Thermochimica Acta, 217 (1993) 207–212
Elsevier Science Publishers B.V., Amsterdam

Non-isothermal devitrification behaviour of diopside glass

F. Branda [*], A. Costantini and A. Buri

Dipartimento di Ingegneria dei Materiali e della Produzione, Università di Napoli, 80125 Naples (Italy)

(Received 7 July 1992)

Abstract

The non-isothermal devitrification of diopside $CaO \cdot MgO \cdot 2SiO_2$ glass has been studied. The crystal growth activation energy has been evaluated as $E_c \pm 137 \pm 10$ kcal mol^{-1}. The devitrification occurs in bulk samples through a surface nucleation mechanism. Surface nuclei behave as bulk nuclei in very finely powdered samples sintered before devitrifying. Optical and scanning electron microscopy support these conclusions.

INTRODUCTION

The non-isothermal devitrification of a glass of composition $CaO \cdot MgO \cdot 2SiO_2$ (the composition of the crystalline phase named diopside) has been studied. Diopside is one of the main crystalline phases that form in glass-ceramics based on the $CaO–MgO–Al_2O_3–SiO_2$ system obtained from natural rocks, mostly basalt, tuff, granite with additions of dolomite, limestone and nucleating agents [1]. Further the non-isothermal devitrification of diopside glass appears to be interesting for the consequences (that are shown here) of the fact that it occurs in the temperature range of efficient powder sintering.

EXPERIMENTAL

A glass of composition $CaO \cdot MgO \cdot 2SiO_2$ was prepared by melting $MgCO_3$, $CaCO_3$ and SiO_2 (analytical grade) at 1400°C in a platinum crucible in an electric oven for 4 h. The melt was quenched by plunging the

---

[*] Corresponding author.

bottom of the crucible into cold water. Differential thermal analysis (DTA) was carried out in air on powdered samples of about 40 mg at various heating rates (1–20°C min^{-1}). A Netzsch heat flux DSC 404 differential thermal analyser with Al_2O_3 powder as reference material was used.

Optical microscopy was performed by using a Leitz Epilux metallographic microscope. Scanning electron microscopy (SEM) was performed by means of a Cambridge model S-240 scanning electron microscope. Polished sections were etched with 5% HF solution.

RESULTS AND DISCUSSION

In Fig. 1 two DTA curves of the glass studied are reported, recorded at 10°C min^{-1} heating rate on fine (63–90 μm) and coarse (315–500 μm) powdered samples. As can be seen, the first slope change in the glass transformation range is followed by a second slope change at a temperature lower than the onset of the devitrification exo-peak. As a matter of fact, the initially powdered samples were recovered from the DSC sample holders as a porous sintered body. Therefore, the second slope change is to be linked to the change in the thermal exchange coefficients when the powders soften and sinter. As can be seen, the effect is much more pronounced in the finer powders.

