Thermochimica Acta, 227 (1993) 125–133
Elsevier Science Publishers B.V., Amsterdam

Non-isothermal kinetic equations applied to crystallization of glasses [1]

L. Barbieri, C. Leonelli, T. Manfredini, M. Romagnoli, G.C. Pellacani * and C. Siligardi

Department of Chemistry, University of Modena, Via Campi 183, 41100 Modena, Italy

(Received 9 February 1993; accepted 1 April 1993)

Abstract

Three of the most important equations for evaluating the activation energy of a chemical reaction are discussed in the present paper: a modification of the Kissinger equation, a graphic method and a derivative method. They are based on thermal analysis measurements under non-isothermal conditions. These mathematical approaches were applied to the study of the crystallization of quaternary glassy systems RO–MgO–Al_2O_3–SiO_2 (where R is Ca, Sr, Ba, Zn), which separate from two to four crystalline phases. The nucleation mechanism was also determined by equations applied to DTA curves. Although the activation energy values obtained are similar to those given in the literature, some significant differences were present that depend on the method used and the nature of the crucibles.

INTRODUCTION

Kinetic studies are necessary both to determine the nucleation mechanism and to verify the crystal growth mechanism of the phases formed. Different equations are used to evaluate the activation energy for the crystallization of glasses. Experiments were performed under non-isothermal conditions in order to consider the trend of many crystallization processes that occur too rapidly to be measured under isothermal conditions. Three of the most important equations were used in this paper to elaborate non-isothermal DTA data. The first equation is the so-called Kissinger method [1], based on the analysis of the variation of the maximum peak temperature with the heating rate. The second equation analysed [2] is a graphic correlation of the advancement of the reaction with

---

* Corresponding author.

[1] Presented at the 14th National Conference on Calorimetry and Thermal Analysis, Udine, Italy, 13–17 December 1992.

the temperature, according to the peak shape. The last equation [3] is a derivative method in which the DDTA data are used to evaluate the reaction kinetic.

Many equations have been proposed for the evaluation in glasses [4] of n, the Avrami parameter, and m, the dimensionality of crystal growth. This is possible by correlating the reaction advancement, e.g. the crystallization peak area and the heating rate.

This mathematical approach to kinetic study was applied in this work to four quaternary glassy systems, deriving from the compositions 25% CaO–14% MgO–11% Al_2O_3–50% SiO_2 and 25% RO–20% MgO–5% Al_2O_3–50% SiO_2 (mol%) [5], where R is Ca, Sr, Ba, Zn. These glasses separated into two (Ca), three (Zn), or even four (Sr, Ba) crystalline phases during a crystallization treatment and, because no nucleating agent was added, a single heating step for both nucleation and crystal growth was required.

EXPERIMENTAL PROCEDURE

The glassy systems (Table 1) were obtained by the traditional method of fusion in an electric kiln. The raw materials, reagent-grade oxides and carbonates of high-quality (Carlo Erba, Milan), were mixed in mullite crucibles and melted at about 1400°C. After quenching in water, the glasses were ground to a fine particle size (<20 μm) and stored in a oven at 120°C to prevent moisture attack until used for DTA measurements. The fine particle size was chosen to avoid any eventual bulk crystallization [6]. The DTA measurements were performed with a Netzsch STA 409 in static air, in both platinum (20 mg sample) and alumina (100 mg sample) crucibles. All the experiments were made in non-isothermal conditions at the different heating rates of 2, 5, 10 and 20°C min^{-1}. The curves were recorded automatically and corrected with a blank run obtained by using calcined kaolin as sample and reference material. Typical DTA curves are reported in Fig. 1, which shows no concomitant formation of different crystalline

TABLE 1

Compositions of the glassy systems (wt.%) and the corresponding main crystalline phases

		R–O	MgO	Al_2O_3	SiO_2	Main cryst. phases
R = Ca	A25-D75	14	24	9	53	Diopside, anorthite
	A50-D50	9	23	18	50	Anorthite, diopside
R = Ba	A25-BaO	47	10	6	37	Celsian, exacelsian
						Sr-celsian
R = Sr	A25-SrO	37	12	8	43	Sr-Mg-silicate
R = Zn	A25-ZnO	32	13	8	47	Gahnite, willemite

