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KINETICS OF CRYSTAL GROWTH IN $Na_2O \cdot 2\ SiO_2$ GLASS. A DTA STUDY

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ABSTRACT

The non-isothermal devitrification of $Na_2O \cdot 2\ SiO_2$ glass is investigated by differential thermal analysis (DTA). The kinetic parameters for the viscous flow of the glass and the temperature of maximum crystallization rate are evaluated from DTA curves. The limits of the Arrhenius-type relationship between the rate constant of crystal growth and the absolute temperature are also discussed.

INTRODUCTION

Differential thermal analysis (DTA) has been extensively used to study the devitrification of glasses.

In previous communications [1–3] several methods have been proposed by the present authors to obtain kinetic data from DTA and derivative differential thermal analysis (DDTA) curves. These methods, as well as other methods reported in the literature, are based on the assumption that the kinetic rate constant for crystal growth is related to the temperature by an Arrhenius-type equation.

The aim of this communication is to show that for the $Na_2O \cdot 2\ SiO_2$ glass devitrification:

(a) the Arrhenius relation holds in a narrow temperature range so that from two sets of experimental measurements, carried out in two different temperature ranges, different values of the activation energy for crystal growth are obtained;

(b) the closer the devitrification temperature range is to the melting point temperature, the further the activation energy for crystal growth is from that of the viscous flow.

EXPERIMENTAL

Samples of $Na_2O \cdot 2\ SiO_2$ glass were prepared by melting analytical grade reagents at 1150°C in a Pt crucible in an electric oven. The melts were cast by plunging the bottom of the crucible in cold water at a high cooling rate. The as-quenched glasses were crushed or cut to obtain powdered (− 170 + 230 mesh) samples and small bulk samples (suitable for the size of the sample holder of the DTA apparatus), respectively.

Very fine powdered samples were also prepared by crushing 300 mg of powdered (− 350 mesh) glass for 30 min in an agata mortar.

Differential thermal analysis curves of 90-mg specimens at different heating rates (5–20°C min^{-1}) in air were recorded. Powdered Al_2O_3 was added to improve the heat transfer between bulk samples and the sample holder. A Netzsch thermoanalyzer (Model 404 M) was used for the analyses, with powdered Al_2O_3 as reference material.

RESULTS AND DISCUSSION

The DTA curves of bulk, coarse-powdered and very fine-powdered samples of $Na_2O \cdot 2\ SiO_2$ glass are presented in Fig. 1.

When a glass crystallizes during a DTA run the heat of crystallization is evolved and an exothermic peak appears on the DTA curve. Two types of crystallization take place in a glass, based on surface and bulk nucleation. In the case of surface nucleation, nuclei are formed only on the surface and their number is proportional to the specific surface area of the sample. In the case of bulk nucleation, in which each crystal particle grows three-dimen-

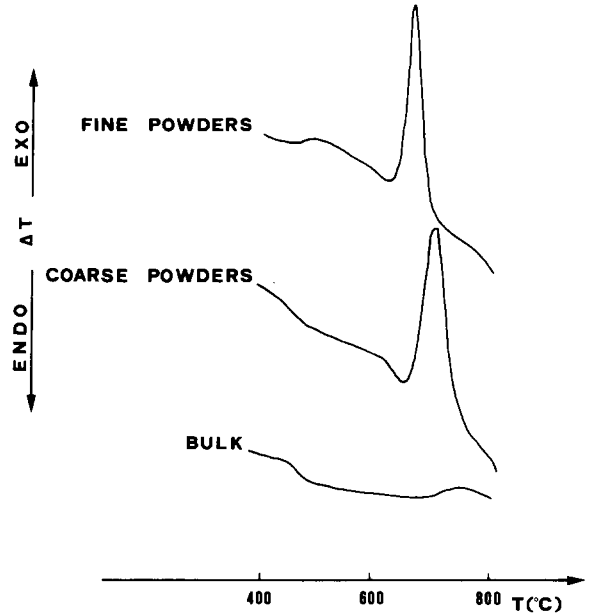

Fig. 1. DTA curves recorded at 20°C min^{-1}.

sionally in the bulk, the number of nuclei is proportional to the time of heating in the nucleation temperature range.

The lack of any exothermic peak on the DTA curve of the bulk (low specific surface area) sample suggests that only surface crystallization occurs during the DTA run. This result is consistent with that obtained under isothermal conditions [4].

When a glass is heated at a constant heating rate, β, the volume fraction of crystal, α, increases with the temperature. In the case of surface crystallization the crystals grow from the surface towards the inside of the glass one-dimensionally. Assuming glass particles as spheres of mean radius R_0 the volume fraction of crystal, α, at temperature T is expressed as [5]

$$1-(1-\alpha)^{1/3}=\frac{\kappa}{\beta R_0} \tag{1}$$

Where the constant κ is related to the absolute temperature, T, by an Arrhenius-type equation

$$\kappa = A_1 \exp(-E/RT) \tag{2}$$

where E is the activation energy for crystal growth, and A_1 is a constant. The condition that at temperature T_p (of the DTA crystallization peak) the crystal volume fraction α reaches the same specific value independent of the heating rate β, leads to [1,6]

$$\ln\beta = -\frac{E}{R}\frac{1}{T_p} + \text{const.} \tag{3}$$

By plotting $\ln\beta$ vs. $1/T_p$ straight lines were obtained for both coarse-powdered and very fine-powdered samples (Fig. 2).

