JOURNAL OF MATERIALS SCIENCE 10 (1975) 961–966

Determination of the activation energy for crystal growth by differential thermal analysis

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A method for determining the activation energy for crystal growth was calculated on the basis of the heat balance in the differential thermal analysis (DTA) measurements and the mechanism of nucleation and growth. The theoretical analysis showed that the term $\ln[C_p d(\Delta T)/dt + K\Delta T]$ should be a linear function of l/T, where C_p is the heat capacity of sample and sample holder, K is the heat transfer coefficient, ΔT is the temperature difference between the sample and reference substance and t is the time. The energy term, E_D, obtained by multiplying the slope of the resulting straight line by R is indicative of the activation energy for crystal growth. It was shown that E_D should be three times the activation energy for crystal growth when bulk nucleation is dominant, and equal to that for crystal growth only when surface nucleation predominates. The result of the analysis was tested by comparing the experimentally determined E_D's with the activation energy for viscous flow, which was known to represent that for crystal growth. The E_D for $Li_2O \cdot 2SiO_2$ glass with dominant bulk nucleation, approached three times the activation energy for viscous flow, as the heating rate in DTA decreased. The E_D for $33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ glass with dominant surface nucleation approached the activation energy for viscous flow as the heating rate increased, suggesting the validity of the analysis.

1. Introduction

Differential thermal analysis (DTA) has been extensively used in the field of chemistry as a rapid and convenient means for detecting the reaction process. The rate of chemical reaction was analysed quantitatively by DTA and the activation energies were obtained [1-4]. Furthermore, this method was used to obtain the activation energy for the crystallization of glass, assuming that the process of crystallization is a first order reaction [5-7]. The physical meaning of the activation energy thus obtained is obscure, however, considering that the crystallization of glass is advanced by nucleation and growth mechanism [8].

In the present study, the method of analysis for obtaining the activation energy for crystal growth from DTA measurements was derived and applied to the crystal growth in $Li_2O \cdot 2SiO_2$ and $33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ glasses. Activation energies thus obtained were compared with the data reported previously, in order to discuss the validity of the present method.

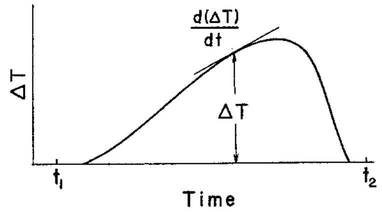

Figure 1 A typical DTA curve. ΔT = temperature difference between sample and reference; t_1 = time before start of crystallization; t_2 = time after completion of crystallization.

2. Theoretical analysis

As the crystallization proceeds in glass, the heat of crystallization is evolved and the exothermic peak appears on the DTA curve. A typical DTA curve is shown in Fig. 1. The heat balance during a time period, dt, in the DTA process can be approximately expressed by the equation [1, 7],

$$d(\Delta H) = C_p d(\Delta T) + K\Delta T dt \qquad (1)$$

where C_p is the heat capacity of the sample and sample holder, ΔT is the temperature difference between the sample and reference material, ΔH is the amount of heat associated with crystallization and K is the heat transfer coefficient. Assuming C_p and K to be independent of temperature and, accordingly, of time over the reaction period, the following expression can be derived,

$$\Delta H = C_\mathrm{p} \int_{t_1}^{t_2} \mathrm{d}(\Delta T) + K \int_{t_1}^{t_2} \Delta T \mathrm{d}t\,. \qquad (2)$$

Since ΔT is zero at both $t = t_1$ and $t = t_2$, the first term of the right hand side of the equation is zero. The integral in the second term means the total area under the curve, A. Therefore,

$$\Delta H = KA\,. \qquad (3)$$

Substituting the relation $\mathrm{d}x = \mathrm{d}(\Delta H)/\Delta H$ (where x is the volume fraction of crystal) and Equation 3 into Equation 1, we obtain,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{KA}\left[C_\mathrm{p}\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t} + K\Delta T\right]. \qquad (4)$$