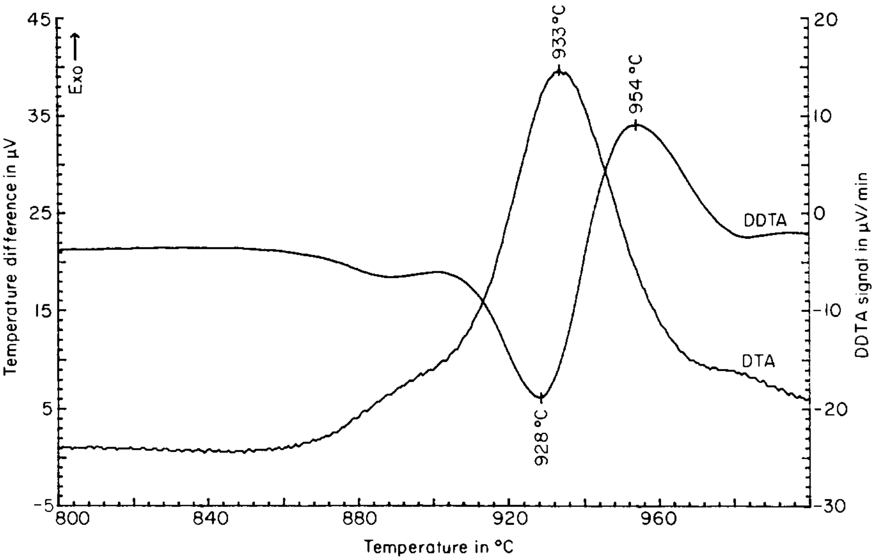

Fig. 1. DTA and DDTA curves for A50-D50 glass (20 μm) heated in alumina crucibles at 10°C min^{-1}.

phases. In the DTA curves of A25-BaO or A25-SrO glasses recorded in alumina crucibles at high heating rates, the exothermic peak is the result of different exothermal events which occur simultaneously, so that graphic and DDTA methods were not applicable.

MATHEMATICAL APPROACH

The so-called Kissinger method

This method [1], derived from the more general Kissinger equation, is the only one of the three considered that refers to the crystallization process in the glass by considering the surface/bulk nucleation mechanism and the dimensionality of crystal growth. The expression given by Matusita and coworkers [7, 8] of the so-called Kissinger equation for a non-isothermal measurement is

$$\ln(\Phi^n/T_p^2) = -mE_c/RT_p + \text{constant} \qquad (1)$$

where E_c is the activation energy for crystallization (cal mol^{-1}); R is the gas constant (1.9872 cal mol^{-1} K^{-1}), T_p is the maximum temperature of the exothermic crystallization peak (K), n is a constant known as the Avrami parameter, m represents the dimensionality of crystal growth, and Φ is the heating rate (°C min^{-1}). When surface crystallization predominates, several papers [4, 7, 8] suggest using $m = n = 1$, so that eqn. (1) becomes

$$\ln(\Phi/T_p^2) = -E_{cK}/RT_p + \text{constant} \qquad (2)$$

where E_{cK} is the correct Kissinger activation energy for crystallization.

The graphic method

This method [9], like the following one, refers to a generic process that shows an exothermic or endothermic peak

$$\ln \Delta t = C' - \frac{E_G}{RT} \tag{3}$$

where E_G is the activation energy of the chemical reaction (cal mol^{-1}), in this case the activation energy of crystallization, C' is a constant, and T is the temperature (K) corresponding to a given value of Δt (cm); Δt values represent the deviation of some points of the DTA curve from the baseline. It is important to note that the Δt values are taken in a range corresponding to a crystallization degree of 40%. The evaluation of the partial area of the peak of crystallization S is chosen so as to obtain a ratio α with the total area S_0 of about 0.4 ($\alpha = S/S_0 = 0.4$).

The DDTA method

The derivative method [3] is applicable when there is the possibility of recording a simultaneous derivative curve (DDTA) together with the DTA measurements. The equation is

$$\frac{E_M}{R}\left(\frac{1}{T_{f_1}} - \frac{1}{T_{f_2}}\right) = 1.59 \tag{4}$$

where E_M is the activation energy, in this case, of crystallization (cal mol^{-1}), and T_{f_1} and T_{f_2} (K) are respectively the DDTA peaks corresponding to the first and the second inflection points of the DTA curve. The factor 1.59 is a constant whose value depends on the devitrification mechanism, and has this value when the surface nucleation mechanism is active.

