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The crystallisation kinetics of iron rich glass in different atmospheres

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Abstract

The crystallisation kinetics of powder and bulk iron-rich glass, based on zinc hydrometallurgy hazardous waste, were investigated in air and nitrogen atmospheres. The activation energy of crystal growth, E_C, and the Avrami parameter, n, were estimated by means of differential thermal analysis. The kind and amount of crystal phases, formed during the thermal treatment and their relative ratio were evaluated by X-ray diffraction analysis. The kinetics results sustain that the pyroxene phase grows on a fixed number of magnetite nuclei. The activation energy of crystal growth on the surface and in the bulk are similar in air and nitrogen atmospheres. When the powder glass sample is heat-treated in air, surface oxidation of Fe^{2+} into Fe^{3+} inhibits crystallisation resulting in the decrease of the percentage of crystal phase and the change of the Avrami parameter value. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The glass forming melts, due to their high viscosity and low transformation rate, are useful tools for the investigation of the crystallisation processes. $Li_2O.2SiO_2$, $BaO.2SiO_2$ and other simple glass compositions are typical systems for investigating the mechanisms of nucleation and crystal growth.[1–4]

The theoretical approach and the experimental results obtained in these studies also acquire particular importance for the synthesis and production of glass-ceramics.[5,6] However, the crystallisation process in commercial glass-ceramics is more complicated than the fundamental studies, due to the complex chemical composition of the parent glass, the variable role of the nucleating agents and the chemical modification of the residual glass during heat-treatment.

In glasses, the crystal growth is controlled either by the rate of aggregation of the structural units to the crystal lattice or by the diffusion. The first case applies when the glass composition does not change during crystallisation, i.e. the crystal growth rate is constant with time. The latter one is characterised by the modification of the glass composition with a rate, function of the square root of time. However, when the scale of the diffusion field becomes constant, the growth rate can be time independent even for diffusion controlled growth.[7] This case is typical of dendritic formation or of fibre like surface crystallisation.[4]

Due to the great number of micro cracks and other surface defects, crystallisation begins from the surface; the formation of surface nuclei is considered as a heterogeneous nucleation.[8] The crystal growth rate for surface and bulk nuclei is in principle similar so the differences in the surface and bulk crystallisation kinetics depend on the number of nuclei formed and their distribution.[9] The surrounding atmosphere might also play an important role in surface crystallisation, by modifying the composition of the surface.[4,8,10]

In the present study, the crystallisation of powder and bulk samples of iron-rich glass composition is investigated. The kinetics of pyroxene formation and the activation energies of the crystal growth are evaluated by means of DTA experiments carried out in air and nitrogen atmospheres.

2. Crystallisation in non-isothermal conditions by means of DTA

Differential thermal analysis (DTA) is a simple tool to determine the glass transition, phase transformation and melting temperatures in glass-forming melts.[11,12]

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The technique can be also used for kinetics investigations, particularly for the determination of the activation energy of crystal growth and the Avrami parameter, n.[13] The method is based on the assumption that the Avrami equation, which is applied to bulk crystallisation in isothermal conditions, can also be employed for non-isothermal crystallisation in a narrow temperature range:[11,13]

$$\alpha(\tau) = 1 - \exp\left(-\mathrm{const}\ I_0 U^{n-1} \tau^n\right) \tag{1}$$

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

The activation energy of crystal growth, E_C, can be estimated carrying out DTA experiments at different heating rates, by using the Kissinger equation:[14]

$$\ln\left(\phi/T_p^2\right) = -E_c/RT + \mathrm{const} \tag{2}$$

where T_p is the crystallisation peak temperature of the DTA trace, ϕ is the heating rate and R is the gas constant. A plot of ln (ϕ/T_p^2) vs. $1/T_p$ is a line, whose slope corresponds to E_C.