It is known that, usually, the rate of crystal nucleation in glasses reaches its maximum at a temperature somewhat higher than the glass transition temperature and then decreases rapidly with increasing temperature [9-12], while the rate of crystal growth reaches its maximum at a temperature much higher than the temperature at which the nucleation rate is highest [11-14]. In other words, for the heating of glass at a constant heating rate, crystal nuclei formed at lower temperatures grow in size at higher temperatures without an increase in number [13, 15]. It should be noted here that there are two types of crystallization; one based on bulk nucleation and the other based on surface nucleation.

In the case of bulk nucleation, the variation of crystal volume fraction is expressed [16] by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 4\pi n r^2(1 - x)\frac{\mathrm{d}r}{\mathrm{d}t} \qquad (5)$$

where n is the number of crystal nuclei per unit volume of the sample formed in the course of heating and r is the radius of crystal particle. In deriving Equation 5, the impingement of crystal particles and reduction of the glass phase are taken into account [16]. The rate of crystal growth, U, is expressed by the formula [8],

$$U = \frac{f}{a_0}D''[1 - \exp(-\Delta G/RT)] \qquad (6)$$

where f is the fraction of site at the interface where molecules can preferentially be added, a_0 is the molecular diameter, D'' is the diffusion coefficient for transport across the crystal-liquid interface and ΔG is the free energy change associated with crystallization. The diffusion coefficient is generally expressed as follows;

$$D'' = D_0 \exp(-E/RT) \qquad (7)$$

where E is the activation energy for diffusion. At relatively low temperatures, the temperature dependence of the term $[1 - \exp(-\Delta G/RT)]$ is negligibly small compared with that of D'' [13]; therefore, Equation 6 can be rewritten as

$$U = U_0 \exp(-E/RT) \qquad (8)$$

where the energy E may be considered as the activation energy for crystal growth. The radius of the crystallite, r, is expressed as follows,

$$r = \int U_0 \exp(-E/RT)\mathrm{d}t = \frac{U_0}{\alpha}\int \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (9)$$

This integral cannot be expressed by any elementary function, and the following approximation is made,

$$r \cong r_0 \exp(-E/RT)\,. \qquad (10)$$

From Equations 5, 8 and 10

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 4\pi n r_0^2 U_0(1 - x)\exp\left(-\frac{3E}{RT}\right). \qquad (11)$$

In the case of surface nucleation, the nuclei are formed at the surface but not in the inner part of the sample. If we assume the glass sphere of radius R_0 in which the surface layer of the thickness r is crystallized, as shown in Fig. 2, the volume fraction of crystal is expressed as

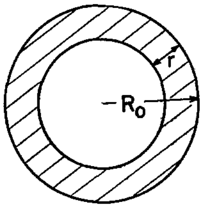

Figure 2 A glass sphere of radius R_0, representing the surface crystalline layer of thickness r.

$$x = 1 - (1 - r/R_0)^3\,. \qquad (12)$$

Then, using Equations 8 and 10

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{3U_0}{R_0}\left(1 - \frac{r}{R_0}\right)^2 \exp\left(-\frac{E}{RT}\right). \qquad (13)$$

Inserting Equations 11 and 13 into Equation 4, we obtain, respectively,

$$\ln\left[C_p\frac{d(\Delta T)}{dt} + K\Delta T\right] = -\frac{3E}{RT} + \ln 4\pi n r_0^2 U_0 (1-x) KA \quad (14)$$

(for bulk nucleation) and

$$\ln\left[C_p\frac{d(\Delta T)}{dt} + K\Delta T\right] = -\frac{E}{RT} + \ln\frac{3U_0 KA}{R_0}\left(1-\frac{r}{R_0}\right)^2 \quad (15)$$

(for surface nucleation).

