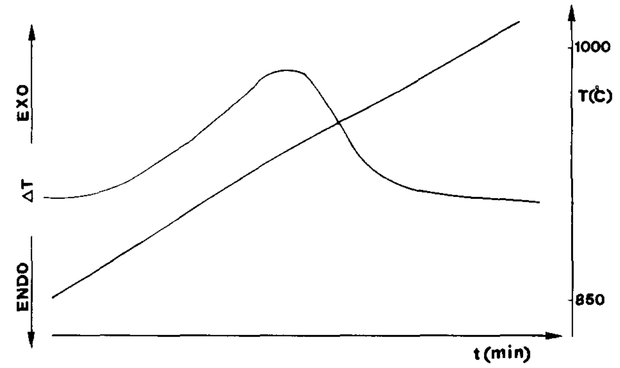

Fig. 1. DTA (20°C/min) and temperature–time curves relative to an as-quenched fine powder sample.

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

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

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

In Figs 1–3 some DTA traces (relative to a heating rate $\beta = 20$°C/min) are reported together with the

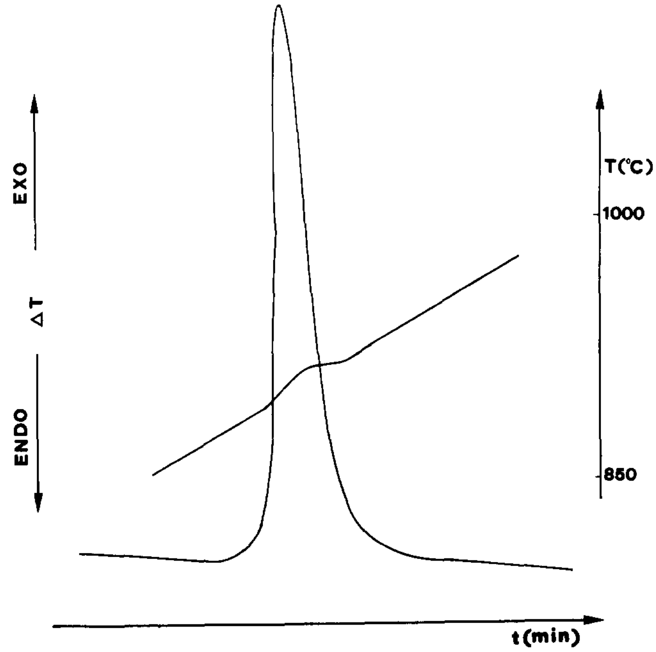

Fig. 2. DTA and temperature–time curves relative to a coarse powder sample heat-treated for 2 h at 735°C.

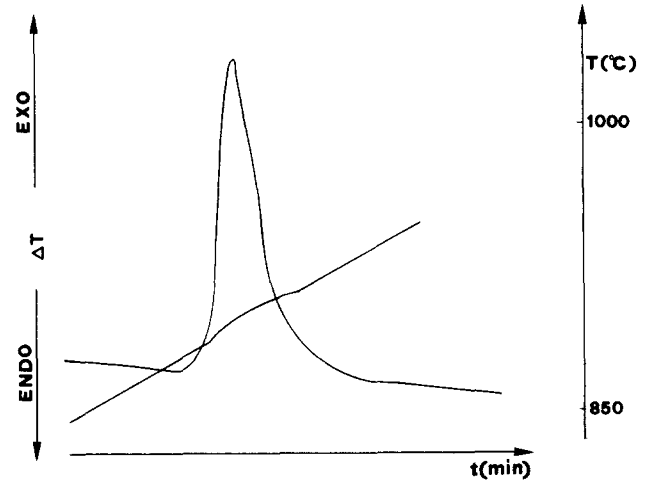

Fig. 3. DTA and temperature–time relative to a coarse powder sample heat-treated for 2 h at 735°C and diluted with Al_2O_3 in a ratio 1:3.

temperature recorded by the thermocouple put under the sample holder. The XRD spectrum relative to a sample submitted to a DTA run stopped at the end of the devitrification peak has been recorded. It differs from the one reported in Ref.[1] (relative to a isothermal treatment of 1 h at $T = 950°C$ of efficient devitrification rate) in the lack of titania reflections. The crystalline phase has been identified as clinoenstatite (JCPDS card 35/610) (which, recently, has been substituted for the 19/769 card also reported as relative to clinoenstatite).