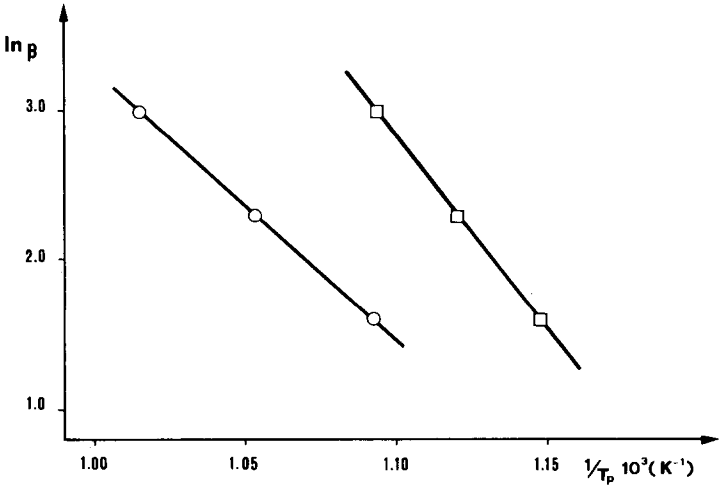

Fig. 2. Plot of ln β vs. $1/T_p$.

TABLE 1

Activation energies (kcal mol^{-1})

Samples	E	E_η	E'_η	ΔT (K)
Coarse powders	36	53	54	200
Fine powders	51	62	58	250

The values of activation energy E calculated from their slopes are reported in Table 1. The value of E for very fine-powdered samples is about 40% higher than that for coarse-powdered samples.

This discrepancy can be explained as follows. The rate of crystal growth, μ, is governed, in the more general case, by the following equation [7]

$$\mu = A_2 \exp\left(-\frac{\Delta G'}{RT}\right)\left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right] \tag{4}$$

where ΔG is the free energy for crystallization, $\Delta G'$ the activation energy, and A_2 a constant. Since ΔG increases proportionally to the undercooling ΔT the factor $1 - \exp(-\Delta G/RT)$ will increase as the undercooling ΔT increases. For small values of ΔT this factor is dominant so initially the rate of crystal growth increases with decreasing temperature. However, eventually the kinetic factor $\exp(-\Delta G'/RT)$ predominates and the rate of crystal growth begins to decrease, passing through a maximum.

The thermodynamic barrier can be approximatively assumed as proportional to the undercooling ΔT [8]

$$1 - \exp\left(-\frac{\Delta G}{RT}\right) \propto \Delta T^{1.75} \tag{5}$$

The kinetic barrier can be assumed to be inversely proportional to the viscosity η [8]

$$\exp\left(-\frac{\Delta G'}{RT}\right) \propto \frac{1}{\eta} \tag{6}$$

The viscosity η is related to the absolute temperature T by the Vogel–Fulcher equation [9]

$$\eta = A_3 \exp\left(\frac{B}{T - T_0}\right) \tag{7}$$

Where A_3, B and T_0 are constants for each glass. From eqns. (5)–(7) the following relationship between the crystallization rate constant, κ, and the absolute temperature, T, can be derived

$$\kappa = A_4 \Delta T^{1.75} \exp\left(-\frac{B}{(T - T_0)}\right) \tag{8}$$

By comparing the first temperature derivatives of the logarithms of eqns. (2) and (8) the following relationship is obtained

$$\frac{E}{R} = B\left(\frac{T}{T - T_0}\right)^2 - \frac{1.75T^2}{\Delta T} \tag{9}$$

It is evident that the Arrhenius-type equation holds only in a narrow temperature range in which the terms $(T/T - T_0)^2$ and $T^2/\Delta T$ can be regarded as constants. From the two E values previously estimated from DTA curves values of $B = 5036$ K and $T_0 = 534$ K can be calculated from eqn. (9). The value of T_0 thus obtained agrees well with that ($T_0 = 523$ K) predicted by the Gutzow rule [10]

$$T_g/T_0 = 4/3$$

assuming for the glass transition temperature the value $T_g = 728$ K. The knowledge of the constants B and T_0 allows the evaluation of the Arrhenius type activation energy for the viscous flow E_η from eqn. (7) in the two temperature ranges investigated.

The values of E_η thus calculated are very close (Table 1) to those E'_η values calculated from the experimental data of viscosity reported in the literature [4].

It should be noted (Table 1) that the lower value is the undercooling ΔT, and the higher value is the difference between the values of activation energy for crystal growth, E, and the values of activation energy for viscous flow, E_η.

Finally the temperature T_M of maximum crystallization rate can be evaluated by setting

$$\frac{d}{dT}\kappa = \kappa\left[\frac{B}{(T - T_0)^2} - \frac{1.75}{\Delta T}\right] = 0 \tag{10}$$

and solving for T_M.

The value of $T_M = 780°C$ thus obtained is in very good agreement with that ($T_M = 800°C$) determined by Scott and Pask [4] with the isothermal techniques currently in use.

CONCLUSIONS

From the above results the following conclusions can be drawn:

(a) in the $Na_2O \cdot 2\ SiO_2$ glass during the DTA run only surface crystallization occurs;

(b) the rate constant of crystal growth is related to the absolute temperature by an Arrhenius-type equation only in a narrow temperature range;

(c) the difference between the values of activation energy for crystal growth, E, and the values of activation energy for viscous flow, E_η, decreases with the increasing in undercooling;

(d) the kinetic constants for the viscous flow and the temperature of maximum crystallization rate can be evaluated from DTA curves.

The results agree well with those reported by other workers who have used the alternative techniques.

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