When these equations are rewritten in a simplified form

$$\ln\left[C_p\frac{d(\Delta T)}{dt} + K\Delta T\right] = -\frac{E_D}{RT} + \text{constant}, \quad (16)$$

it is easily seen that the term E_D obtained by plotting the $\ln[C_p d(\Delta T)/dt + K\Delta T]$ versus $1/T$ should be three times the activation energy for crystal growth in the case of bulk nucleation, while it is equal to that for crystal growth in the case of surface nucleation. It should be noticed that the crystal volume fraction should be small in order for the second term of the right-hand side of Equations 14 and 15 to be regarded as constant and, accordingly, for Equation 16 to hold.

3. Experimental methods

Glasses of the compositions $Li_2O \cdot 2SiO_2$ and $33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ in mol % were used. The crystallization mechanism of these glasses is already well known [9-15, 17]. The method of preparation of the glasses were described in the previous paper [13].

DTA measurements were made with a Shimadzu micro-DTA apparatus type DTA-20B which has a platinum sample holder of 5 mm i.d. and 2 mm depth. The bulk glass was used as the sample, instead of powder, in order to avoid the possible effect of the particle radius distribution found in powder. To fill the sample holder with glass, the glass melt of about 120 mg was poured into it, remelted in an electric furnace at 1400° C for about 20 min, and allowed to cool in air.

In order to evaluate the degree of surface crystallization, the glass cubes with 5 mm sides were heated at a constant heating rate to given temperatures and the polished surface of the specimen was observed under an optical microscope.

Estimation of the value of K was made from DTA curves of NaCl and Li_2SO_4.

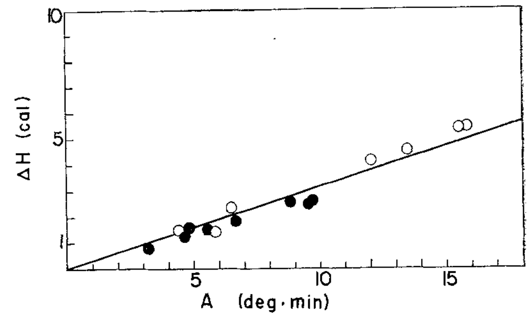

Figure 3 Relation between DTA peak area, A, and latent heat, ΔH, for fusion of NaCl (○) and solid-solid transition of Li_2SO_4 (●). Quantities of the sample were varied from 10 to 50 mg and two different heating rates (5 and 10° C min^{-1}) were employed.

4. Results and discussion

Fig. 3 shows the relation between the peak area in DTA curves and ΔH calculated from the amount of the sample for fusion of NaCl (temperature of fusion 801° C, $\Delta H_f = 6.9$ kcal mol^{-1}) as well as for solid-solid transition of Li_2SO_4 (temperature of transition 560° C, $\Delta H_f =$ 6.8 kcal mol^{-1}). Data points plotted in Fig. 3 were obtained by varying the quantity of the sample (10 to 50 mg) and the heating rates (5 and 10° C min^{-1}). It is seen that a straight line can be well fitted. The slope of the straight line gave 0.30 cal min^{-1} $°C^{-1}$ for K.

The DTA curves of $Li_2O \cdot 2SiO_2$ and $33.3 Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ glasses are shown in Fig. 4a and b, respectively, for various heating rates. The exothermic peak shifts to higher temperatures with increasing heating rate. It is also noticed that the peak for the TiO_2 containing glass lies at higher temperatures than that for the non-TiO_2 containing glass for the corresponding heating rate.

