ELSEVIER

Thermochimica Acta 280/281 (1996) 237–242

thermochimica acta

Devitrification behaviour of $CaO{\cdot}0.1P_2O_5{\cdot}0.9SiO_2$ glass [1]

A. Costantini *, R. Fresa, A. Buri, F. Branda

Dipartimento di Ingegneria dei Materiali e della Produzione, Università "Federico II" di Napoli, P.le Tecchio, Napoli, Italy

Abstract

In this paper the non-isothermal devitrification of a glass of composition $CaO{\cdot}0.1P_2O_5{\cdot}0.9SiO_2$ has been studied. Comparison with literature data about the glass $CaO{\cdot}SiO_2$ enables discussion of the influence of the equimolar substitution of P_2O_5 for SiO_2. The crystal growth activation energy is $E_c = 128 \pm 14\,\mathrm{Kcal\,mol^{-1}}$ and is lower than that for $CaO{\cdot}SiO_2$. The experimental results suggest that this effect can be linked to an analogous compositional effect on the viscous flow activation energy. A surface nucleation mechanism is operative as in the case of the parent glass $CaO{\cdot}SiO_2$. However the nucleation rates would be reduced as a result of the need for diffusion in the non-stoichiometric glass.

Keywords: Bioactive glasses; $CaO{\cdot}0.1P_2O_5{\cdot}0.9SiO_2$ glass; $CaO{\cdot}SiO_2$ glass; Crystal growth activation energy; DTA; Non-isothermal devitrification; Surface nucleation; Viscous flow activation energy; X-ray diffraction

1. Introduction

Growing interest in "bioactive glasses" is found in the literature. This term refers to glasses which enable the preparation of medical prostheses that differ from the traditional ones in their ability to form chemical bonds with bones [1, 2]. Glasses of the system $CaO–P_2O_5–SiO_2$ have been demonstrated to be bioactive and the composition range of bioactivity, in this system, has been defined [3]. In this paper devitrification behaviour is studied for the glass $CaO{\cdot}0.1P_2O_5{\cdot}0.9SiO_2$, whose composition lies in the bioactivity composition range. The results are compared with those of $CaO{\cdot}SiO_2$ glass published elsewhere [4] in order to evaluate the influence on the devitrification behaviour of substitution of small amounts of P_2O_5 for SiO_2.

---

* Corresponding author.

[1] Dedicated to Professor Hiroshi Suga.

SSDI 0040-6031(95)02645-2

2. Experimental

The glass of composition $CaO \cdot 0.1P_2O_5 \cdot 0.9SiO_2$ was prepared by melting analytical grade reagents $CaCO_3$, $NH_4H_2PO_4$ and SiO_2 in a platinum crucible in an electric oven for 2 h at 1600 °C. The melt was quenched by plunging the bottom of the crucible into cold water. A transparent glass was so obtained.

Differential thermal analysis (DTA) was performed by means of a Netzsch model 404 M differential scanning calorimeter on about 50 mg powdered samples at various heating rates (2–20 °C min^{-1}). Fine (63–90 μm) and coarse (315–500 μm) powdered samples were used. Powdered Al_2O_3 was used as reference material.

The devitrified sample was analysed in a computer-interfaced X-ray (CuKα) powder diffractometer (XRD) using a Philips model PW1710 diffractometer with a scan speed of 1 °C min^{-1} using a built-in computer search program. The crystalline phases were identified by means of JCPDS cards.

3. Results

In Fig. 1 the DTA curve is reported for a finely powdered sample. After a slope change in the glass transformation range, an exothermic peak appears as a result of devitrification.

In Fig. 2 the XRD pattern is reported for a sample submitted to a DTA run stopped just after the exothermic peak. The lines have been attributed by means of the JCPDS cards. As can be seen, wollastonite (JCPDS card 19/248) is formed but in a crystalline form different from that (JCPDS card 29/371) which forms in the stoichiometric glass. Cristobalite (JCPDS card 11/695) is also found.

