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NUCLEATION IN GLASS-FORMING SYSTEMS. A DTA STUDY.

A. MAROTTA, A. BURI, F. BRANDA and S. SAIELLO

Istituto di Chimica, Facoltà di Ingegneria, Università di Napoli, 80125 Napoli (Italy).

ABSTRACT

A simple method recently proposed (ref.1) for evaluating the temperature of maximum nucleation rate is applied to several different glass-forming systems. The results well agree with those obtained by means of traditional methods.

INTRODUCTION

In this work a method for evaluating the effectiveness of the nucleation heat treatment from the temperature of DTA crystallization peak is described. The proposed procedure allows the estimation of temperature of maximum nucleation rate to be made more quickly than is usually the case.

The nucleation behaviour of $Li_2O \cdot 2SiO_2$, $30Li_2O \cdot 70SiO_2$, $30Li_2O \cdot 69SiO_2 \cdot 1P_2O_5$, $Na_2O \cdot SiO_2$, $BaO \cdot 2SiO_2$, $Na_2O \cdot 2CaO \cdot 3SiO_2$ and $2Na_2O \cdot CaO \cdot 3SiO_2$ glasses has been investigated.

The experimental procedure of glass preparation and thermal analysis were described elsewhere (ref.1).

THEORETICAL CONSIDERATIONS AND RESULTS

The non isothermal devitrification of glass is the result of the two individual processes: nucleation and crystals growth. The number of nuclei for unit volume is the sum of surface nuclei N_s, bulk nuclei formed during the DTA run N_h and bulk nuclei formed during a previous heat treatment of nucleation N_n.

$$N = N_s + N_h + N_n \qquad (1)$$

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The values of N_s, N_h and N_n are respectively proportional to the sample specific surface S, to the reciprocal of DTA heating rate β and to the time t_n of the nucleation heat treatment. The process of crystal growth can be described by the following equation (ref.2)

$$-\ln(1-\alpha) = A \frac{N}{\beta^n} \exp\left(-\frac{nE_c}{RT}\right) \qquad (2)$$

where α is the volume fraction crystallized at temperature T, E_c the activation energy for crystal growth, n is a parameter related to the crystallization mechanism, β is the DTA heating rate and A a constant.

The condition that at temperature T_p (of the DTA crystallization peak) the crystal volume fraction α reaches the some specific value indipendent of β and n, leads to (ref.1,3)

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

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

$$\ln(N_o + N_n) = \frac{nE_c}{R} \frac{1}{T_p} + \text{const.} \qquad (4)$$

and for an as-quenched sample (N_n=0)

$$\ln N_o = \frac{nE_c}{R} \frac{1}{T^\circ_p} + \text{const.} \qquad (5)$$

From Eqs.(4) and (5) the following equation can be drawn

$$\ln \frac{N_o+N_n}{N_o} = \frac{nE_c}{R} \left(\frac{1}{T_p} - \frac{1}{T^\circ_p}\right) \qquad (6)$$

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

$$N_n >> N_o \qquad (7)$$

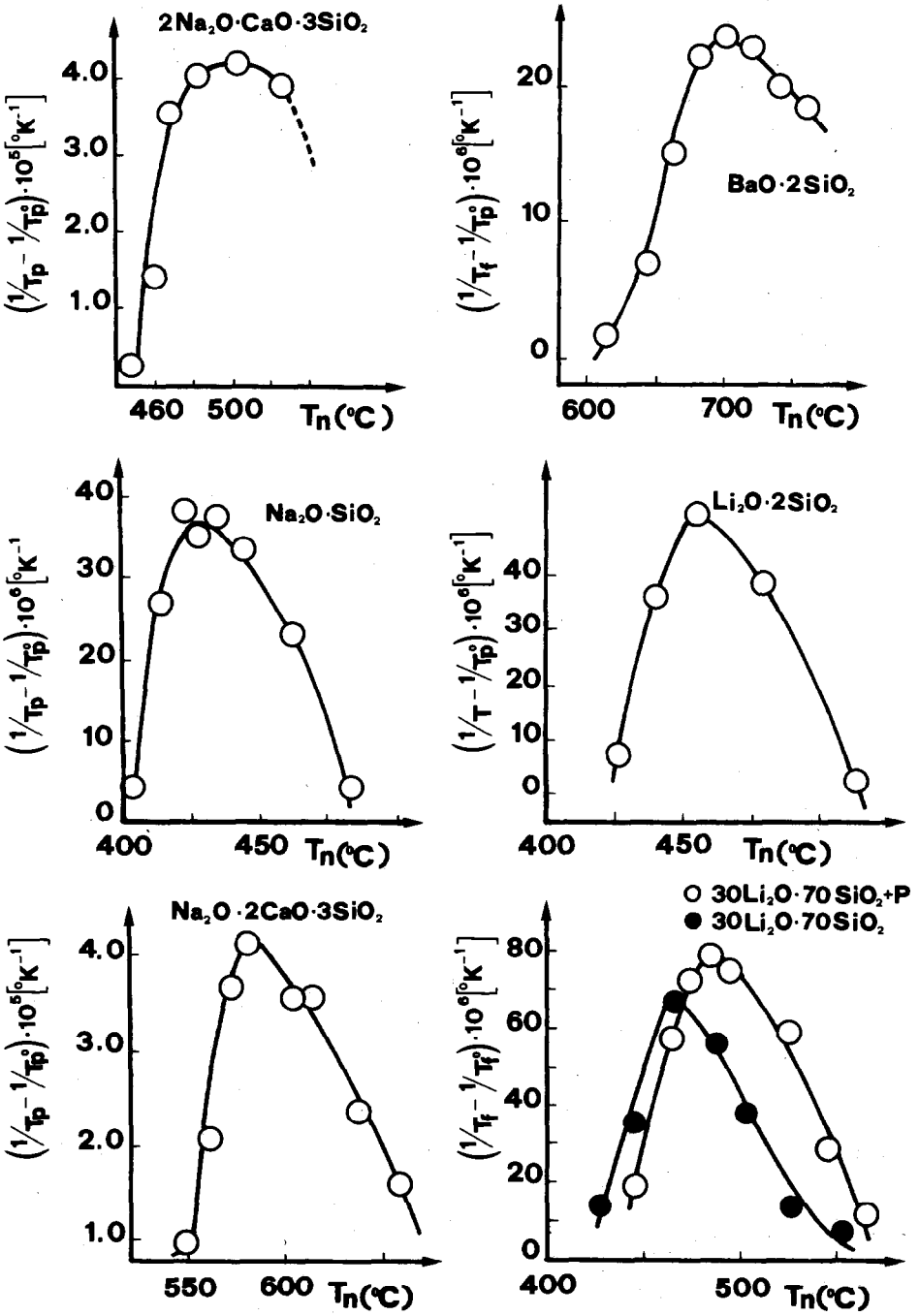

Fig.1-Nucleation rate-temperature like curve of studied glasses

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

$$N_n = I t_n^b \tag{8}$$

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

$$\ln I = \frac{nE_c}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^\circ}\right) + \text{const.} \tag{9}$$

By plotting $(1/T_p)-(1/T_p^\circ)$ vs.the T_n of the nucleation heat treatment, a nucleation rate-temperature like curve is obtained (fig. 1).

The results well agree with those reported in literature (ref.4).

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