Evaluation of the heat content C_p, necessary for analysis by Equation 16, was made using the reported data of specific heat. The specific heat is 26.0 cal $SiO_2^{-1} \cdot °C^{-1}$ for $Li_2O \cdot 2SiO_2$ [18] and $C_p = 5.74 + 1.34 \times 10^{-3}T + 0.1 \times 10^5 T^{-2}$ (cal $°C^{-1}$ mol^{-1}) for platinum (sample holder) [19]. The term, $C_p d(\Delta T)/dt$, was found to be negligibly small compared with the term $K\Delta T$ for the heating rate of 1° C min^{-1}. It was about

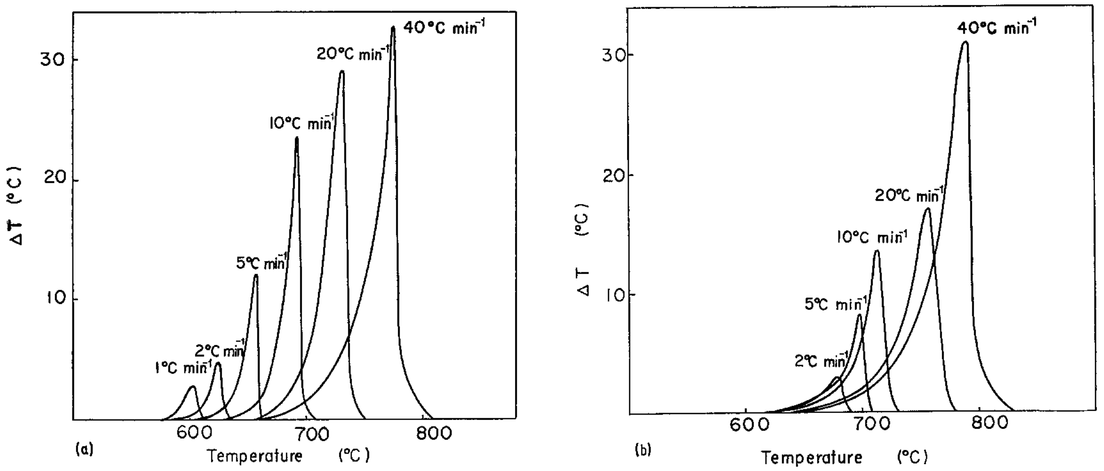

Figure 4 DTA curves at various heating rates for (a) $Li_2O \cdot 2SiO_2$ and (b) $33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ glasses.

one-fifth of the latter for the heating rate of 20°C min^{-1}. The ratio was kept almost constant for the temperature range lower than that corresponding to the maximum peak height. The plot of $\log[C_p d(\Delta T)/dt + K\Delta T]$ versus $1/T$ for $Li_2O \cdot 2SiO_2$ and $33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ glasses heated at 5°Cmin^{-1} are shown in Fig. 5, as examples. The values of E_D obtained from the slope of these straight lines are shown in Table I, and was reproduced within the error of ± 5%.

It was already shown that in $Li_2O \cdot 2SiO_2$ glass the activation energy for diffusion across the crystal-liquid interface, and accordingly that for crystal growth in Equation 8, was equal to that for viscous flow [13, 14], and the latter is used instead of the former since it is better known as a function of temperature. The viscosity of $Li_2O \cdot 2SiO_2$ glass is expressed by the formula [14];

$$\log \eta = -1.44 + \frac{3.37 \times 10^3}{T - 460} \text{P} \qquad (17)$$

where T is absolute temperature. This formula makes it possible to calculate the activation energy for viscous flow, $E\eta$, at each peak temperature. The ratio, E_D/E_η, is plotted against the heating rate in Fig. 6. It is seen that for $Li_2O \cdot 2SiO_2$ glass, the E_D/E_η ratio is close to three at low heating rates and decreases gradually

