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A STUDY OF NUCLEATION AND DEVITRIFICATION KINETICS OF A LOW-MELTING-POINT SOLDER–GLASS SYSTEM $PbO–ZnO–B_2O_3$ BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

Non-isothermal differential thermal analysis (DTA) was used to evaluate the kinetic parameters and nucleation rate. The temperature of the maximum nucleation rate of $PbO–ZnO–B_2O_3$ glasses was found to be near 320 ° C.

The activation energy of crystal growth and the values of the parameter m depending on the mechanism and morphology of crystal growth, were also obtained: the activation energy ranged from 35 to 65 kcal mol^{-1}; and the values of m ranged from 0.9 to 1.4.

It was found that surface crystallisation occurred in two finely powdered glasses and also in coarsely powdered glass from a glass rod, but not in the quenched coarsely powdered glass.

INTRODUCTION

Thermal analysis has been used for studying the kinetics of chemical reaction and the crystallisation of glass [1]. Differential thermal analysis has been extensively used to study the devitrification of glass [2] because it can be used at temperatures above 1500 ° C. Many authors have described methods of analysis using DTA curves for determining the activation energy of crystal growth and the mechanism of crystallisation, bulk or surface nucleation [3–6]. Recently, a method was proposed for evaluating the effectiveness of nucleation with heat using crystallisation peaks obtained from DTA [7,8].

$PbO–ZnO–B_2O_3$ glass forms the matrix of low-melting solder glasses. Its physical properties have been described by many researchers [9–11], but the crystallising behaviour of $PbO–ZnO–B_2O_3$ glasses has rarely been considered. This research examines the crystallising behaviour and the nucleation rate of $PbO–ZnO–B_2O_3$ when subjected to heat, using differential thermal analysis for the data collection.

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EXPERIMENTAL

$PbO–ZnO–B_2O_3$ (mole ratio = 3.12 : 1.28 : 1) glasses were prepared by melting at 1100 ° C for 2 h in a platinum crucible in an electric furnace. The melts were quenched by placing them in ice-cold distilled water, which is below 0 ° C, for 10 s. Another method was to cast the glasses in graphite moulds which were kept at 380 ° C and then cooled to room temperature to obtain a high cooling rate. The quenched glasses were then crushed with a ball miller and then sieved to obtain a fine powder under 325 mesh and a coarse powder between 30 mesh and 50 mesh.

Glass rods which were prepared from the graphite moulds were crushed to a fine powder under 325 mesh and a coarse powder between 30 mesh and 50 mesh. X-ray diffraction failed to detect any crystalline phase in the samples before the DTA runs.

Differential thermal analysis was used on ~ 30 mg of fine glass powder or coarse glass powder in an air atmosphere using heating rates from 1° C min^{-1} to 20 ° C min^{-1}.

Four sets of DTA curves were recorded. In the first two sets, the quenched samples were used and in the second, the fine and coarse powder samples from the glass rods were used. A Rikagu-Denki differential thermal analyser, model 8121, was used and α-Al_2O_3 powder was used as the reference material.

RESULTS AND DISCUSSION

Crystal growth

When different glasses are heated at a constant rate, the crystal nuclei form at temperatures higher than the glass transition temperature and increase in size at higher crystallisation temperatures without any increase in number [1]. If we consider classical theory, applied to a moderate degree of undercooling, the crystal growth rate U can be expressed

$$U = U_0 \exp(-E_g/RT) \qquad (1)$$

where E_g is the activation energy of crystal growth. If the number of nuclei is not dependent on the heating rate, the following equation can be applied to the non-isothermal devitrification of glasses [4]

$$-\ln(1-\alpha) = AN/\phi^m \exp(-mE_g/RT) \qquad (2)$$

where α is the volume fraction crystallised at temperature T, ϕ is the heating rate of the DTA and A is a constant whose value depends on the pre-exponential factor U_0 in eqn. (1). N is the number of nuclei and can be expressed

$$N = N_s + N_h + N_n \tag{3}$$

where N_s is the number of surface nuclei, proportional to the specific sample surfaces, N_h is inversely proportional to the heating rate and N_n is the number of nuclei formed in previous heat treatments.