Determination of the m *and* n *parameters*

The value of n is determined from the Ozawa equation [10]

$$\left.\frac{\mathrm{d}\ln(-\ln(1-x))}{\mathrm{d}\ln\Phi}\right|_T = -n \tag{5}$$

where x is the volume fraction crystallized at temperature T when heated at a heating rate Φ, i.e. x is the ratio of the partial area S (at T) to the total area S_0 of the crystallization peak. To obtain n, it is necessary to plot $\ln(-\ln(1-x))$ versus $\ln\Phi$ at different temperatures.

The *m* parameter is obtained using the equation [7]

$$\ln(-\ln(1-x)) = -mE_c/RT + \text{constant} \qquad (6)$$

where *x* is determined in the same way as for eqn. (5), but at a different temperature *T* (K) for each single crystallization peak.

Considering eqn. (6) and (2), once *n* is known the *m* parameter can be evaluated using the expression

$$E_c = (n/m)E_{cK}$$

a relation which, for most oxide–glass systems, is within the error range of the DTA experiment.

RESULTS AND DISCUSSION

The nucleation mechanism of the base compositions with calcium has been shown to be surface catalysed [6]; as a consequence it should be assumed that $m = n = 1$. This equality was confirmed by evaluating these parameters experimentally when R is Ba, Sr, and Zn, by applying eqns. [5] and [6] to their DTA curves. For example, for the A25-SrO system, it was found that $n = 0.85 \simeq 1$ and $m = 0.74 \simeq 1$. The results of these kinetic studies were also confirmed by scanning electron microscopy. Figure 2 shows an SEM micrograph of A25-SrO glass ceramic in which a surface-crystallized layer and the presence of glass in the core are evident.

The activation energy values for crystallization were determined using

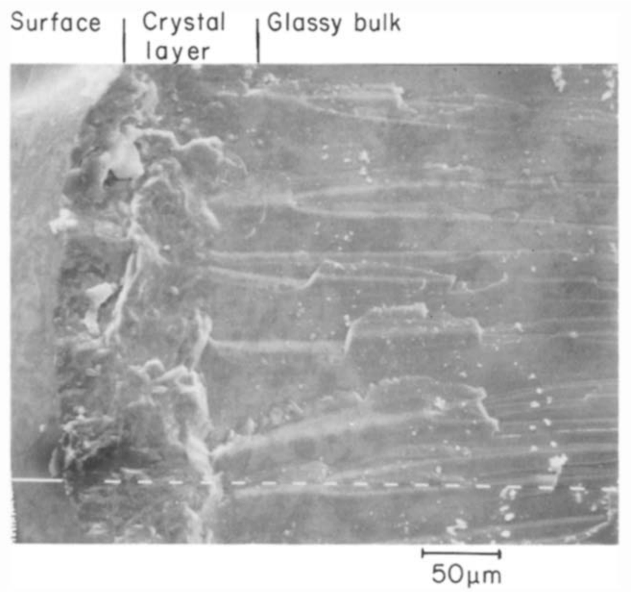

Fig. 2. SEM micrograph of freshly fractured A25-SrO glass-ceramic rod treated at 1100°C for 1 h (original magnification, ×320).

TABLE 2

Average activation energy values (kcal mol^{-1}) obtained using the so-called Kissinger equation E_{cK}, and the graphic E_G and the DDTA E_M methods in platinum and alumina crucibles

	Platinum crucible		
	E_{cK} (5, 10, 20°C min^{-1})	$\bar{E}_G$ (5, 10, 20°C min^{-1})	$\bar{E}_M$ (5, 10, 20°C min^{-1})
A25-D75	117	234	185
A50-D50	122	226	269
A25-BaO			
A25-SrO			
A25-ZnO	115	215	98
	Alumina crucible		
	E_{cK} (2, 5, 10, 20°C min^{-1})	$\bar{E}_G$ (2, 5, 10, 20°C min^{-1})	$\bar{E}_M$ (2, 5, 10, 20°C min^{-1})
A25-D75	113	108	116
A50-D50	125	151	160
A25-BaO	98, 85	121	
A25-SrO	81	163	
A25-ZnO	124	195	193

the three different equations mentioned above, once the nucleation mechanism was identified. From the data elaboration, it was apparent that the activation energy values (mean values for the graphic and DDTA methods) are different and depend on the mathematical approach (Table 2), as already observed by Chakraborty et al. [11]. For all the compositions, both the so-called Kissinger and the graphic methods gave a plot with a linear trend, verifying their suitability (Figs. 3 and 4). Figure 3 reports