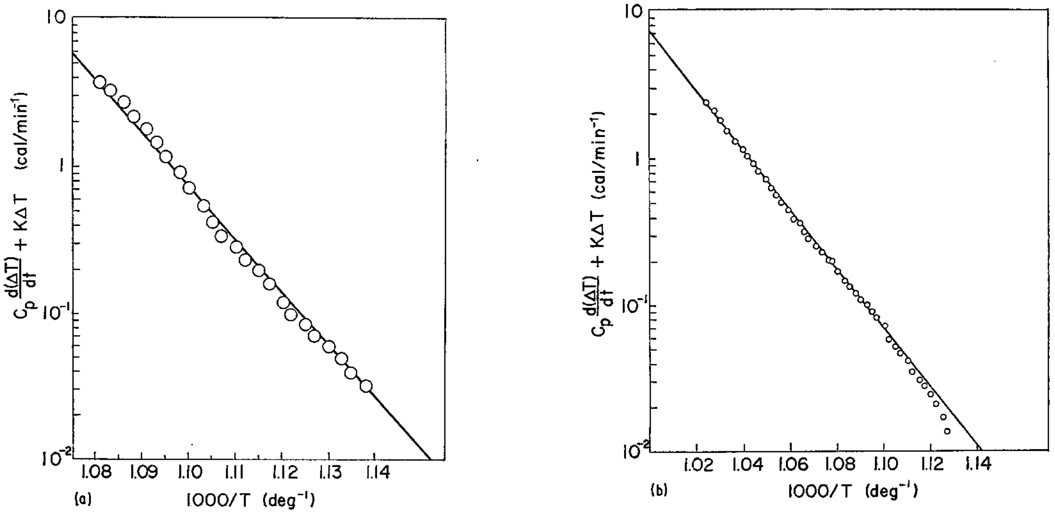

Figure 5 The term $(C_p d\Delta T/dt + K\Delta T)$ plotted against reciprocal of absolute temperature for the heating rate of 5°C min^{-1}. (a) $Li_2O \cdot 2SiO_2$ glass. (b) $33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$ glass.

TABLE I The values of E_D(kcal mol^{-1}) obtained by using Equation 16

Heating rate (°C min^{-1})	$Li_2O \cdot 2SiO_2$	$33.3Li_2O \cdot 66.7SiO_2 \cdot 3TiO_2$
1	209	
2	182	91
5	163	92
10	150	80
20	117	73
40	80	68

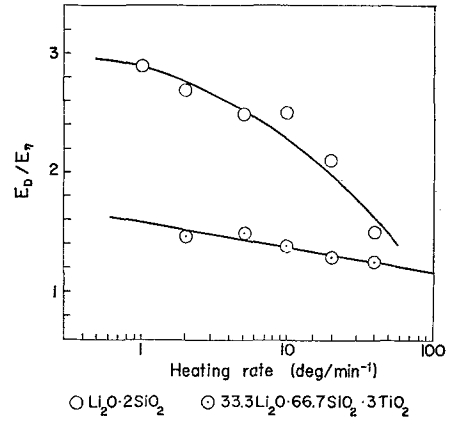

Figure 6 E_D/E_η ratio as a function of heating rate.

as the heating rate increases. For the glass containing TiO_2, the E_D/E_η ratio is close to unity at high heating rates and increases as the heating rate decreases.

These tendencies can be explained on the basis of nucleation mechanism revealed by the microscopic observation. Fig. 7 shows the photomicrographs of a section of the crystallized sample. It is seen in the photomicrographs that the higher the heating rate, the thicker the surface crystalline layer. This is also clearly seen in Fig. 8, which shows the relation between the thickness of the surface crystalline layer and the heating rate. That is, the bulk nucleation is dominant in $Li_2O \cdot 2SiO_2$ glass, especially at low heating rates, and each particle grows three-dimensionally, which agrees with the fact that E_D/E_η is close to 3. The contribution of surface crystallization gradually increases as the heating rate increases, which also agrees with the gradual decrease in the E_D/E_η ratio. In the glass containing TiO_2, surface crystallization is dominant and the crystal grows one-dimensionally, which agrees with the fact that E_D/E_η is close to unity in this glass.

