A NEW PARAMETER TO EVALUATE NUCLEATION IN GLASSES FROM DTA CURVES

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ABSTRACT

Non-isothermal kinetic data relative to five silicate glasses are compared. The analysis of data suggests the use of a new parameter to obtain a rough estimate of the ability of different glass compositions to form nuclei and to select glass compositions which can, easily, give fine-grained glass ceramics.

INTRODUCTION

Methods have recently been proposed for studying the devitrification of glasses by means of differential thermal analysis (DTA). They are very rapid and, if compared with the traditional isothermal methods, require a very small amount of glass. These methods make it possible to evaluate the crystal growth activation energy and to obtain information about the devitrification mechanism; they have been used successfully several times [1–5]. It is also possible to distinguish the temperature range in which nucleation occurs with appreciable rates and, within it, the maximum nucleation rate temperature [6]. In this work, the crystal growth activation energy values of five silicate glasses are compared. Analysis of data suggests the use of a new parameter to obtain rough estimates of the ability of different glass compositions to form nuclei and hence to select glass compositions which can easily give fine-grained glass ceramics.

RESULTS AND DISCUSSION

When a glass is heated in a DTA apparatus, a curve like the one shown in Fig. 1 is recorded. At first a slope change is observed in the glass transformation range, where the glass is converted from a rigid body into a plastic one. Afterwards, when the viscosity has become low enough to allow rearrangements in the structure, devitrification occurs and the heat evolved is revealed by the appearance of an exo-peak on the DTA curve.
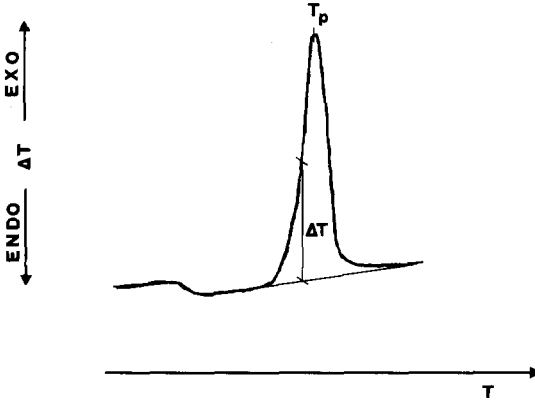
Fig. 1. Typical DTA curve of a glass.

Following classical theory, for not too small degrees of undercooling, the crystal growth rate U can be expressed as

$$U = U_0 \exp(-E_c/RT) \tag{1}$$

where E_c is the crystal growth activation energy; this is very often equal to the viscous flow activation energy. It is worth noting that the Arrhenius dependence of the viscosity on the temperature holds only in narrow temperature ranges. According to the Vogel equation, the viscous flow activation energy would decrease with temperature as

$$E_\eta = BR(T/T - T_0)^2 \tag{2}$$

where B and T_0 are the parameters of the Vogel equation [7]

$$\log \eta = A + \frac{B}{T - T_0}$$

If eqn. (1) holds and the number of nuclei is not dependent on the heating rate, the following equation correctly describes the non-isothermal devitrification of glasses [8,9]

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

where α is the volume fraction crystallized at temperature T, β is the DTA heating rate, A is, for each glass, a constant whose value depends on the preexponential factor U_0 of eqn. (1). N is the number of nuclei and can be expressed as [1]

$$N = N_s + N_h + N_n$$

where N_s is the surface nuclei number, which is proportional to the sample specific surface, N_h is the number of nuclei formed during the DTA run, which is inversely proportional to the heating rate, and N_n is the nuclei

number formed in a previous heat treatment. The parameter m depends on the mechanism and morphology of crystal growth. For the growth controlled by the reaction at the glass-crystal interface it ranges from $m = 1$, for one-dimensional growth (or growth from surface nuclei) to $m = 3$ for three-dimensional growth. For the diffusion-controlled growth the corresponding m range is 0.5–1.5.

Taking into account [10] that at peak temperature, T_p, the crystallization degree reaches the same specific value, independent of the heating rate, the following equation can be derived

$$\ln \beta = -\frac{E_c}{RT_p} + \text{const} \tag{4}$$

Moreover, as the deflection from the baseline ΔT is proportional to the instantaneous reaction rate [11] and, in the initial part of the DTA crystallization peak, the change in temperature has a much larger effect than α on the ΔT deflection [12], the following equation is obtained

$$\ln \Delta T = \frac{mE_c}{RT} + \text{const} \tag{5}$$

By means of eqns. (4) and (5), as described elsewhere [1–5], it is possible, by changing the specific surface or heat treating the glass samples, to get information about the devitrification mechanism. The crystal growth activation energy can be evaluated, by means of eqn. (4), when using samples of high specific surface, provided $N_s \gg N_h + N_n$, or samples heat treated at a temperature of high nucleation rate for a long enough time to have $N_n \gg N_s + N_h$.

