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Influence of the nucleation time-lag on the activation energy in non-isothermal crystallization

Alexander Karamanov*, Mario Pelino

Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, 67040 Monteluco di Roio L'Aquila Italy

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Abstract

In the present work, the influence of the nucleation time-lag on the non-isothermal glass crystallization is discussed. Differential thermal analysis (DTA) results of an iron-rich glass nucleated by Cr_2O_3 were obtained at different heating rates. The activation energy of crystallization, E_c , and the Avrami parameter, m , estimated by Kissinger's and Ozawa's equations were shown to be dependent on the heating rate. The value of E_c , obtained at 2.5, 5 and 7.5 K/min heating rates was calculated as 299 kJ/mol, while the value of E_c , obtained at 10, 15 and 20 K/min was as 499 kJ/mol. The value of m for 'low' and 'high' heating rates were 2.57 and 1.45, respectively. The results were interpreted on the basis of the non-steady state nature of the nucleation process. It was assumed that at high heating rates no nucleation takes place and the crystals grow on an existing fixed number of nuclei; the activation energy of crystal growth, E_g , can be estimated by applying the Kissinger equations. At low heating rates nucleation occurs and the number of nuclei formed is influenced by the heating rate; E_g can be estimated by the Matusita and Sakka equation. © 2001 Published by Elsevier Science B.V.

1. Introduction

Iron-rich glasses are characterized by spontaneous liquid–liquid immiscibility; one of the phases is richer in iron and promotes the formation of the magnetite spinel as the first crystal phase [1–6]. The magnetite formation depends on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the parent glass [3,6], as well as on the presence of TiO_2 and ZnO oxides [4,5]. By prolonged thermal treatment, pyroxenes precipitate on the spinel crystals, which act as nuclei for the crystallization.

A small addition of Cr_2O_3 affected the spinel formation, reducing the time of the thermal treatment and enhancing the degree of crystallization [7]. The nucleation mechanism is influenced by the low solubility of Cr_2O_3 in silicate melts; i.e., some Cr–Fe spinel crystals, named 'primary' nuclei, precipitated near the liquidus temperature, while at low temperatures the formation of 'secondary' nuclei takes place [8]. The above mentioned behavior was confirmed, for iron-rich compositions, by differential thermal analysis (DTA) [7]. The addition of 0.4–1.0 wt% Cr_2O_3 in as-quenched glasses leads to 40–50 K decrease of the crystallization peak temperature, T_p , compared with the glass without Cr_2O_3 . This shift can be related to the fast formation of primary nuclei. After nucleation treatment at 903 K the T_p shift reached 70 K due to the formation of secondary

* Corresponding author. Tel.: +39-0862 434 224; fax: +39-0862 434 203.

E-mail addresses: karama@ing.univaq.it (A. Karamanov), pelino@ing.univaq.it (M. Pelino).

nuclei. The formation of both primary and secondary spinel nuclei was highlighted by X-ray diffraction (XRD) [7].

In the present work DTA experiments with an iron-rich glass, nucleated with Cr_2O_3 are reported. The values of the crystallization activation energy and Avrami parameter, obtained at different heating rates, are evaluated and discussed.

2. Isothermal and non-isothermal crystallization in glasses

The isothermal crystallization kinetics in glasses are usually investigated by the KJMA (Kolmogorov, Johnson, Mehl, Avrami) equation in the form [9,10]

$$\alpha(\tau) = 1 - \exp(-\text{const}I_0U^n\tau^{n+1}), \quad (1)$$

where $\alpha(\tau)$ is the degree of transformation at time τ , I_0 is the rate of steady-state nucleation, U is the rate of crystal growth and n is an integer number, depending on the mechanism and direction of crystal growth.

If no nucleation takes place during heat-treatment and the crystals grow on an fixed number nuclei, N , previously formed, the following equation applies [9,10]:

$$\alpha(\tau) = 1 - \exp(-\text{const}NU^n\tau^n). \quad (2)$$

If clusters with critical radius are not formed in the parent glass during quenching, the nucleation cannot be considered as a steady state process [9–11]. A certain time-lag, t , is needed, before the formation of clusters with size corresponding to the critical radius. In this case the overall crystallization can be described by the following equation [11]:

$$\alpha(\tau) = 1 - \exp[-\text{const}I_0U^n(\tau - bt)^{n+1}], \quad (3)$$

where t is the time-lag, and $b = \pi^2/6$. The time-lag value may be estimated through the following approximation [11]:

$$t = \text{const}(T_m/\Delta T)^2\eta, \quad (4)$$

where T_m is the melting temperature and η is the viscosity at undercooling $\Delta T = T_m - T$.