The non-isothermal devitrification is well described by the well known equation [5, 6]:

$$-\ln(1-\alpha) = (AN/\beta^m)\exp(-mE_c/RT) \qquad (1)$$

where α is the degree of crystallization, N is the nucleus number, A is a constant and β is the heating rate. As in inorganic glasses the exothermic devitrification peak occurs in

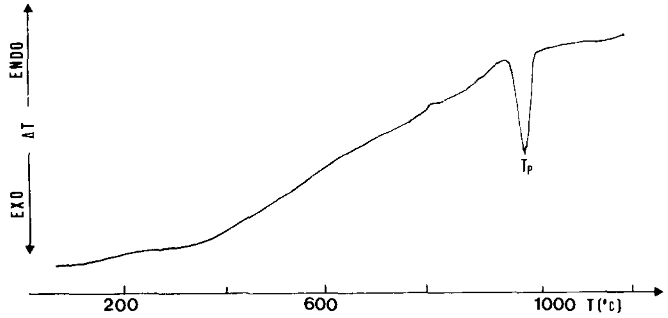

Fig. 1. DTA curve recorded at 10 °C min^{-1} heating rate on fine (63–90 μm) powdered sample.

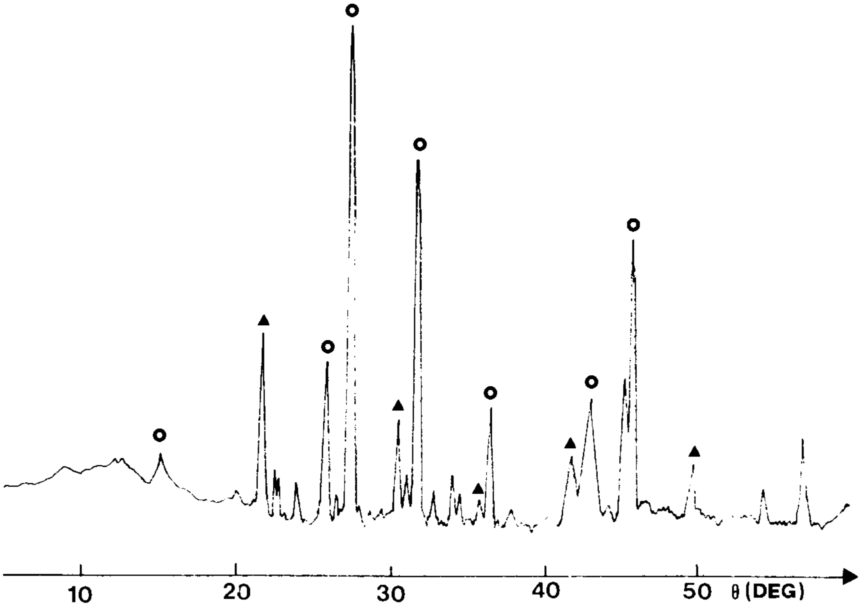

Fig. 2. XRD pattern after a DTA run stopped just after the exothermic peak. (○) CaO·SiO$_2$ (JCPDS card 19/248); (▲) cristobalite (11/695).

a temperature range higher than that of efficient nucleation [5], 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 1-dimensional growth (or growth from surface nuclei) to $m = 3$ for 3-dimensional growth [5, 6].

If the value of α at the peak temperature is not dependent on the heating rate [7] Eq. (1) gives:

$$\ln \beta = -E_c/RT_p + \text{const} \qquad (2)$$

where T_p is the peak temperature.

If the deflection from the baseline, ΔT, is proportional to the instantaneous reaction rate [8, 9] and, in the initial part of the DTA crystallization peak, the change in the temperature has a much greater effect than α on the ΔT [10], Eq. (1) also gives:

$$\ln \Delta T = -mE_c/RT + \text{const} \qquad (3)$$

In Fig. 3 the plots of $\ln \beta$ vs $1/T_p$ are reported; in Fig. 4 the plots of $\ln \Delta T$ vs $1/T$ are reported for finely and coarsely powdered samples. In accordance with Eqs. (2) and (3) straight lines were obtained.

The values of E_c are reported in Table 1; the same Table also reports values of mE_c, T_g and T_p taken from a DTA curve recorded at 10 °C min^{-1}. In Table 2 the same values are reported for CaO·SiO$_2$ glass; these values are taken from the literature [4].