The parameter m depends on the mechanism and morphology of crystal growth. For growth controlled by the reaction at the glass–crystal interface, m ranges from a value of 1 for one-dimensional growth, or growth from surface nuclei, to 3 for three-dimensional growth. For diffusion-controlled growth, the corresponding m range is ~ 0.5 to ~ 1.5 [12].

If we take into account [13] the fact that at the peak temperature T_m the degree of crystallisation reaches the same specific value independent of the heating rate, the following equation can be derived

$$\ln \phi = -E_g/RT_m + \text{const.} \tag{4}$$

Moreover, because the deflection from the baseline ΔT is proportional to the instantaneous reaction rate [14] and because the change in temperature in the initial part of the DTA crystallisation peak has a much larger effect than α on the ΔT deflection, the following equation can be obtained

$$\ln \Delta T = -mE_g/RT + \text{const.} \tag{5}$$

By plotting ln ΔT against $1/T$ as shown in Fig. 1, and ln ϕ against $1/T_m$ as shown in Fig. 2, straight lines were obtained and the values of the kinetic parameters E_g and m were calculated from the slopes of these lines; the results are reported in Table 1.

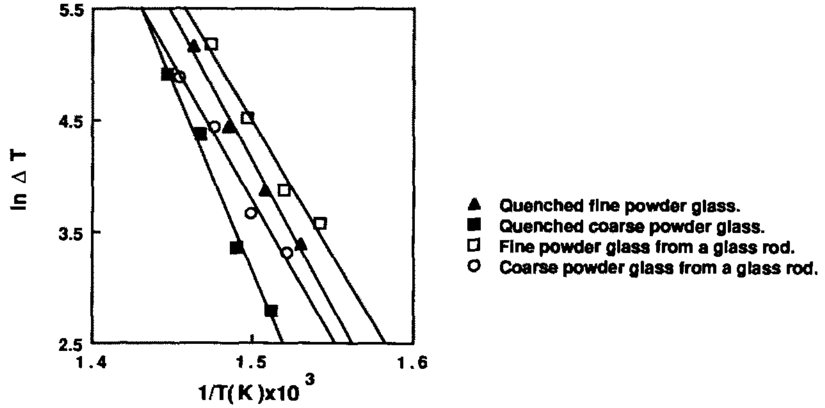

Fig. 1. Plot of ln ΔT against $1/T$ used to determine the value of mE_g.

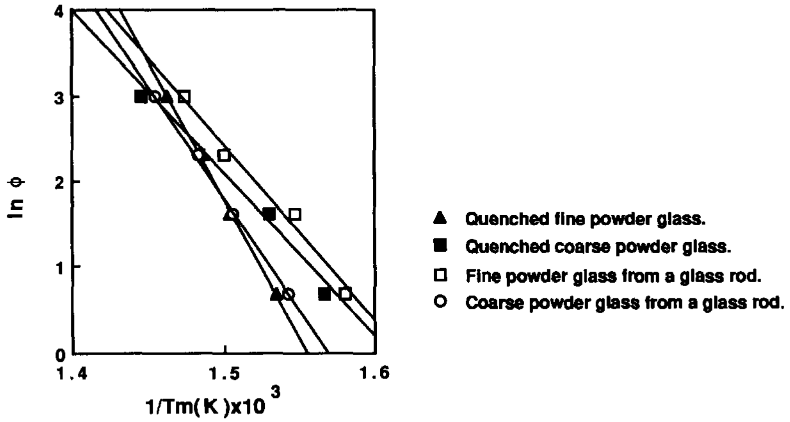

Fig. 2. Plot of ln ϕ against $1/T_m$ used to determine the activation energy of crystallisation by heating rate.

The values of m suggest that only surface crystallisation takes place in the two finely powdered glasses and in the coarsely powdered glass made from the glass rod ($m = 1$). However, both surface and bulk crystallisation occur in the quenched coarse glass ($m > 1$).

These results confirm that, for the glass composition studied, devitrification starts mainly from surface nuclei. This is seen in the photograph in Fig. 4, where the longer the time of heat treatment, the thicker the surface crystalline layer.