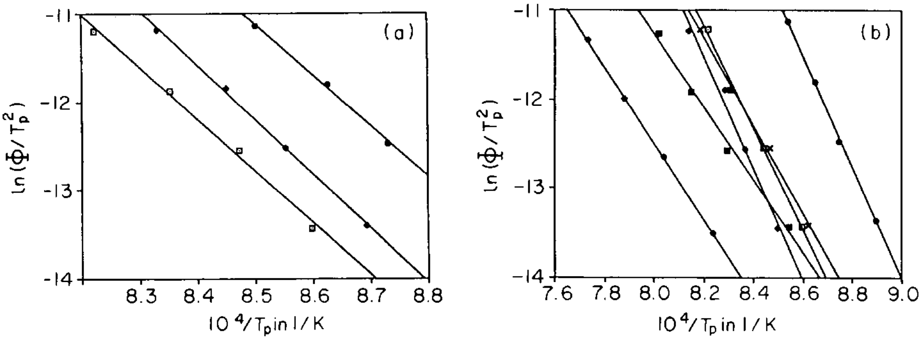

Fig. 3. The so-called Kissinger plots, ln(Φ/T_p^2) vs. 10000/T_p, for the different glassy compositions in (a) platinum and (b) alumina crucibles: □, A25-D75; ◆, A50-D50; ●, A25-ZnO; ×, A25-BaO first peak; ◇, A25-BaO second peak; ■, A25-SrO.

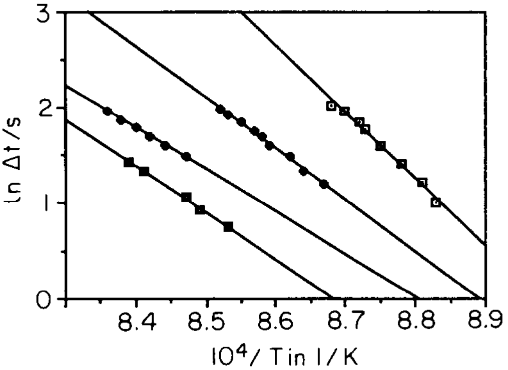

Fig. 4. Graphic method plot, ln Δ*t* versus 1/*T* × 10000, for composition A25-D75 in alumina crucibles at: ⊡, 2; ◆, 5; ▣, 10; and ◇, 20°C min^{-1}.

Kissinger plots, $\ln(\Phi/T_p^2)$ versus $10^4/T_p$, for the different glassy compositions in platinum and alumina crucibles. The figure shows that the lines are almost parallel to each other, suggesting the formation of isomorphous crystalline phases [4]. In the alumina crucible, a lower slope is evident for the data relative to the barium and strontium feldspars, in comparison to that of calcium feldspar, suggesting a lower activation energy. In Fig. 4, ln Δ*t* is plotted against 1/*T* and the slope of the curves is shown to be dependent on the heating rate. When the slope, which is proportional to E_G, is reported for different compositions (Fig. 5), it can be seen that the dependence of the activation energy on the heating rate is greater when an alumina crucible is used. The dispersion of points is very high when a high heating rate, 20°C min^{-1}, is used: the range for E_G values is from 50 to 220 kcal mol^{-1}. This observation suggests a problem related to the material from which the crucible is made: the heat conductivity of Al_2O_3 is lower than that of platinum.

For the values derived from the DDTA method, it can be observed from Table 2 that such values are generally closer to those derived from the

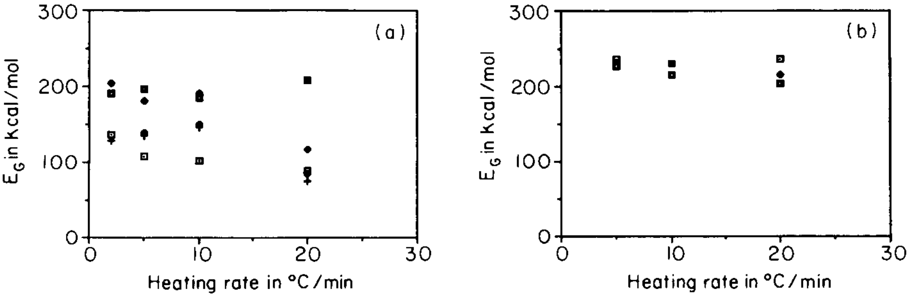

Fig. 5. Activation energy E_G from the graphic method in (a) alumina and (b) platinum crucibles at different heating rates: ⊡, A25-D75; ◆, A50-D50; +, A25-BaO; ◇, A25-SrO; and ▣, A25-ZnO.

