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Crystallization kinetics of gehlenite glass

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Isothermal and non-isothermal kinetics of gehlenite glass devitrification have been studied. A Johnson–Mehl–Avrami rate equation was assumed. The values of kinetic parameters obtained from XRD patterns and DTA curves are in a good agreement. The crystallization process is thought to proceed by a rod-like growth controlled by diffusion from a fixed number of nuclei.

1. Introduction

In previous papers [1, 2] the devitrification behaviour of melilitic glasses was studied. Their compositions, expressed by the formula $2\,CaO \cdot (1-x)\,MgO \cdot xAl_2O_3 \cdot (2-x)\,SiO_2$ with $0 \leqslant x \leqslant 1$, fall in the range of solid solutions between the end members akermanite ($Ca_2Mg\,Si_2O_7$) and gehlenite ($Ca_2Al_2\,SiO_7$). Conclusions were drawn about the crystallization mechanism taking into account that: (a) all the as-quenched glasses revealed a phase separation and (b) glasses with $x \leqslant 0.6$ crystallized through a metastable intermediate phase, $Ca_3Mg\,Si_2O_8$.

The aim of the present paper was to analyse the crystallization kinetics of gehlenite glass by means of isothermal and non-isothermal methods, in order to suggest a reaction mechanism consistent with the experimental results.

2. Experimental procedure

Gehlenite glass was prepared by melting pure reagents at 1700° C in a graphite crucible in an electric oven. The melt was cast in distilled water at a high cooling rate.

The heat treatments were performed in a DTA furnace on 100 mg powdered specimens to eliminate temperature gradients. Moreover temperatures and times were easily and exactly evaluated on isothermal DTA curves. The samples were heated at $20°\,C\,min^{-1}$ up to the selected growth temperatures. Growth times were measured from the time at which the samples reached the desired temperatures.

The quantitative determinations of the transformation was done by means of X-ray diffraction (XRD) analysis by the powder method using a Philips PW 1011 apparatus. $CuK\alpha$ radiation was used in all cases.

The calibration curve of X-ray peak intensity versus weight per cent of crystalline phase was obtained by using mixtures of glass and 100% crystalline gehlenite, in different proportions. The crystalline standard was prepared by heating gehlenite glass up to 1100° C in a DTA apparatus. To verify the degree of crystallinity a second run up to the same temperature was carried out. As no thermal effect was recorded and no difference in the X-ray patterns of crystallized samples after the first and the second run was found, a 100% degree of crystallinity was assumed. To eliminate the effect of preferred orientations of the crystals the three stronger peaks ($d = 2.85; 1.75; 3.07$ Å) were selected. Each intensity value was averaged over five measurements. Plotting the ratio of the diffracted intensity from mixtures to that from a completely crystalline sample against the weight per cent of crystalline phase present, a single calibration curve, i.e. a straight line with a slope nearly 1, for all the three peaks examined, was obtained as shown in Fig. 1.

Differential thermal analysis (DTA) curves at different heating rates (2 to $20°\,C\,min^{-1}$), in air,

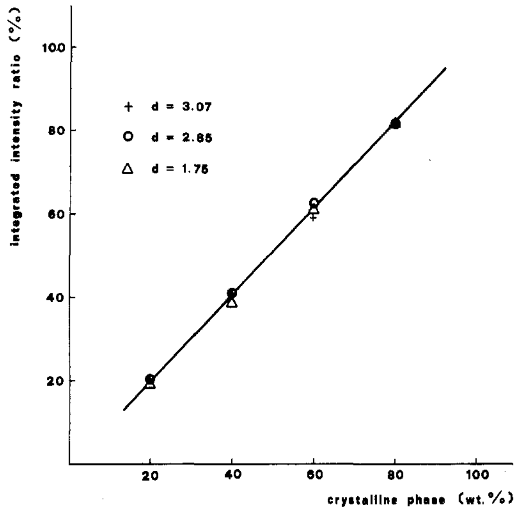

Figure 1 X-ray calibration curve for mixtures of crystalline and amorphous gehlenite.

of 90 mg powdered specimens were recorded; the particles were − 170 to + 230 mesh and the reference material was Al_2O_3. A Netzch thermoanalyser 404M was used.

3. Results and discussion

3.1. Isothermal kinetics

The percentage of crystallization detected by XRD analysis is shown in Fig. 2 as function of time. Growth temperatures ranged from 895 to 946° C.