TABLE 1

The m and E_g values of PbO–ZnO–B_2O_3 glasses

	Quenched finely powdered glass	Quenched coarsely powdered glass	Finely powdered glass from a glass rod	Coarsely powdered glass from a glass rod
E_{g1} [a] (kcal mol^{-1})	64.40	47.11	47.53	52.00
E_{g2} [b] (kcal mol^{-1})	61.62	44.51	44.95	49.24
E_{g3} [c] (kcal mol^{-1})	62.36	49.58	44.35	53.83
mE_g (kcal mol^{-1})	51.94	66.82	47.31	49.20
E_g, av. (kcal mol^{-1})	62.79	47.07	45.61	51.69
m	0.827	1.420	1.037	0.952

[a] E_{g1} is the activation energy obtained by plotting ln ϕ versus $1/T_m \times 10^3$.

[b] E_{g2} is the activation energy obtained by plotting ln ϕ/T_m^2 versus $1/T_m \times 10^3$, (see Fig. 3, Kissinger method).

[c] E_{g3} is the activation energy calculated from $[T_m T'_m(\phi/\phi' + 2 \ln T_m/T'_m)R]/(T'_m - T_m)$ where T_m and T'_m are the peak temperatures at heating rates ϕ and ϕ', respectively (Levskii method) and R is the gas constant.

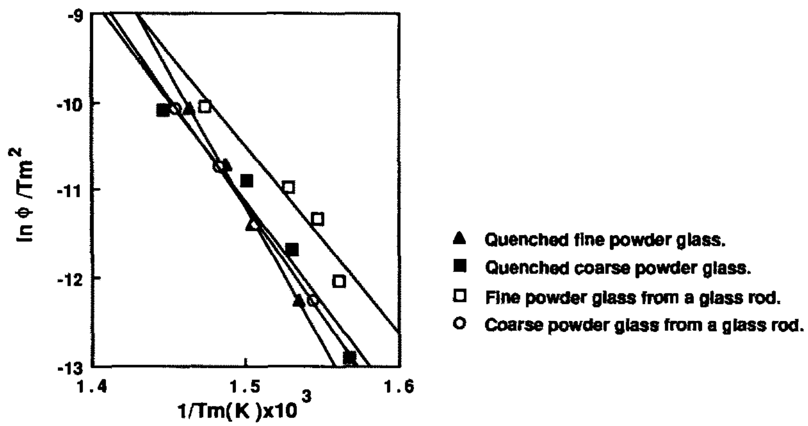

Fig. 3. Plot of ln ϕ/T_m^2 against $1/T_m$ used to determine the activation energy of crystallisation by heating rate.

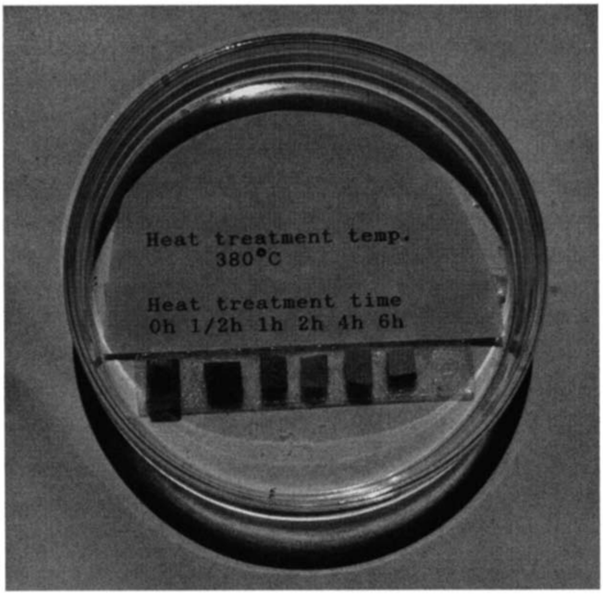

Fig. 4. The devitrification of PbO–ZnO–B_2O_3 glass kept at 380 °C, with various sintering times.