The applicability of Eqs. (1)–(3) was confirmed by many experiments, carried out in isothermal conditions [9,10]. The data relative to I , U , t , n , as well as the activation energy of crystal growth, E_g , and the activation energy of nucleation were obtained for several glassy systems.

Alternatively, non-isothermal investigations, carried out with DTA or differential scanning calorimetry (DSC) are widely applied [12]. These methods are based on the assumption that the formal theory of isothermal transformation kinetics is nearly valid in non-isothermal conditions. This approximation can be only used in a relatively short temperature range, assuming a constant value of the activation energy in this interval.

These techniques are used to evaluate the activation energy of the crystallization and the reaction order, m , also called Avrami parameter. In the case of simultaneous nucleation and crystal growth (Eq. (1)) $m = n + 1$; in the case when the crystals grow on fixed number of nuclei (Eq. (2)) $m = n$.

The DTA method usually involves non-isothermal heat-treatments, carried out at different heating rates. The activation energy of crystallization, E_c , can be estimated by the Kissinger equation [13]:

$$\ln(\phi/T_p^2) = -E_c/RT_p + \text{const}, \quad (5)$$

where T_p is the crystallization peak temperature of the DTA trace, ϕ is the heating rate and R is the gas constant. The plot of $\ln(\phi/T_p^2)$ vs. $1/T_p$ is a straight line, whose slope corresponds to E_c .

When surface crystallization takes place (powder samples) or when the crystals grow on fixed number of nuclei the value of E_c obtained with Eq. (5) corresponds to the activation energy of crystal growth, E_g [12]. However, when nucleation takes place during heating, the E_c value evaluated by Kissinger has a considerable lower value compared with the value of E_g . This is a consequence of the fact that the number of nuclei is influenced by the heating rate; the lower the rate, the bigger the number of the nuclei formed during heating. In the case of nucleation during DTA measurement, Matusita and Sakka proposed the following modification of the Eq. (4) [14]:

$$\ln(\phi^m/T_p^2) = -nE_g/RT + \text{const.} \quad (6)$$

The value of the activation energy obtained by Kissinger's equation, E_c , can be related to the activation energy of the crystal growth, E_g , by the following approximation [15]:

$$E_g \approx \frac{m}{n} E_c. \quad (7)$$

This relationship can be used in oxide systems, where E_g has a relatively high value. In the silicate glass forming melts can be assumed that the associated error related to the application of Eq. (7) is less than 10% [15].

The Avrami parameter, m , can be evaluated using Ozawa's equation [16]

$$\left. \frac{d[\ln(-\ln(1-\alpha))]}{d(\ln \phi)} \right|_T = -m, \quad (8)$$

where α is estimated at a fixed temperature, T , from exotherms obtained at different heating rates. The value of α is calculated as the ratio of partial area of the crystallization peak at the temperature T to the total area of the crystallization exotherm.

3. Experimental

A glass with the following composition: SiO₂ – 52.2, Al₂O₃ – 3.9, (Fe₂O₃ + FeO) – 21.6, CaO – 12.1, MgO – 0.2, ZnO – 2.4, PbO – 1.5, Na₂O – 4.9, K₂O – 1.0 was prepared by mixing jarosite, a zinc hydrometallurgy waste, granite mud, a waste arising from the cutting of the blocks, sand, limestone and Na₂CO₃. A 0.7 wt% Cr₂O₃, was added in the batch as nucleating agent.

The batch, about 100 g, was melted at 1723 K utilizing a corundum crucible (99.8% Al₂O₃) in a super-kanthal furnace for 2 h. The glass was obtained by quenching on a cold stainless steel mold.

The crystallization process was investigated by DTA technique at 2.5, 5, 7.5, 10, 15 and 20 K/min heating rates. In order to minimize the effect of surface oxidation of Fe²⁺, which takes place on the glass powder [6], bulk samples of about 100 mg were used.

DTA experiments were also carried out on samples previously nucleated at 913 K for 2 h. This

heat-treatment was sufficient to allow a complete nucleation [7].

Isothermal treatments were carried out at 923 and 973 K for different holding times. The crystalline fraction was evaluated by measuring the change of the density between the parent glass and the heat-treated sample using the following equation [17]:

$$x = 100 \frac{1/\rho_g - 1/\rho_{gc}}{1/\rho_{g(cr)} - 1/\rho_{cr}}, \quad (9)$$

where ρ_g is the density of parent glass, ρ_{gc} is the density of measured sample, $\rho_{g(cr)}$ is the density of a hypothetical glass with the composition of the formed crystal glass and ρ_{cr} is the density of the crystal phase.

