Thermochimica Acta, 203 (1992) 373–378
Elsevier Science Publishers B.V., Amsterdam

Nucleation and crystal growth in inorganic glass-forming systems. A DTA study

F. Branda

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

Abstract

In this paper, a method for studying devitrification processes by means of DTA is reported, together with the results obtained for a large number of glassy systems. When literature isothermal data are available, a comparison is made. Good agreement is always found among the results of the two methods. A method based on thermoanalytical data is suggested for the rapid comparison of the stability of glasses of unlike compositions on heating.

INTRODUCTION

The usual method of obtaining kinetic data involves a series of experiments carried out under isothermal conditions at different temperatures, which is a laborious process. There is considerable interest in the study of devitrification kinetics by a dynamic method such as differential thermal analysis (DTA).

The aim of this paper is to show how devitrification has been successfully studied in a great number of glassy systems by means of DTA, with good agreement between non-isothermal and isothermal results. In addition, it is shown that a parameter can be defined which allows rapid comparision of the kinetics in glasses of unlike composites.

THEORETICAL EQUATIONS AND RESULTS

The process of crystal growth can be described by the following equation [1,2]

$$-\ln(1-\alpha) = A(N/\beta^n)\exp(-nE_c/RT) \qquad (1)$$

where α is the volume fraction crystallized at temperature T, E_c is the

---

Correspondence to: F. Branda, Dipartimento di Ingegneria dei Materiali e della Produzione, Università di Napoli, Italy.

Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

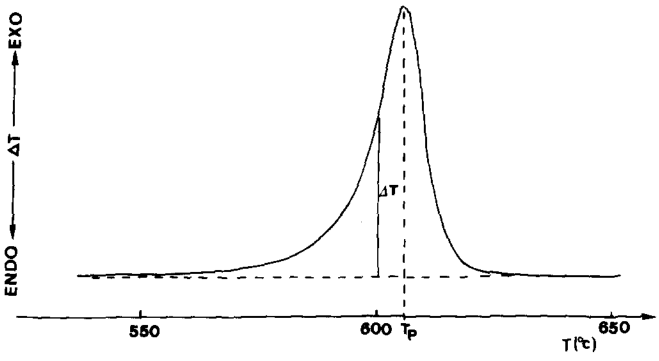

Fig. 1. Typical DTA curve.

activation energy for crystal growth, n is a parameter related to the crystallization mechanism, β is the DTA heating rate and A is a constant. Some relations can be derived [3] from eqn. (1), as reported below, which allow the devitrification kinetic parameters to be evaluated. It should be noted that the same relations can also be obtained [4,5] by using the well-known Johnson–Mehl–Arrhenius equation $-\ln(1-\alpha) = Kt^n$, and taking into account that, on a DTA curve, the deflection from the baseline ΔT is proportional to the instantaneous reaction rate [6,7], $\Delta T = C_1\, \mathrm{d}\alpha/\mathrm{d}T$, and that at the DTA peak temperature, $\mathrm{d}\Delta T/\mathrm{d}T = 0$.

Crystal-growth kinetic parameters

The deflection from the baseline ΔT taken as indicated in Fig. 1, is proportional to the instantaneous reaction rate [6,7] and, in the initial part of the DTA crystallization peak, the change in temperature has a much greater effect than α on the deflection [8]; therefore, eqn. (1) leads to

$$\ln \Delta T = (nE_c/RT) + \text{const.} \qquad (2)$$

The condition that at the DTA crystallization peak temperature T_p the crystal volume fraction α reaches the same specific value independent of β and n, leads to [9]

$$\ln N - \ln \beta^n = (nE_c/R)1/T_p + \text{const.} \qquad (3)$$

If DTA runs are carried out at different heating rates, provided the number of nuclei can be considered constant, the following equation is obtained

$$\ln \beta = -(E_c/RT_p) + \text{const.} \qquad (4)$$

Equations (2) and (4) can be used to determine the values of E_c and n from plots of $\ln \beta$ versus $1/T_p$ and $\ln \Delta T$ versus $1/T$.