To obtain kinetic parameters the following rate equation was assumed:

$$\frac{dy}{dt} = k^n t^{n-1}(1-y) \qquad (1)$$

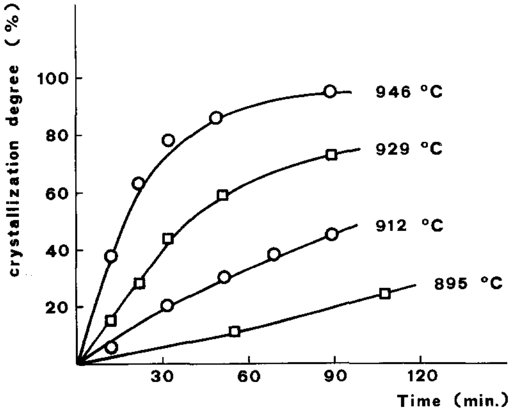

Figure 2 Isothermal devitrification curves.

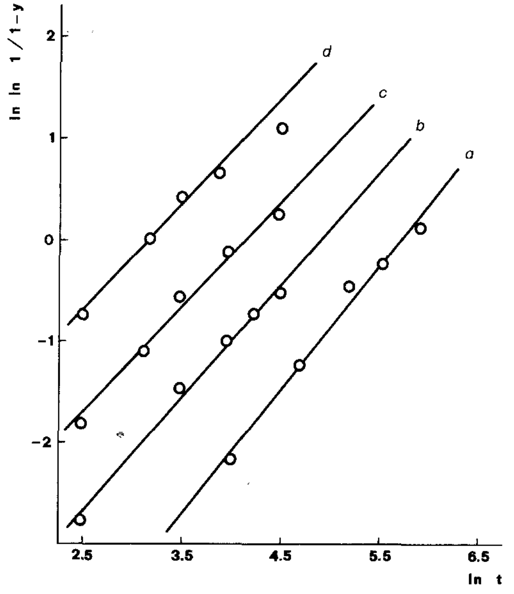

Figure 3 Johnson–Mehl–Avrami equation plot (a) 895° C; (b) 912° C; (c) 929° C; (d) 946° C.

where y is the fraction reacted at time t, n the reaction order and k is related to temperature T by an Arrhenius-type equation:

$$k = A\exp(-E/RT), \qquad (2)$$

where E is the activation energy and A a constant.

The integrated form of Equation 1

$$\ln\left(\frac{1}{1-y}\right) = (kt)^n \qquad (3)$$

is the well-known Johnson–Mehl–Avrami (JMA) [3, 4] equation which describes a wide number of solid state reactions [5].

Taking the logarithms of Equation 3

$$\ln\ln\left(\frac{1}{1-y}\right) = n\ln k + n\ln t \qquad (4)$$

and plotting $\ln\ln\left(\frac{1}{1-y}\right)$ versus $\ln t$, straight lines at each temperature, with nearly the same slope, were obtained as shown in Fig. 3. From their slopes and intercepts, a reaction order n and kinetic constant k could be evaluated. A plot of $\ln k$ versus $1/T$, Fig. 4, gave, in accordance with Equation 3, a straight line with slope $-E/R$.

The reaction order and activation energy values so calculated, are reported in Table I.

TABLE I Kinetics parameters

Investigation method	E (kcal mol^{-1})	n
Isothermal kinetics (XRD)	148	1
Non-isothermal kinetics (DTA)	135	1

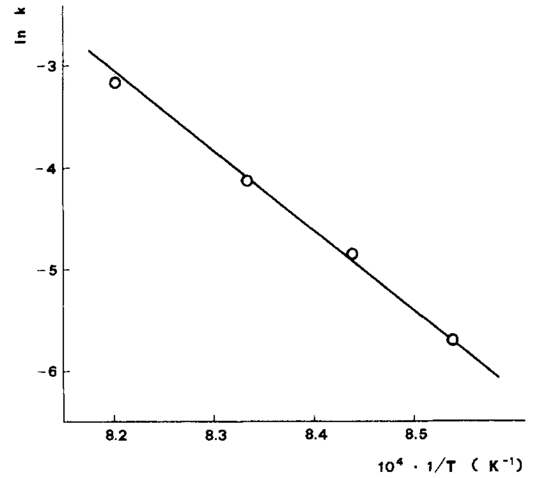

Figure 4 Arrhenius equation plot.

3.2. Non-isothermal kinetics

Kinetic parameters were also evaluated by means of DTA analysis. The method [6] is based on some theoretical assumptions. In a DTA curve, Fig. 5, the ΔT deflection from the base line at any given instant is proportional to the instantaneous reaction rate [7]; during a DTA run the time of heating t at each temperature T is inversely proportional to the heating rate h if the latter is constant [6]. In the advancing part of the crystallization peak the change in T has a much greater effect on the change in ΔT than on the change in y [8]. Also taking into account that at the peak temperature T_M, the ΔT deflection has a null temperature derivative, for kinetics governed by a JMA equation, the following two equations can be derived;

$$\ln \Delta T = -\frac{nE}{RT} + C \tag{5}$$

$$\ln h = -\frac{E}{RT_M} + C' \tag{6}$$

where C and C' are constants.