As it is known, in a DTA apparatus, the temperature difference between the sample and a reference material (usually Al_2O_3) heated at a constant heating rate is recorded. As can be seen, owing to a too high value of the devitrification heat, in some experimental conditions (Fig. 2) the temperature–time dependence is, in correspondence of the devitrification peak, markedly changed from that programmed. As can be seen the effect is much less pronounced in the case of a fine powder sample (Fig. 1). The explanation should be that, in this case, devitrification is due predominantly to crystal growth of nuclei formed at the surface of the sample particles, that is,[8] the Avrami parameter should be $m = 1$. Therefore, taking into account eqn (1), the devitrification rate changes more slowly with the temperature, the overall process is accomplished in a larger range of temperatures and so the developed heat is less able to affect the heating rate. As can be seen (Fig. 3) a way to reduce this effect is to dilute the sample with Al_2O_3 powder. Therefore the kinetic study was lead on 'diluted' samples in a ratio to Al_2O_3 1:3.

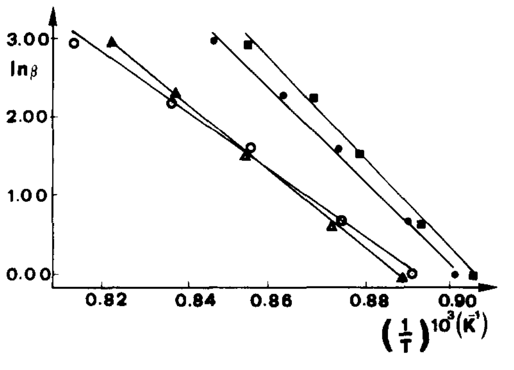

Fig. 4. In B versus $1/T_p$ curve. ○, As-quenched fine powder sample; △, as-quenched coarse powder sample; ●, coarse powder sample after 2 h at 730°C; ■, coarse powder sample after 15 h at 730°C.

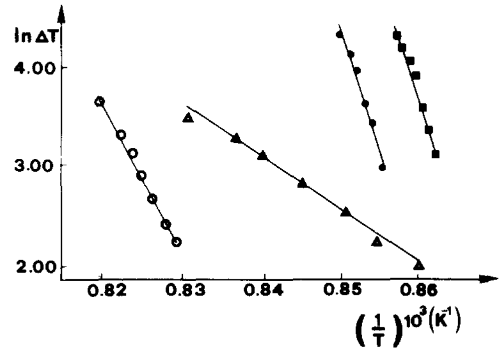

Fig. 5. In ΔT versus $1/T$ curve (20°C/min). ○, As-quenched fine powder; △, as-quenched coarse powder sample; ●, coarse powder sample after 2 h at 730°C; ■, coarse powder sample after 15 h at 730°C.

Two sets of DTA have been performed on fine and coarse powdered as quenched samples. The results have been plotted as $\ln \beta$ versus $1/T_p$ (Fig. 4) and $\ln \Delta T$ versus $1/T$ (Fig. 5). As predicted by eqns (2) and (3), straight lines have been obtained. The E and mE values calculated from their slopes are reported in Table 1. As can be seen, the powder size affects the Avrami parameter causing it to change from $m = 1$ to $m = 3$. This can be explained by taking into account that the devitrification from surface nuclei, whose number is proportional to the specific surface, is always in competition with that from bulk nuclei. Therefore, for samples of high specific surface, the surface devitrification becomes dominant and the Avrami parameter is reduced.[8] It is worth noting that, as pointed out previously, variations in the range $m = 1$–3 suggest that the devitrification should be controlled by the reaction at the glass–crystal

Table 1. Kinetic parameters

	E_c(*kJ/mole*)	mE_c(*kJ/mole*)
Fine powders	367	430
Coarse powder	321	1 177
Coarse powder (2 h at 730°C)	449	2 034
Coarse powder (15 h at 730°C)	484	1 966

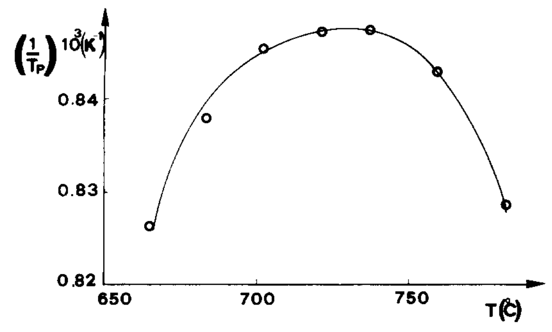

Fig. 6. Nucleation rate-like curve.

interface. In Fig. 4 the results relative to a series of coarse powder samples heat treated for the same length of time ($t = 2\,\text{h}$) at different temperatures in the glass transformation range are reported. All peak temperatures are lower than the as-quenched one. This is to be ascribed to differentiated nuclei formation during the reported heat treatments. Equation (1) can be rearranged as follows:[9]

$$\ln N = \frac{mE}{R}\left(\frac{1}{Tp}\right) + \text{const.} \tag{4}$$

Therefore the plot of $1/T_p$ versus the temperature of the nucleation heat treatment, reported in Fig. 6, indicates that the temperature of the more efficient nucleation rate is close to $T_N = 720°\text{C}$.