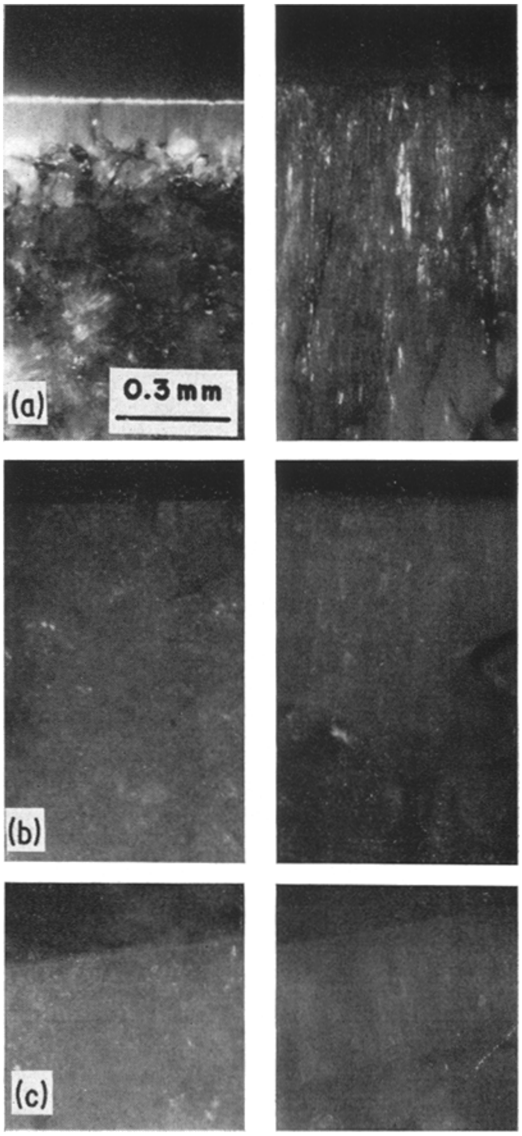

Figure 7 Polished cross-sections of samples crystallized by heating at various heating rates. (a) 10°C min^{-1}, (b) 5°C min^{-1}, (c) 1°C min^{-1}.

In general, determination of the activation energy for crystal growth normally needs data on the growth rate at various temperatures. The method derived in the present study is very convenient compared with such a method. Only a small quantity of sample is necessary and the DTA measurement is easy to carry out. Furthermore, the present method enables one to obtain the activation energy in glasses in which so many

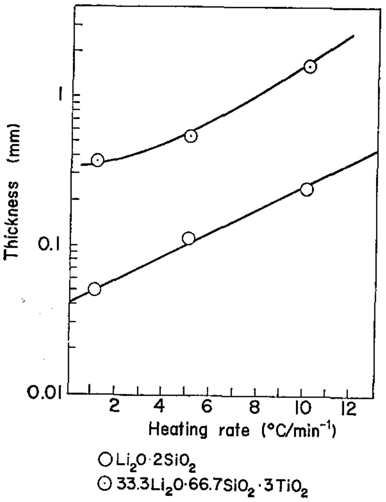

Figure 8 Variation of thickness of surface crystalline layer with heating rate.

nuclei are formed that the microscopic measurement of the growth rate of each particle is very difficult.

5. Conclusion

A formula $\ln[C_p d(\Delta T)/dt + K\Delta T] = -E_D/RT$ + constant was derived which connects DTA measurement with the activation energy for crystal growth. It was shown that the activation energy for crystal growth is $\frac{1}{3}E_D$ when bulk nucleation is dominant and E_D when surface nucleation is dominant. Thus the meaning of the energy term is distinct when either of the nucleation mechanisms is dominant, while it is somewhat obscure when both the mechanisms operate to a comparable degree. The results of the theoretical analysis were confirmed to be valid by the measurement on glass of lithium disilicate composition in which bulk nucleation is dominant for low heating rates and TiO_2-containing glass in which surface nucleation is dominant for high heating rates.

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Received 11 October and accepted 5 November 1974.