The non-isothermal devitrification has been studied by using the two

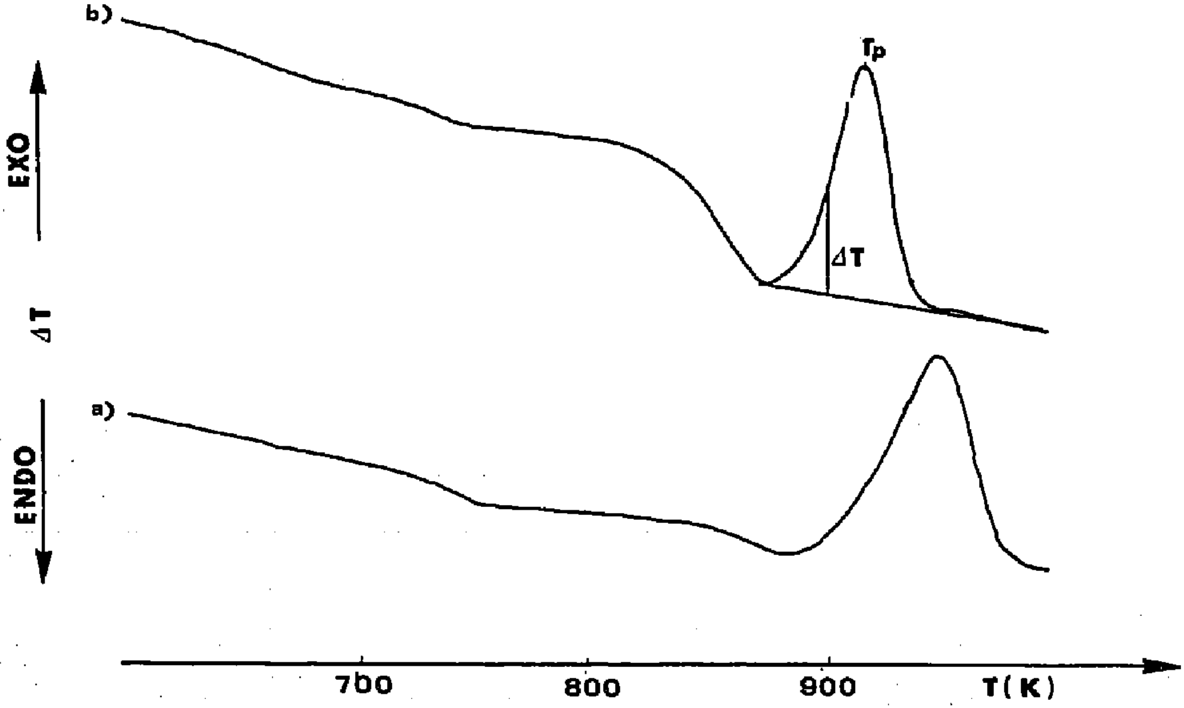

Fig. 1. DTA curves recorded at 10°C min^{-1} heating rate on 315–500 μm (a) and 63–90 μm (b) powdered samples.

equations

$$\ln \beta = -\frac{E_c}{RT_p} + \text{constant} \tag{1}$$

$$\ln \Delta T = -\frac{mE_c}{RT} + \text{constant} \tag{2}$$

where β is the heating rate, ΔT and T_p are the deflection from the baseline and the peak temperature taken as indicated in Fig. 1 respectively, and T is the temperature. As in inorganic glasses, the devitrification exo-peak occurs in a temperature range higher than that of efficient nucleation [2]; E_c is the crystal growth activation energy. The parameter m depends on the mechanism and morphology of crystal growth; it ranges from $m = 1$ for one-dimensional growth (or growth from surface nuclei) to $m = 3$ for three-dimensional growth.

When the number of nuclei is not dependent on the heating rate [2, 3]

$$-\ln(1-\alpha) = \frac{AN}{\beta^m}\exp\left(-\frac{mE_c}{RT}\right) \tag{3}$$

where α is the crystallization degree, N is the nuclei number and A is a constant.

Equations (1) and (2) can be derived from eqn. (3) by supposing: (i) α at peak temperature is not dependent on the heating rate [4]; (ii) ΔT is

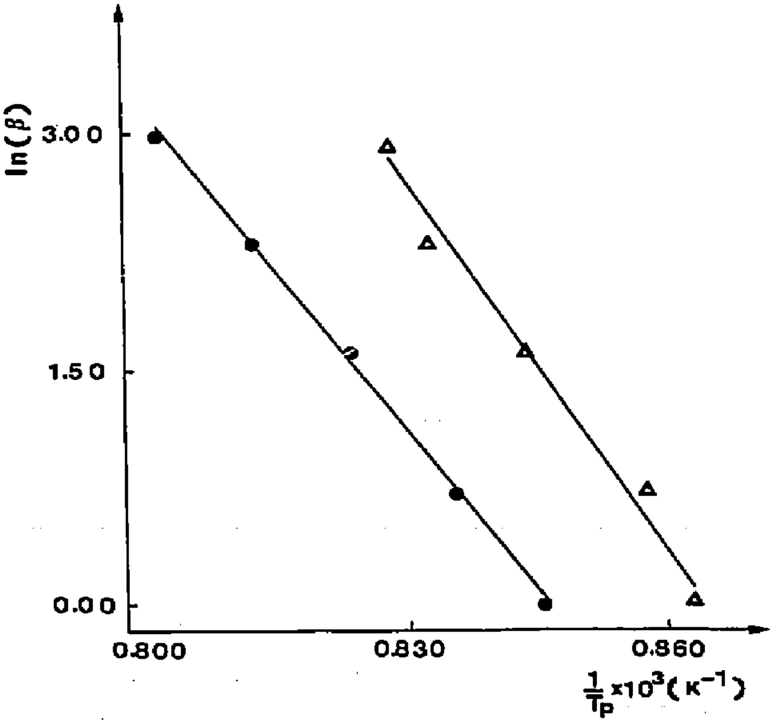

Fig. 2. Plot of $\ln \beta$ vs. $1/T_p$ relative to powdered samples: (●) 315–500 μm; (△) 63–90 μm.