The method used is based on the variation of density during the crystallization process. It is assumed that the volume of the parent glass, V_g , consists of two parts: $V_{g(cr)}$ – with the composition as the crystal phase which is going to be formed and $V_{g(r)}$ – with the composition of the residual glass. Then, during the crystallization, only the part $V_{g(cr)}$ is transformed in crystal phase with volume V_{cr} . A detailed description of the methodological approach and application to the crystallization of iron-rich glasses is reported elsewhere [17].

The applicability of the method depends on the density difference between the amorphous phase $g(cr)$ and the corresponding crystalline phase and on the accuracy of the density measurements. In case of pyroxene formation the density variation is extremely high, which allows the detection of differences of about 1–2% crystal phase in the crystallized samples. For this series of tests, a He displacement Pycnometer was utilized. The experimental associated error to the measurements, employing a 3–4 g glass sample, was evaluated as $\pm 0.001 \text{ g/cm}^3$.

4. Results

The experimental DTA curves, obtained at 2.5, 5, 7.5, 10, 15 and 20 K/min heating rates, respectively, are shown in Fig. 1. Fig. 2 reports the

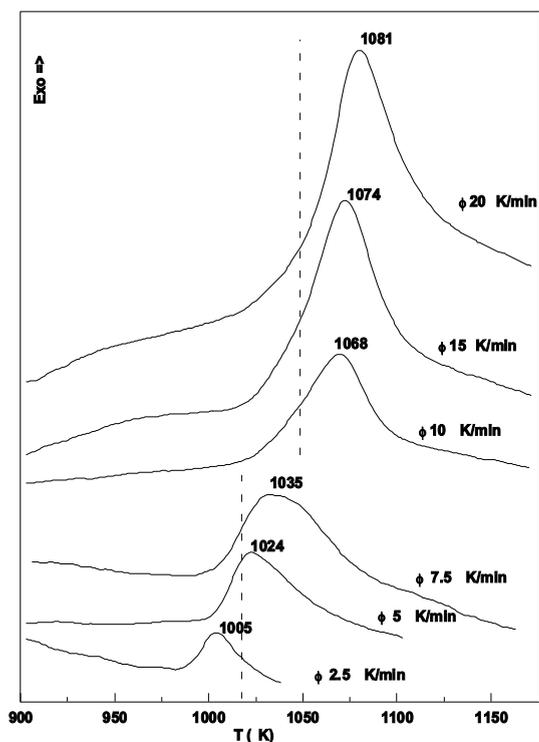


Fig. 1. DTA plots of glass samples, heat-treated at different heating rates.

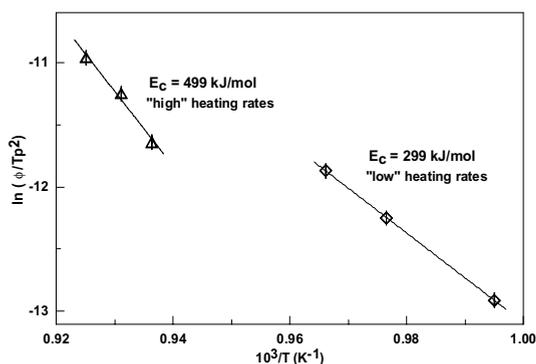


Fig. 2. Activation energy of crystallization, E_c , obtained by Kissinger equation at low (2.5, 5 and 7.5 K/min) and high (10, 15 and 20 K/min) heating rates.

corresponding plots of $\ln(\phi/T_p^2)$ vs the inverse of the peak temperature ($1/T_p$), and the values of the activation energy of crystallization, obtained according to the Kissinger equation. It is evident that

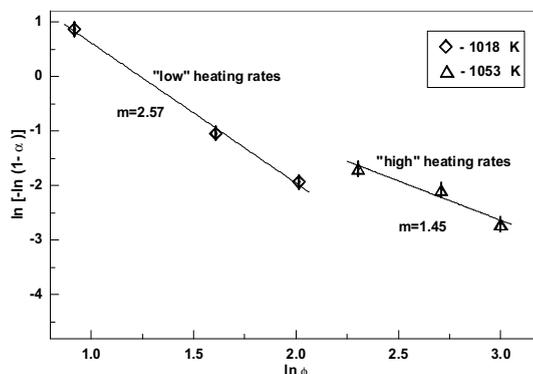


Fig. 3. Avrami parameters, m , obtained by Ozawa equation at low (2.5, 5 and 7.5 K/min) and high (10, 15 and 20 K/min) heating rates.

the DTA curves can be separated in two groups: traces obtained at 'low' heating rates (2.5, 5 and 7.5 K/min) and traces obtained at 'high' heating rate (10, 15 and 20 K/min).