Plotting $\ln \Delta T$ versus $1/T$ and $\ln h$ versus $1/T_M$ two straight lines were obtained as shown in Figs. 6 and 7 respectively. The values of E and n calculated from their slopes are reported in Table I.

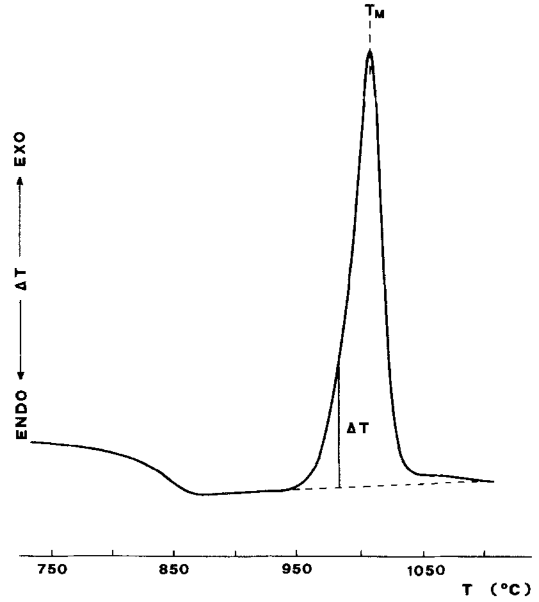

Figure 5 Crystallization peak of gehlenite glass detected by DTA.

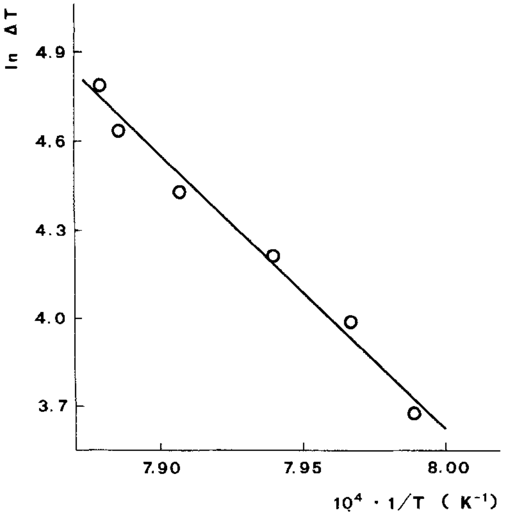

Figure 6 Plot of $\ln \Delta T$ versus $1/T$ (the values of ΔT and T are derived from a DTA curve recorded at 20° C min^{-1}).

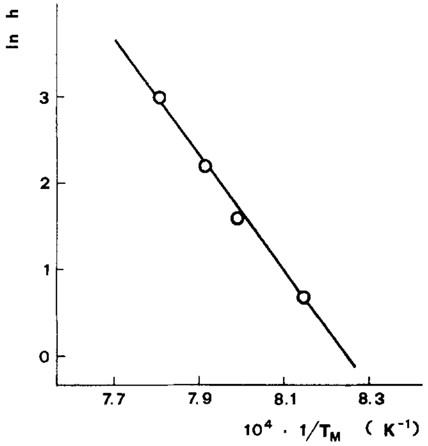

Figure 7 Plot of $\ln h$ versus $1/T_M$ (the values of T_M are read on DTA curves recorded at different heating rates).

3.3. Reaction mechanism

From isothermal and non-isothermal results a reaction order $n \simeq 1$ can be estimated. A JMA equation with $n = 1$ describes a rod-like growth controlled by diffusion from a fixed number of nuclei [5, 9].

As the crystalline phase and the glass examined have the same composition no long range diffusion should have been needed. SAXS measurements revealed the presence of discrete and independent droplets of a separated phase [1]. Guinier analysis identified 2 particle sizes with a radii of 120 and 270 Å respectively [2]. Moreover the calculated value of activation energy is of the same order of magnitude as for viscous flow in molten silicates [10].

The growth from a fixed number of nuclei is consistent with the above described heating process in DTA furnace. If the temperature of nucleation is lower than that of crystallization, the glass first passes through a region of high nucleation rate and subsequently crystallizes at a higher temperature where the formation of nuclei is very unlikely.

Finally as the crystalline morphology is spherulitic [11], the growth of very fine and densely packed fibres is well described as a rod-like crystallization.

4. Conclusions

The usual method of obtaining kinetic data involves, as reported in the experimental procedure, a laborious series of measurements under isothermal conditions at different temperatures. The good agreement between isothermal and non-isothermal results confirms the convenience of obtaining kinetic parameters from the relatively quick dynamic method of DTA analysis.

The experimental results, interpolated by a JMA equation with $n = 1$ suggest, at least in the range of temperatures and degrees of devitrification examined, a rod-like growth controlled by diffusion from a fixed number of nuclei.

Such a reaction mechanism is consistent with the phase separation in the glass and with the crystalline phase morphology.

Further investigations to identify the nature of the dispersed phase in as-quenched glass are required.

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