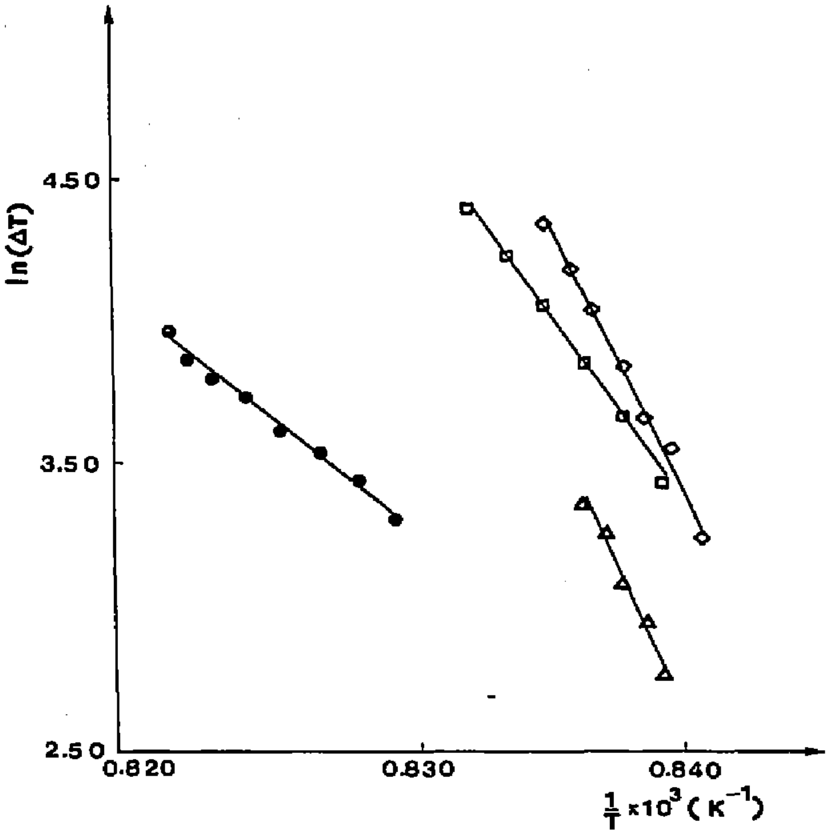

Fig. 3. Plot of ln ΔT vs. $1/T$. (●) 315–500 μm; (□) 90–125 μm; (△) 63–90 μm; (◇) 45–63 μm.

proportional to the instantaneous reaction rate [5, 6]; (iii) in the initial part of the DTA crystallization peak the change in the temperature has a much lower effect than α on ΔT [7].

In Figs. 2 and 3 the plots of ln β vs. $1/T_p$ and ln ΔT vs. $1/T$ are shown. The values of E_c and mE_c obtained from such plots by means of eqns. (1) and (2) are shown in Table 1.

The mE_c values appear to increase as the specific surface area of the samples is increased. The opposite result is usually obtained, owing to the

TABLE 1

Kinetic parameters

Powder diameter (μm)	E_c (kcal mol^{-1})	mE_c [a] (kcal mol^{-1})
315–500	127	155
90–125		274
63–90	148	426
45–63		392

[a] Taken from DTA recorded at 10°C min^{-1}.