The Avrami parameter, n, can be determined by using the equation proposed by Ozawa:[15]

$$\frac{d[\ln(-\ln(1-\alpha))]}{d(\ln\phi)}\Big|_T = -n \tag{3}$$

where α is estimated by evaluating the partial area of the crystallisation peak from exotherms, obtained at different heating rates and at a fixed temperature, T.

The value of n can also be evaluated by a single DTA experiment using the Augis and Bennett equation[16] in the form:

$$n = (2.5/\Delta w)\left(RT_p^2/E_C\right) \tag{4}$$

where Δw is the width of the crystallisation peak at half height.

3. Experimental

A glass with the following composition (wt%): SiO_2 52.9; Al_2O_3 4.1; (Fe_2O_3 + FeO) 24.1; CaO 5.2; MgO 1.8; ZnO 2.7; PbO 1.7; Na_2O 6.4; K_2O 1.1 was prepared by mixing Jarosite,[17] a hazardous industrial waste arising from the hydrometallurgy of zinc ores, granite scraps and glass cullet. The melting was carried out in a methane furnace at 1400°C, utilising mullite crucibles. The raw material characterisations and the melting conditions were reported elsewhere.[18]

The crystallisation process has been investigated in non-isothermal conditions by means of DTA technique in air and nitrogen atmospheres. About 100 mg of powder sample (122–212 μm particle size) obtained after crushing, milling and sieving of glass tile were used. The experiments were carried out in "Netzsch STA 409" apparatus at 5, 10, 15 and 20°C/min heating rates. DTA analyses have also been carried out on bulk samples, in air.

The crystalline phases formed and their relative ratio were determined by XRD technique, using a Philips-1830 apparatus and CuK_α radiation. Firstly the crystalline fractions developed during the thermal treatment were evaluated comparing the areas of amorphous and crystalline phases in the XRD spectra,[19] then the ratio between the phases has been estimated using the relative intensities of the major peaks.[20]

4. Results and discussion

The experimental DTA curves for the powder samples obtained in air (P-air) and nitrogen atmospheres (P-N_2) are shown in Figs. 1 and 2, respectively. Fig. 3 reports the DTA trace obtained for bulk sample in air (B-air).

In a previous work,[21] it was highlighted that the crystallisation ability of powder iron rich glasses in air decreases due to the surface oxidation of Fe^{2+}. This process influences the pyroxene formation by changing the melt composition, viscosity and liquidus temperature. In the present investigation the oxidation of Fe^{2+} into Fe^{3+} is indicated in P-air sample by the exo-effects in the 620–740°C region (Fig. 1). A similar effect is not noticeable in P-N_2 and is negligible in B-air samples, due to the presence of a neutral atmosphere in the first case and small specific surface area in the latter, respectively. The DTA traces also highlight that crystallisation is inhibited when powder samples are thermally treated

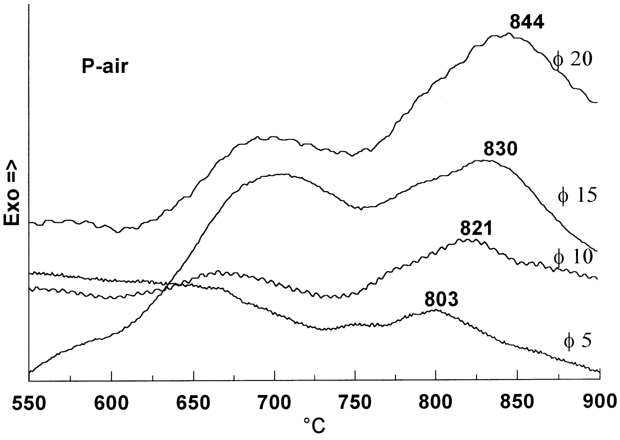

Fig. 1. DTA plots of powder glass, heat treated in air at different heating rates.

in air; the exo- peak is not as sharp as in P-N_2 and B-air and appears at higher temperatures.