Nucleation-like curves

A nucleation-like curve can be obtained from thermoanalytical data and the temperature of maximum nucleation rate can be evaluated [3,5]. The non-isothermal devitrification of a glass is the result of two individual processes: nucleation and crystal growth. The number of nuclei per unit volume is the sum of the surface nuclei N_s, the bulk nuclei formed during the DTA run N_h, and the bulk nuclei formed during a previous heat treatment of nucleation N_n

$$N = N_s + N_h + N_n \tag{5}$$

If the DTA runs are carried out on samples of the same specific surface at the same heating rate β, the sum N_o of the surface nuclei N_s, and the bulk nuclei formed during the DTA run N_h, is constant, and eqn. (3) becomes, for a previously nucleated sample

$$\ln(N_o + N_n) = (nE_c/R)(1/T_p) + \text{const.} \tag{6}$$

and for an as-quenched sample ($N_h = 0$)

$$\ln N_o = (nE_c/R)(1/T_p) + \text{const.} \tag{7}$$

From eqns. (4) and (5), the following equation can be derived

$$\ln(N_o + N_n)/N_o = (nE_c/R)(1/T_p - 1/T_p^\circ) \tag{8}$$

If bulk samples (low specific surface) are used, the DTA runs carried out at a high heating rate (20°C min^{-1}) and the samples nucleated for a long time ($t_n = 2$ h)

$$N_n \gg N_o \tag{9}$$

Because the number of nuclei N_n is related to the time t_n of nucleation heat-treatment by

$$N_n = It_n^b \tag{10}$$

where I is the kinetic rate constant of nucleation and b is a parameter related to the nucleation mechanism, then if the samples are held for the same time t_n at each temperature T_n of the heat treatment, the following approximated equation can be derived from eqn. (6)

$$\ln I = (nE_c/R)(1/T_p - 1/T_p^\circ) + \text{const.} \tag{11}$$

By plotting $(1/T_p) - (1/T_p^\circ)$ against the T_n of the nucleation heat-treatment, a nucleation rate–temperature-like curve is obtained (Fig. 2) and the temperature of maximum nucleation rate can be determined [3].

Evaluation of glass stability

Equation (1) can be written

$$E_c/RT_p = ((1/n)\ \ln(AN/\beta^n)) - \left(\ln\left(-\ln(1-\alpha_p)\right)/n\right) \tag{12}$$

where A depends on the pre-exponential factor U° of the growth rate (U) equation [1,2]:

$$U = U^\circ \exp(-E_c/RT) \tag{13}$$

using eqn. (12), a rapid comparison of the glass stability of unlike glass compositions can be made [10]. It is worth noting that for α_p variations in the range 0.2–0.8, the corresponding variations of $\ln(-\ln(1-\alpha_p))/n$, usually affect the (E_c/RT_p) value by less than 2%. Therefore when T_p is taken from DTA curves (recorded at the same heating rate) relative to samples of unlike compositions in which bulk crystallization is dominant ($m = 3$), greater values of E_c/RT_p are indicative of greater values of N formed on heating and/or greater crystal growth rates, i.e. a greater tendency to devitrify on heating.

If T_p values are taken from DTA curves, recorded at the same heating rates, relative to samples of unlike composition previously heat-treated for the same time at the temperatures of the maximum nucleation rate, eqn. (12) leads to

$$(E_c/RT_p)_i - (E_c/RT_p)_j = (1/n)\ \ln(I_iA_i/I_jA_j) \tag{14}$$

where subscripts i and j refer to unlike glass compositions. Equation (14) can be used to determine rapidly those compositions that are more likely, from a kinetic point of view, to give glass ceramics [11].

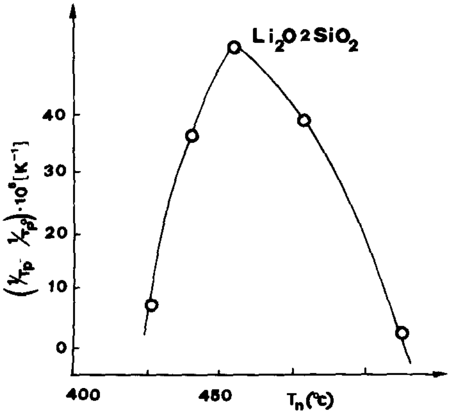

Fig. 2. Nucleation-like curve of $Li_2O\cdot 2SiO_2$ glass.

TABLE 1

Activation energies E_c and E_c' (kcal mol^{-1}), Avrami parameters n and n', and temperature of maximum nucleation rates, T_N and T_N' (°C) of reported glasses evaluated by means of isothermal and non-isothermal methods; superscript refers to literature isothermal data

	E_c	T_N	n	Ref.	E_c'	T_N'	n'	Ref.
$Ca_2Al_2SiO_7$	135		1	12	148		1	12
GeO_2	55		1	13	54		1	14
$3BaO\cdot5SiO_2$	92		2.7	13	100		3	15, 16
$Li_2O\cdot2SiO_2$	65	455	1.0–3.9	5, 17	65	455		18, 19
$Na_2O\cdot2CaO\cdot3SiO_2$	89	580	1.0–3	20	78	580		21, 22
$2Na_2O\cdot CaO\cdot3SiO_2$	107	500	1.8–2.8	23	102	500		24
$Na_2O\cdot2SiO_2$	51	–	1	25	58			26
$Na_2O\cdot SiO_2$	74	430	1	27			1	28
$Na_2O\cdot P_2O_5$	22		2	29	20		2	30, 31
$BaO\cdot2SiO_2$	99	700	–	32	–	700	–	33
$0.9Li_2O\cdot0.1BaO_2SiO_2$	70	480	1.0–2.5	34	–	480		33

RESULTS

Equations (2), (4) and (11) have been applied to study nucleation and crystal growth in many glassy systems. Table 1 reports the results relative to systems whose isothermal data are available in the literature. As can be seen, good agreement was always found.