Finally two sets of DTA runs (1–20°C/min) were performed on coarse powder samples heat treated at $T = 730°\text{C}$. The data are plotted in Figs 4 and 5 and the kinetic parameters obtained are reported in Table 1. An increase in the activation energy value is observed. This is to be expected, because eqn (2) is derived by supposing that the number of nuclei is not dependent on the heating rate. This is true only when a suitable nucleation heat treatment has been performed on the samples. Therefore the correct activation energy value is $E_c = 467 \pm 20\,\text{kJ/mole}$, obtained from samples treated for 2 h and 15 h at $T = 730°\text{C}$ close to the maximum of the curve of Fig. 6. The obtained mE values are, nevertheless, consistent with the suggested devitrification mechanism.

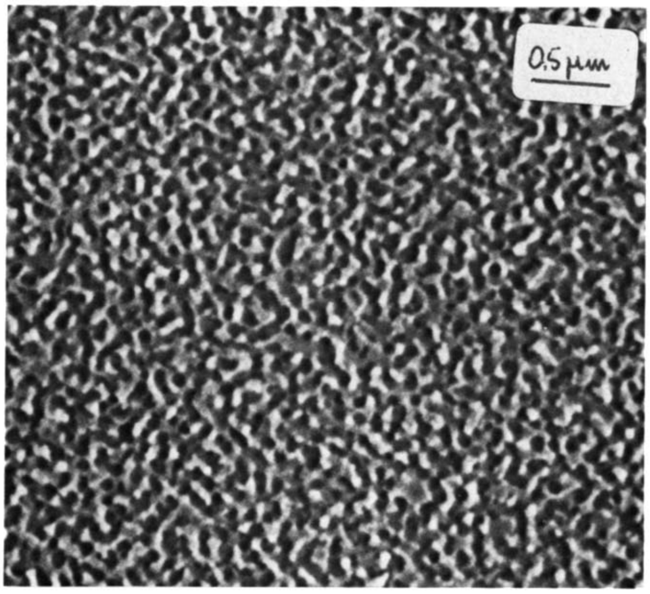

Fig. 7. SEM photograph of a sample heat-treated for 15 h at 735°C.

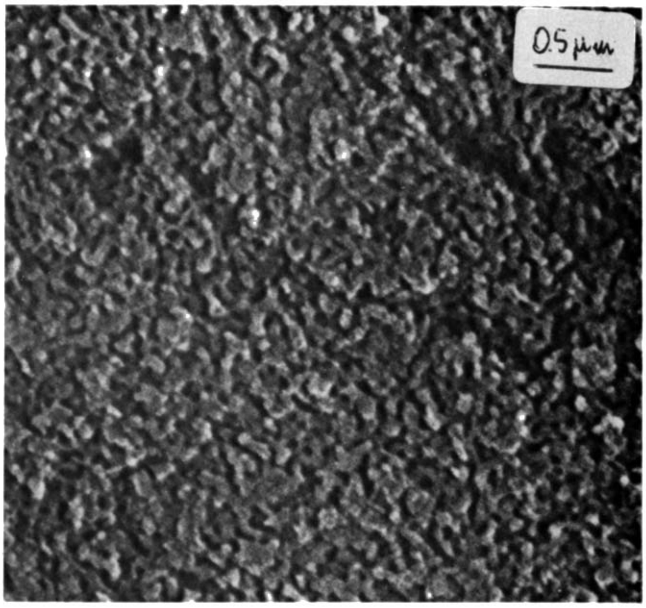

Fig. 8. SEM photograph of a sample after heat treatment for 15 h at 735°C and a DTA run stopped at the end of the devitrification peak.

In Fig. 7 the SEM photograph relative to a sample heat treated for 15 h at 735°C is reported. No difference is observed with respect to the as-quenched sample: the glass shows it to be demixed on a very fine scale. It is worth noting that, differently from the behaviour of the lower MgO-content glass,[2] the glass morphology appears not to be affected by the performed heat treatment. In Fig. 8 the SEM photograph relative to a devitrified sample is reported. The microstructural morphology confirms the thee-dimensional crystalline growth of bulk nuclei expected from the Avrami parameter values found.

4 Conclusions

The experimental data suggest the following conclusions:

(1) The crystals grow three-dimensionally with a mechanism controlled by the crystal–glass interface reaction.

(2) The crystal growth activation energy is $E_c = 467 \pm 20$ kJ/mole.
(3) The temperature of more efficient nucleation is $T_N = 720°C$.

No proof has been found of crystals growing from the glass–glass interfaces as in the mentioned lower MgO-content glass.[2]

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