As is known, in silicate glasses nucleation and crystal growth occur in well separated temperature ranges. Nucleation occurs just above T_g. In fact, usual assumption in

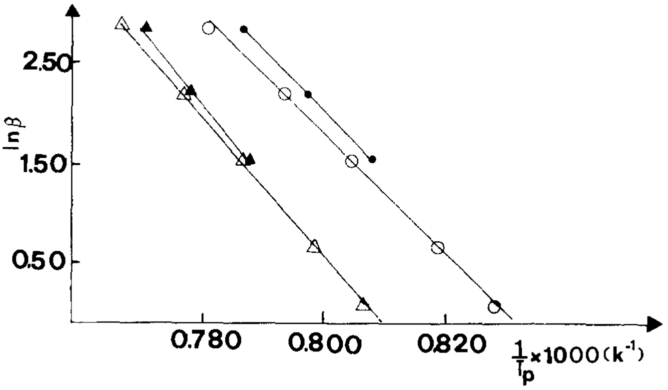

Fig. 3. ln β vs $1/T_p$ curves for quenched fine (○) and coarse (△) powders; fine (●) and coarse (▲) powders after DTA at $\beta = 1$ °C min until the onset of the exothermic peak, and cooling at 1 °C min^{-1}.

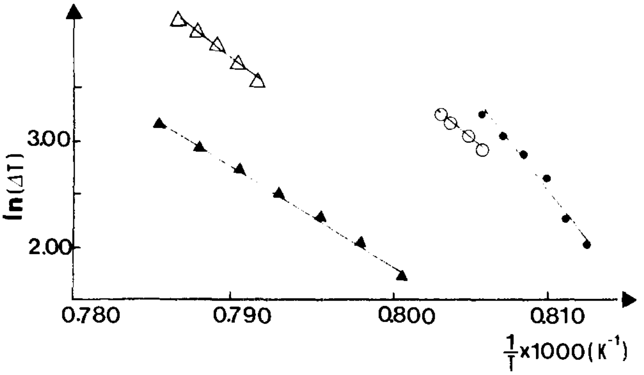

Fig. 4. ln ΔT vs $1/T$ curves. Symbols as in Fig. 3.

non-isothermal devitrification [5] is that the number of nuclei already formed at the onset of the DTA devitrification peak remains constant during devitrification. However their number can change depending on β [5], that is on the time spent in the temperature range of efficient nucleation. This has relevant consequences on the peak temperature–the effect is an error in the evaluation of E_c through Eq. (2). Otherwise in non-stoichiometric glasses, demixing can be expected to happen when the glass transformation range is entered. In this case E_c is expected to change. These are the reasons why two sets of fine- and coarse-powdered samples were heat treated at 1 °C min^{-1} up to the temperature of the onset of the exothermic peak and cooling at 1 °C min^{-1}. They were successively submitted to a DTA run at heating rates $\beta = 5$–20 °C min^{-1} so that the time spent in the glass transformation range, before devitrification occurred was not greater than 10% of the time spent during the previous heating-cooling cycle at 1 °C min^{-1}. The plots of ln β vs $1/T_p$ and ln ΔT vs $1/T$ are

Table 1
Glass transformation temperature, T_g/°C, peak temperature, T_p/°C, mE_c/(Kcal mol^{-1}) and E_c/(Kcal/mol^{-1}) for the CaO·0.1 P_2O_5·0.9SiO_2 glass

	E_c	mE_c	T_p	T_g
Fine powder	114	218	980	770
Coarse powder	126	208	1009	–
Fine powder[a]	120	272	974	–
Coarse powder[a]	142	160	1010	–

[a] after heating at 1 °C min^{-1} to the onset of the exothermic devitrification peak and cooling at 1 °C min^{-1}.

Table 2
Glass transformation temperature, T_g/°C, softening temperature, T_s/°C, peak temperature, T_p/°C, mE_c/(Kcal mol^{-1}) and E_c/(Kcal/mol^{-1}) for the CaO·SiO_2 glass

	E_c	mE_c	T_p	T_g	T_s
Fine powders	160	360	912	775	862
Coarse powders		250	940		

reported in the Figs. 3 and 4. The calculated values of E_c and mE_c are reported in Table 1. As can be seen, the value $E_c = 128 \pm 14$ Kcal mol^{-1} can be assumed.