CONCLUSIONS

The kinetic data obtained by means of the thermoanalytical methods are in good agreement with those obtained under isothermal conditions. They can be used to compare rapidly the glass stability of unlike compositions or to assess the ability, from a kinetic point of view, of the glass to form ceramic materials.

REFERENCES

1 K. Matusita and S. Sakka, Bull. Inst. Chem. Res. Kyoto Univ., 59 (1981) 159.
2 D.R. McFarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
3 A. Marotta, A. Buri, F. Branda and S. Saiello, Thermochim. Acta, 85 (1985) 231.
4 A. Marotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
5 A. Marotta, A. Buri and F. Branda, J. Mater. Sci., 16 (1981) 341.
6 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
7 K. Akita and M. Kase, J. Phys. Chem., 72 (1968) 906.
8 F.O. Piloyan, I.V. Ryabchica and O.S. Novikova, Nature, 212 (1966) 1229.
9 P.G. Boswell, J. Therm. Anal., 18 (1980) 353.
10 F. Branda, A. Marotta and A. Buri, J. Non-Cryst. Solids, 134 (1991) 123.
11 F. Branda, A. Marotta and A. Buri, Thermochim. Acta, 144 (1989) 117.
12 A. Marotta, A. Buri and G.L. Valenti, J. Mater. Sci., 13 (1978) 2483.

13 A. Marotta, A. Buri and P. Pernice, Phys. Chim. Glasses, 21 (1980) 94.
14 P.J. Vergano and D.R. Ulhmann, Phys. Chem. Glasses, 11 (1970) 30.
15 J.F. MacDovell, Proc. Br. Ceram. Soc., 3 (1965) 229.
16 S.W. Freiman, G.Y. Onada and A.G. Pincus, J. Am. Ceram. Soc., 55 (1972) 354.
17 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
18 P. Hantjavi, A. Velianon, V. Komppa and E. Pajanni, J. Non-Cryst. Solids, 29 (1978) 365.
19 P.F. James, Phys. Chem. Glasses, 15 (1974) 95.
20 A. Marotta, S. Saiello, F. Branda and A. Buri, Thermochim. Acta, 46 (1981) 123.
21 C.J.R. Gonzales Oliver, P.J. Johnson and P.F. James, J. Mater. Sci., 14 (1979) 1159.
22 C.J.R. Gonzales Oliver and P.F. James, J. Non-Cryst. Solids, 38/39 (1980) 699.
23 A. Marotta, S. Saiello, F. Branda and A. Buri, Verres Refract., 35 (1981) 477.
24 A.M. Kalinina, V.N. Filipovich and V.M. Fokin, J. Non-Cryst. Solids, 38/39 (1980) 723.
25 F. Branda, A. Buri, A. Marotta and S. Saiello, Thermochim. Acta, 77 (1984) 13.
26 W.D. Scott and J.A. Pask, J. Am. Ceram. Soc., 44 (1956) 181.
27 F. Branda, A. Buri, A. Marotta and S. Saiello, Verres Refract., 38 (1984) 589.
28 A.N. Winchell and H. Winchell, The Microscopical Characters of Artificial Inorganic Solid Substances: Optical Properties of Artificial Minerals, Academic Press, New York, 1964, p. 268.
29 F. Branda, A. Buri, A. Marotta and G. Mascolo, Thermochim. Acta, 98 (1986) 363.
30 A.E.R. Westman and M. Krishna-Murthy, in M.K. Reger, G. Smith and A. Insley (Eds.), Symp. on Nucleation and Crystallization in Glasses and Metals, American Ceramic Society, Columbus, OH, 1962, p. 91.
31 L.B. Morgan, Philos. Trans. R. Soc. London Ser. A., 247 (1954) 12.
32 F. Branda, A. Buri, A. Marotta and S. Saiello, J. Mater. Sci. Lett., 3 (1984) 654.
33 P.F. James, in J.H. Simmons, D.R. Uhlmann and G.H. Beall (Eds.), Nucleation and Crystallization in Glasses, Advances in Ceramics, Vol. 4, The American Ceramic Society, Columbus, 1982, p. 1.
34 F. Branda, A. Buri and A. Marotta, Thermochim. Acta, 120 (1987) 217.