Nucleation

At the temperature T_m (the DTA crystallisation peak), the crystal volume fraction α reaches the same specific value independent of ϕ and m, giving

$$\ln N - \ln \phi^m = mE_g/RT_m + \text{const}. \qquad (6)$$

If the DTA runs are carried out on samples of the same specific surface S at the same heating rate ϕ, the sum (N_0) of the surface nuclei (N_S) and the bulk nuclei (N_h) formed during the DTA run, is constant, and eqn. (6) becomes

$$\ln(N_0 + N_n) = mE_g/RT_m + \text{const.} \tag{7}$$

For a previously nucleated sample and for a quenched sample ($N_n = 0$), the following equation is true

$$\ln N_0 = mE_g/RT_m^{\ominus} + \text{const.} \tag{8}$$

From eqns. (7) and (8), the following equation can be derived

$$\ln(N_0 + N_n)/N_0 = mE_g/R(1/T_m - 1/T_m^{\ominus}) \tag{9}$$

Using the same specific surface sample, if the DTA runs are carried out at a high heating rate (20 °C min^{-1}) and the samples are nucleated for a longer period of time ($t_n = 2$ h), the following relationship results

$$N_n \gg N_0$$

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

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

where I is the kinetic rate constant of nucleation and b is a parameter related to the nucleation mechanism. If the samples are kept for the same time t_n at each temperature T_n of the heat treatment, the following approximated equation can be derived from eqn. (9)

$$\ln I = mE_g/R(1/T_m - 1/T_m^{\ominus}) + \text{const.} \tag{11}$$

By plotting $1/T_m - 1/T_m^{\ominus}$ versus the temperature T_n of the nucleation heat treatment, a nucleation rate–temperature-like curve was obtained (Fig. 5) and the heat treatment temperature of maximum nucleation rate was found to be near 320 °C, which is very close to the T_g value of PbO–ZnO–B_2O_3 glasses (Fig. 6).

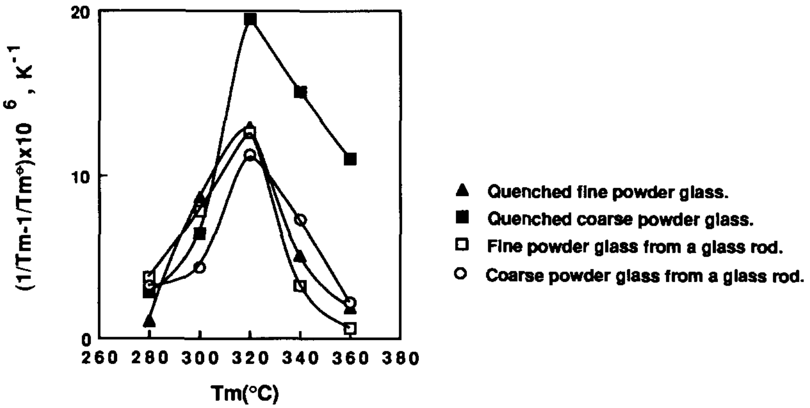

Fig. 5. Nucleation rate–temperature-like curve of PbO–ZnO–B_2O_3 glasses.

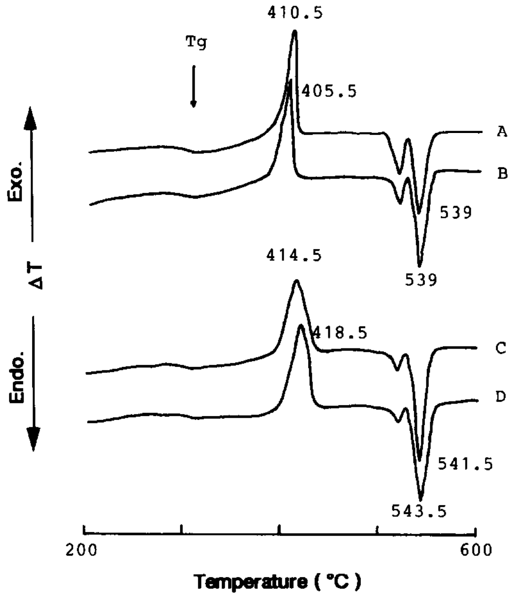

Fig. 6. DTA curves of different glass samples with 20 °C min^{-1} heating rate: A, fine glass from a glass rod; B, quenched fine glass; C, quenched coarse glass; and D, coarse glass from a glass rod.

CONCLUSIONS

The experimental results suggest that in the two finely powdered glasses made from glass rods, crystal growth occurs by a surface crystallisation mechanism. However, this was not the case for the quenched coarsely powdered glass.

The maximum nucleation-rate temperature was found to be approximately 320 °C.

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