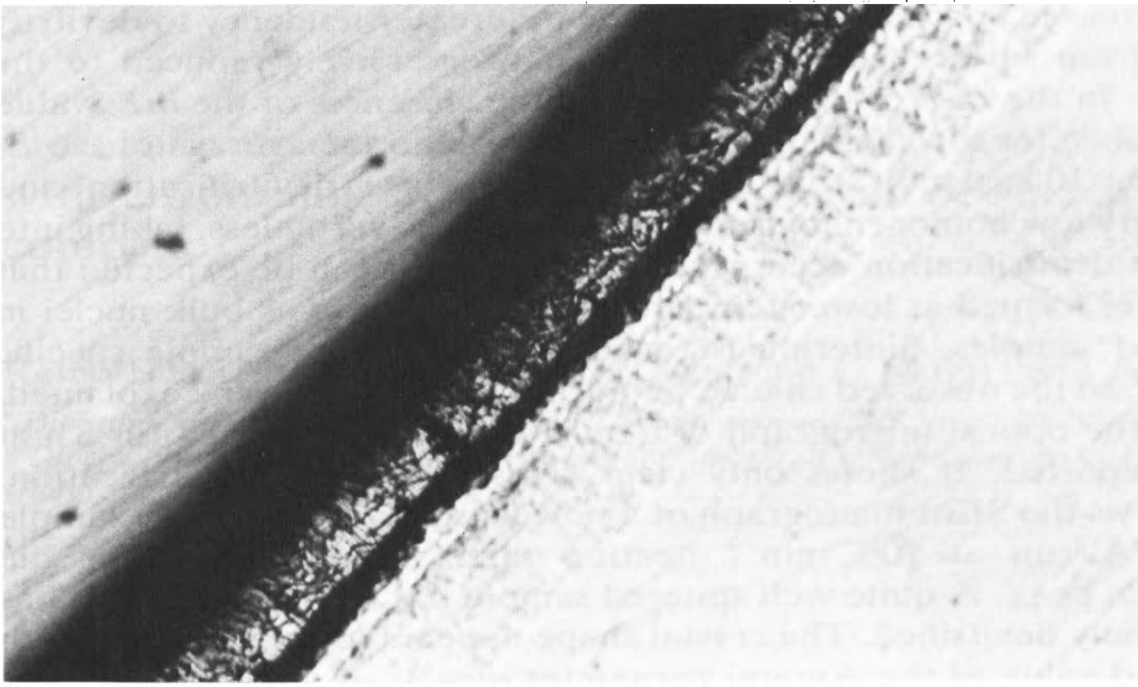

Fig. 4. Optical micrograph of bulk sample after 3 h at 1000°C (1 min etching, original magnification 200×).

Fig. 5. Scanning electron micrograph of powdered sample sintered and devitrified during a DTA run (3 min etching, original magnification 4000×).

fact that increased specific surface area means greater tendency to devitrify by growth from surface nuclei so that m is progressively reduced to the value $m = 1$. In the case of the glass studied the closeness of the mE_c value (155 kcal mol^{-1}) for the coarsely powdered sample to the average of the E_c values (137 ± 10 kcal mol^{-1}) is indicative of surface devitrification and therefore very low homogeneous nucleation rates. Nevertheless, taking into account that devitrification occurs during sintering, it can be expected that surface nuclei formed at lower temperatures, can behave as bulk nuclei in well sintered samples. Sintering is favoured by a higher sample specific surface area, so the observed change of m from 1 to 3 can thus be explained.

In Fig. 4 the optical micrograph of a bulk sample heat treated for 3 h at 1000°C is reported. It shows only clear signs of surface devitrification. Figure 5 shows the SEM micrograph of a powdered (170–230 mesh) sample after a DTA run at 10°C min^{-1} heating rate, stopped just after the devitrification peak. A quite well sintered sample has been obtained. It has been very finely devitrified. The crystal shape appears to be consistent with the measured value of the Avrami parameter $m = 3$.

CONCLUSIONS

The following conclusions can be drawn from the experimental results.

(1) The crystal growth activation energy $E_c = 137 \pm 10$ kcal mol^{-1}.

(2) The homogeneous nucleation rates are very low. Nevertheless, surface nuclei can behave as bulk nuclei in powdered samples that sinter before devitrifying.

REFERENCES

1 Z. Strnad, Glass-Ceramic Materials, Elsevier, Amsterdam, 1986.
2 K. Matusita and S. Sakka, Bull. Inst. Chem. Res. Kyoto Univ., 59 (1981) 159.
3 D.R. MacFarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
4 P.G. Boswell, J. Therm. Anal., 18 (1980) 353.
5 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
6 K. Akita and M. Kase, J. Phys. Chem., 72 (1968) 906.
7 F.O. Piloyan, I.V. Ryabchica and O.S. Novikova, Nature, 212 (1966) 1229.