The Avrami parameter was evaluated by the Ozawa method (Eq. (8)) at two different temperatures, indicated in Fig. 1 by the dashed lines. For the low heating rates, the degree of transformation, α , was evaluated at 1018 K while for the high heating rates at 1053 K, respectively. The results and the corresponding values of the Avrami parameter, m , are reported in Fig. 3.

DTA experiments were also carried out on nucleated glass. The results for the samples, treated at 7.5 and 10 K are plotted in Fig. 4, together with the traces of the corresponding non-nucleated samples.

The crystallization process was investigated in isothermal conditions. The density variation and the corresponding percentage of crystal phase formed as a function of the holding time at 923 and 973 K are shown in Figs. 5 and 6, respectively. The highest density, 2.96 g/cm³, was obtained after 1200 min at 923 K and 110 min at 973 K, respectively. The XRD analysis highlighted that pyroxene is the main crystalline phase and the percentage of crystallization is 30 ± 2 wt%.

5. Discussion

In the present work, the overall kinetics of an iron-rich glass, nucleated with 0.7 wt% Cr₂O₃ are

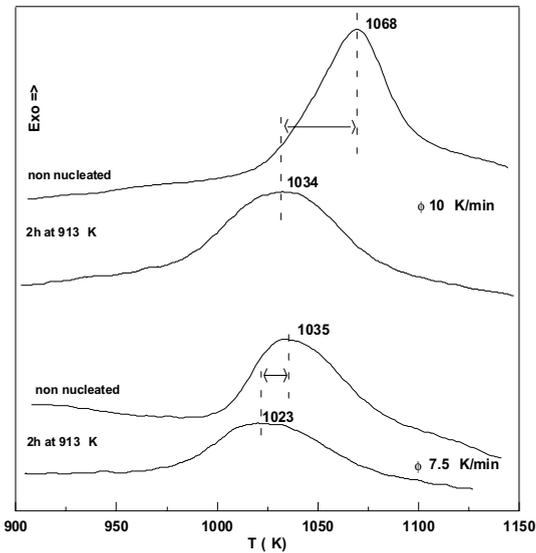


Fig. 4. DTA plots of nucleated and non-nucleated glass samples, heat-treated at 7.5 and 10 K/min.

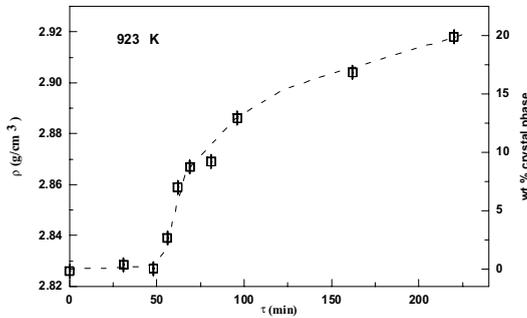


Fig. 5. Variation of the density and the corresponding percentage of crystal phase as function of the time at 923 K.

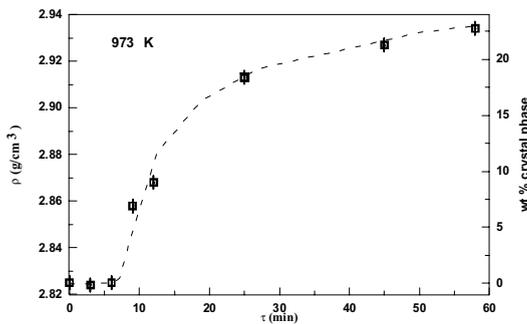


Fig. 6. Variation of the density and the corresponding percentage of crystal phase as function of the time at 973 K.

investigated by DTA at different heating rates. The value of E_c , obtained by the Kissinger equation for the low heating rates (2.5, 5 and 7.5 K/min) is 299 kJ/mol, while the value for the high heating rates (10, 15 and 20 K/min) is considerably higher, 499 kJ/mol. Similarly, the value of the Avrami parameter, m , obtained by Ozawa's equation for the low rates is 2.57, while for the high rates is 1.45.