4. Discussion

One difference between the behaviour of P_2O_5-substituted glass and that of the parent is that although the difference $T_p - T_g$ is increased, no softening effect is observed on the DTA curve before the exothermic devitrification peak occurs. Otherwise, in the case of CaO·SiO_2 glass, the initially finely powdered samples were taken out from the sample holder as well-sintered disks of glass ceramic [4]. This occurrence has been shown to have relevant consequences on the non-isothermal devitrification behaviour. In fact, surface nuclei formed just above the glass transformation temperature behave as bulk nuclei in the case of finely powdered samples that soften before devitrifying [4, 11]. In the present case, after the DTA cycle, the sample showed only slight signs of sintering. The addition of P_2O_5, therefore, influences the viscosity–temperature relationship. As long as an Arrhenius dependence of the viscosity, η, on the temperature holds, the addition of P_2O_5 reduces the activation energy for viscous flow, E_η.

The results reported in Table 1 show that an average value for the crystal growth activation energy can be assumed to be $E_c = 128$ Kcal mol^{-1}. This value is lower than that reported for the parent CaO·SiO_2 glass $E_c = 160$ Kcal mol^{-1}. The decrease can be explained if one admits that, as usually happens, $E_c = E_\eta$ [12]. Moreover the comparison of the exothermic peak temperatures, reported in Tables 1 and 2, shows that the

P_2O_5-substituted glass devitrifies in an higher temperature range than the $CaO \cdot SiO_2$ glass. This is another reason for the decrease of the E_c value. In fact it is known that an Arrhenius-type relationship of η on T holds in narrow temperature ranges. In large temperature ranges the viscosity depends on the temperature according to the Vogel-Fulker-Tamman equation [13] which implies that E_η decreases as the temperature range considered is increased.

Comparison of the mE_c values with those of E_c gives values $1 \leqslant m \leqslant 2$. The values for finely powdered samples are higher than those for coarsely powdered samples. These results suggest that a surface nucleation mechanism ($m = 1$) is operative as in the case of the $CaO \cdot SiO_2$ glass. One explanation of the higher values for finely powdered samples can be that, as in the case of the parent glass $CaO \cdot SiO_2$ [4], sintering enables surface nuclei to behave as bulk nuclei. The shift of the devitrification peak to an higher temperature range, although T_g is, lowered, suggests that the substitution of P_2O_5 for SiO_2 causes the nucleation rate to be decreased. This probably occurs because diffusion is required in the non-stoichiometric glass.

5. Conclusions

The activation energy for crystal growth is $E_c = 128 \pm 14\,\mathrm{Kcal\,mol^{-1}}$. A surface nucleation mechanism is operative, as in the case of the parent glass $CaO \cdot SiO_2$. The experimental results suggest that the addition of P_2O_5 has significant influence on the viscosity-temperature relationship and on the nucleation rate: the viscosity changes more slowly; the nucleation rates would be reduced as a result of the need for diffusion in the non-stoichiometric glass.

References

[1] L.L. Hench, J. Am. Ceram. Soc., 74 (7) (1991) 1487–1510.
[2] T. Kokubo, Bol. Soc. Esp. Ceram. Vidrio, Proc. XVI Int. Congr. Glass, Vol. 1, 31–C 1 (1992) 119–137.
[3] C. Ohtsuki, T. Kokubo and T. Yamamuro, J. Non-Cryst. Solids, 143 (1992) 84.
[4] F. Branda, A. Costantini, A. Buri and A. Tomasi, J. Therm. Anal., 41 (1994) 1479.
[5] K. Matusita and S. Sakka, Bull. Inst. Chem. Res., Kyoto Univ., 59 (1981) 159.
[6] D.R. MacFarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
[7] P.G. Boswell, J. Therm. Anal., 18 (1980) 353.
[8] H.J. Borchardt and F. Daniels, J. Am. Chem. Soc. 79 (1957) 41.
[9] K. Akita and M. Kase, J. Phys. Chem., 72 (1968) 906.
[10] F.O. Piloyan, I.V. Ryabchica and O.S. Novikova, Nature, London, 212 (1966) 1229.
[11] F. Branda, A. Costantini and A. Buri, Thermochim. Acta, 217 (1993) 207.
[12] K. Matusita and S. Sakka, J. Non-Cryst. Solids, 38/39 (1980) 741.
[13] H. Scholze (Ed.) "Le Verre", Institut du verre, Paris, 1980, p. 69.