The above type of analysis was performed on the five glass compositions reported in Table 1. All reported data are taken from the original papers [1–5]. All glasses showed a three-dimensional crystal growth controlled by the glass–crystal interface reaction ($m = 3$). The temperature of the heat treatment reported in the table footnotes is, for each system, very near to the maximum nucleation rate temperature; the nucleation time was always

TABLE 1

Non-isothermal kinetic data for the glasses studied

Glass compositon	E_c kcal mol^{-1}	T_p (K)	$\dfrac{E_c}{RT_p}$	N (m^{-3})
Li$_2$O·2SiO$_2$ [a]	59	899	33	9×10^{13}
0.9Li$_2$O·0.1BaO·2SiO$_2$ [b]	70	933	38	2×10^{14}
BaO·2SiO$_2$ [c]	99	1119	44	8×10^{15}
Na$_2$O·2CaO·3SiO$_2$ [d]	89	982	45	3×10^{15}
2Na$_2$O·CaO·3SiO$_2$ [e]	107	864	62	8×10^{16}

[a] 14 h at 475°C. [b] 750 h at 480°C. [c] 2 h at 700°C. [d] 2 h at 580°C. [e] 2 h at 480°C.

sufficient to have $N_n \gg N_s + N_h$. The reported E_c values were obtained by means of eqn. (4) using samples heat treated as indicated in the table footnotes. The peak temperature was detected on DTA curves recorded at $10\,^\circ C\ min^{-1}$ for the same kind of sample. In the last column is reported the number of nuclei which, following references 13 and 14, should be present in the glass sample after the specified heat treatment. As can be seen the values of crystal growth activation energy and the values of the DTA peak temperature vary widely from glass to glass, but the values of the dimensionless ratio E_c/RT_p appear to be correlated to the number of nuclei: the greater is N, the higher is the value of E_c/RT_p. A simple explanation can be given, as follows. The devitrification peak appears on the DTA curve when the number of nuclei, N, and the crystal growth rate, U, are great enough to allow devitrification to be performed. Therefore, when a glass is heated in a DTA apparatus the devitrification temperature range is dependent on the number of nuclei present in the glass; in particular, as long as variations in U_0 can be neglected, there must be a relation between the number of nuclei formed and the devitrification temperature range, which, taking into account eqn. (2), would also depend on the form of the glass viscosity–temperature curve.
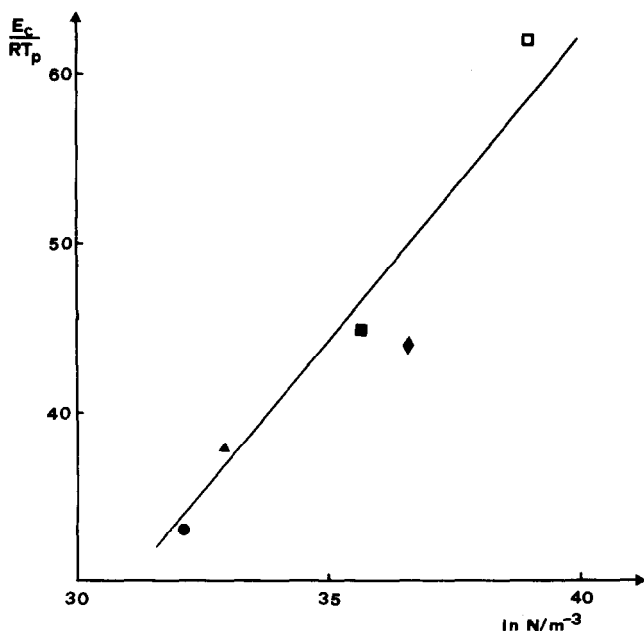

Fig. 2. Plot of the parameter E_c/RT (defined in the text) against the natural logarithm of the nuclei present, after the heat treatments reported in Table 1, in the following glasses: $Li_2O\cdot2SiO_2$ (●), $0.9Li_2O\cdot0.1BaO\cdot2SiO_2$ (▲), $BaO\cdot2SiO_2$ (◆), $Na_2O\cdot2CaO\cdot3SiO_2$ (■), $2Na_2O\cdot CaO\cdot3SiO_2$ (□).

Equation (3) can be rearranged

$$\frac{E_c}{RT_p} = \frac{1}{m} \ln \frac{AN}{\beta^m} + \text{const} \tag{6}$$

At the same heating rate and when m assumes the same value, if A is constant, a straight line should be obtained by plotting E_c/RT_p against $\ln N$. As shown in Fig. 1 this trend is obtained for the glasses studied.

The values of A are linked to the preexponential factor of eqn. (1) and cannot, a priori, easily be predicted. For glasses having very different compositions its value could vary widely. However the results suggest that an experimental evaluation of A could be very interesting. The knowledge of the values of A and E_c/RT_p could allow a rough estimate of the ability of different glass compositions to form nuclei and could be very useful in selecting glass compositions suitable for producing fine-grained glass ceramics.

REFERENCES

1 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
2 A. Marotta, S. Saiello, F. Branda and A. Buri, Thermochim. Acta, 46 (1981) 123.
3 A. Marotta, S. Saiello, F. Branda and A. Buri, Verres Réfract., 35 (1981) 477.
4 F. Branda, A. Buri, A. Marotta and S. Saiello, J. Mater. Sci. Lett., 3 (1984) 654.
5 F. Branda, A. Buri and A. Marotta; Thermochim. Acta, 120 (1987) 217.
6 A. Marotta, A. Buri, F. Branda and S. Saiello, Thermochim. Acta, 85 (1985) 231.
7 H. Sholze, Le Verre, nature, structure et propriétés, deuxième édition, Institut du Verre, Paris, 1980.
8 K. Matusita and S. Sakka, Bull. Inst. Chem. Res., Kyoto Univ., 59 (1981) 159.
9 D.R. Macfarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
10 T. Ozawa, Polymer, 12 (1971) 150.
11 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
12 F.O. Piloyan, I.V. Ryabchicov and O.S. Novikova, Nature (London), 212 (1966) 1229.
13 P.F. James, Nucleation and Crystallization in Glasses, American Ceramic Society, Ohio, 1982, p. 1.
14 A.M. Kalinina, V.N. Filipovich and V.M. Fokin, J. Non-Cryst. Solids, 38-39 (1980) 723.