At high heating rates the Avrami parameter, m , is near to the value of 1.5; at low heating rates is near to the value of 2.5. The first number may be related to three-dimensional parabolic growth on a fixed number of nuclei while the second one to simultaneous nucleation and three-dimensional parabolic growth [9,10].

Three-dimensional spherulitic growth is typical for the pyroxenes and was confirmed in many iron-rich compositions [1–5]. At the same time, the low percentage crystal phase formed in the investigated composition, 30 ± 2 wt%, indicates that the crystal growth is controlled by diffusion, i.e., a square root temperature dependence of the growth rate may be expected.

The difference in the m values at low and high heating rates can be explained assuming that, for the investigated composition, the nucleation process is time dependent. When the heating rate is high, the sample stays in the temperature region of nucleation for a time shorter than the time-lag; as a result no nucleation can take place and the pyroxene crystals grow only on the primary spinel nuclei. Vice versa when the heating rate is low; the samples stay in the temperature region of nucleation for times longer than the time-lag and the formation of secondary nuclei might take place.

It is known that the time-lag is not constant and depends on the temperature [9–11]. However in non-isothermal conditions there exists one critical quench/heating rate that limits the significance of the time-lag effect [18].

The differences in the activation energies, at low and high heating rates, also can be explained assuming a non-steady state behavior of the nucleation process. At 'high' heating rates, the value of the activation energy by the Kissinger equation is not influenced by the formation of secondary spinel nuclei; pyroxene crystals grow only on primary spinel nuclei and E_c corresponds to the value of

activation energy of crystal growth, E_g . At low heating rates, the formation of secondary nuclei takes place and, as a result, E_c value decreases.

For the low heating rates the activation energy of crystal growth, E_g , was estimated by the Matusita and Sakka equation, assuming the values of 1.5 and 2.5 for n and m , respectively. The results are shown in Fig. 7. The obtained E_g value of 514 kJ/mol is in very good agreement with the value of 499 kJ/mol, obtained for the high heating rates by the Kissinger equation.

Similar E_g value, 498 kJ/mol, was obtained directly through Eq. (7) using the value of 299 kJ/mol, obtained by Kissinger's equation at low heating rates and the values of 1.5 and 2.5 for n and m , respectively.

The time-lag effect was confirmed by the results of the nucleated samples. Fig. 4 shows that the T_p shift after 2 h nucleation step is about 12 K for the sample heated at 7.5 K/min, while it is more than 30 K for the sample heated at 10 K/min. This difference might be explained assuming that in the non-nucleated sample, heated at 10 K/min, the crystals grow only on primary nuclei while in the non-nucleated sample, heated at 7.5 K/min, crystals grow also on secondary nuclei.

The nucleation time-lag effect was clearly highlighted by the isothermal experiments. Fig. 5 shows that the density variation, i.e., the formation of the crystal phase, is negligible after 45–50 min holding at 923 K while 15% of the crystal

phase, half of the total amount, is formed after 110–115 min. At 973 K, as highlighted by Fig. 6, the density variation starts after 6–7 min and 15% crystal phase is obtained after 16–18 min. This crystallization behavior can be explained assuming that non-steady state nucleation takes place.

6. Conclusions

The present work showed that the values of the activation energy of crystallization, E_c , by the Kissinger equation and of the Avrami parameter, m , by the Ozawa equation depend on the heating rate.

At low heating rate, the nucleation process might take place; the activation energy of crystal growth, E_g , can be estimated by the Matusita and Sakka equation. The Avrami parameter indicates a simultaneous nucleation and crystal growth.

At high heating rate, due to the non-steady state nature of the nucleation, the crystals grow on a fixed number of already existing nuclei. The E_g value can be estimated directly by the Kissinger equations and the Avrami parameter is relative to crystal growth only.

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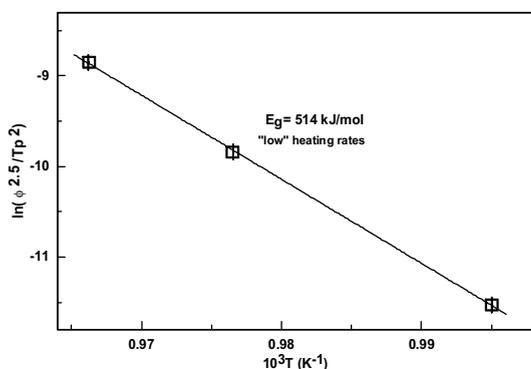


Fig. 7. Activation energy of crystal growth, E_g , obtained by Matusita and Sakka equation for the glass samples heat-treated at 2.5, 5 and 7.5 K/min.

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