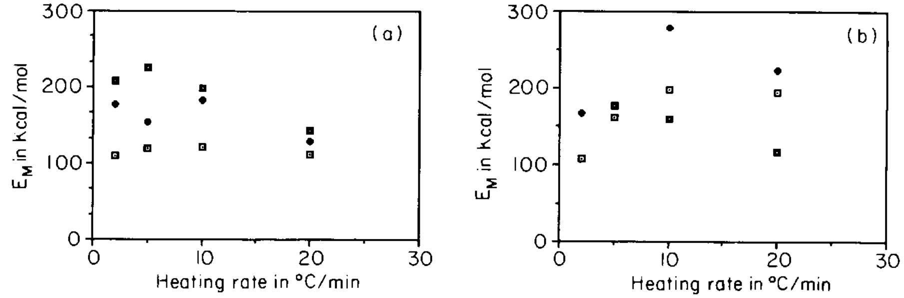

Fig. 6. Activation energy E_M from the DDTA method in (a) alumina and (b) platinum crucibles at different heating rates: ⊡, A25-D75; ◆, A50-D50; and ■, A25-ZnO.

so-called Kissinger equation than to those of the graphic method. When the E_M values are plotted against the heating rate (Fig. 6), the data dispersion is very high for both the alumina and platinum crucibles, ranging approximately from 100 to 300 kcal mol^{-1}.

CONCLUSIONS

The crystallization mechanism developed by starting from the surface of the glass and moving inwards, has been confirmed both experimentally and mathematically. In the evaluation of the activation energy for crystallization, different results were obtained from different methods, so that it is very difficult to define unequivocally the exact activation energy of the investigated compositions. However, it has been possible to individuate an approximate range of values for the different compositions analysed, namely 90–280 kcal mol^{-1}. The most reliable method seem to be the so-called Kissinger method, while the other two methods can only provide a reliable indication of the range of the activation energy values. However, a good correlation with the literature data for the different feldspar glass-ceramics was found, namely 86–313 kcal mol^{-1}, depending on the method, for magnesium calcium aluminium silicate glasses [11], 130–132 kcal mol^{-1} for barium aluminium silicate glasses [12], and 125 kcal mol^{-1} from strontium aluminium silicate glasses [13].

ACKNOWLEDGEMENT

The authors thank MURST for financial support.

REFERENCES

1 H.E. Kissinger, J. Res. Natl. Bur. Stand., 57 (1956) 217; Anal. Chem., 29 (1957) 1702.
2 T. Ozawa, Polymer, 12 (1971) 150.
J. Šesták, Phys. Chem. Glasses, 6 (1974) 137.
3 F. Branda, A. Buri, A. Marotta and S. Saiello, J. Mater. Sci., 17 (1982) 105.

4 X.J. Xu, C.S. Ray and D.E. Day, J. Am. Ceram. Soc., 74 (1991) 909.
5 C. Leonelli, T. Manfredini, M. Paganelli, P. Pozzi and G.C. Pellacani, J. Mater. Sci., 26 (1991) 5041.
6 L. Barbieri, C. Leonelli, T. Manfredini, M. Paganelli and G.C. Pellacani, J. Therm. Anal., 38 (1992) 26.
7 K. Matusita, S. Sakka and Y. Matsui, J. Mater. Sci., 10 (1975) 961.
8 K. Matusita and S. Sakka, Phys. Chem. Glasses, 20 (1979) 81; J. Non-Cryst. Solids, 38–39 (1980) 741.
9 G.O. Piloyan, I.D. Ryabchikov and O.S. Novikova, Nature, 212 (1966) 1229.
10 H. Yinnon and D.R. Uhlmann, J. Non-Cryst. Solids, 54 (1983) 253.
11 N.K. Chakraborty, S.K. Das, S.K. Niyogi and R.L. Thakur, in Proc. 10th Int. Congr. on Glass, Kyoto, Japan, 9 July 1974, Vol. 14, 1974, p. 75.
12 N.P. Bansal and M.J. Hyatt, J. Mater. Res., 4 (1989) 1257.
13 C.H. Drummond III and N.P. Bansal, Bol. Soc. Esp. Ceram. Vidrio, 31-C/2 (1992) 41.