The activation energy of crystal growth, E_C, has been estimated by the Kissinger equations [Eq. (2)]. Fig. 4 reports the plots of $\ln\left(\phi/T_p^2\right)$ vs the shifts of the peaks $(1/T_p)$ and the values obtained for the activation energy of crystal growth. From the results obtained it appears that the E_C value is similar for the three samples. It can be concluded that the diffusion process, connected with the crystal growth in iron rich compositions, is similar when bulk or powder glasses are heat-treated in an air or nitrogen atmosphere.

The shift at lower temperatures of the crystallisation peak in P-N_2, compared with B-air sample, can be explained by the greater number of nuclei formed due to the higher specific surface.

The E_C value for P-N_2 and P-air are similar, but in P-air the crystallisation occurs at higher temperatures because of the higher viscosity induced by the surface oxidation process. The shape of the P-air crystallisation peak is also broader than that for P-N_2 indicating a lower reaction order.

In the previous work[18] the kinetics of bulk crystallisation of the same glass composition were investigated by isothermal treatments at 620, 640 and 660°C. The results highlighted a high immiscibility of the initial melt, leading to the formation of magnetite as first crystal phase, followed by the precipitation of pyroxene as the major phase. Using DTA and density measurements it was demonstrated that there is no typical nucleation process and the pyroxene crystals grow on a fixed number of nuclei. In the 620–660°C temperature range, a 1.5 value was obtained for the Avrami parameter, which corresponds to three dimensional parabolic growth. Electron microscopy imaging confirmed this hypothesis. In the same work, the amounts of magnetite and pyroxene formed at 660°C were estimated by density[22] and XRD measurements as 8–10 wt% and 43–45 wt%, respectively.

In the present work, the Avrami parameter was evaluated at higher temperatures. The results obtained by the Ozawa method [Eq. (3)] at 825°C for B-air, at 750°C for P-air and at 740°C for P-N_2 are shown in Fig. 5. The Avrami parameter, n, has also been evaluated by the

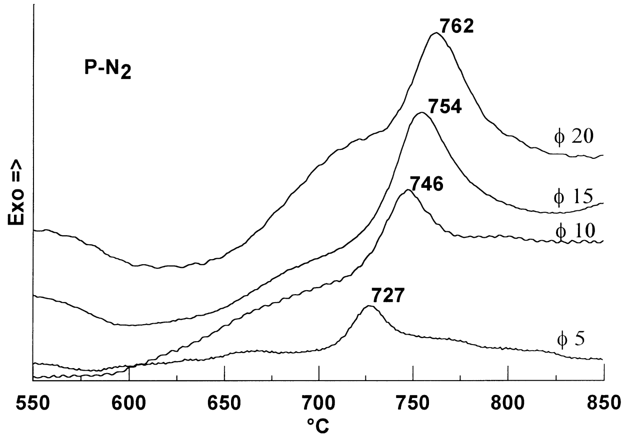

Fig. 2. DTA plots of powder glass, heat treated in nitrogen atmosphere at different heating rates.

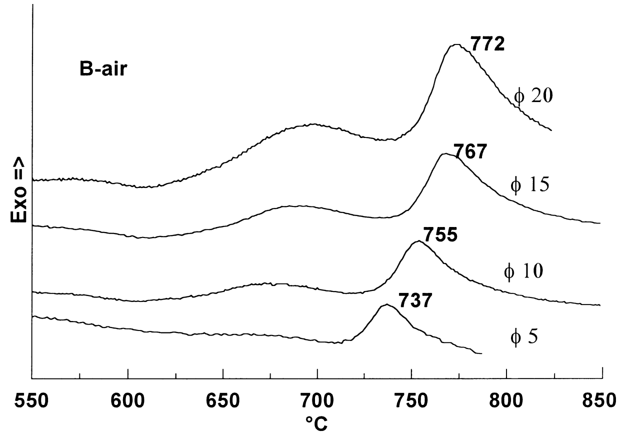

Fig. 3. DTA plots of bulk glass, heat treated in air at different heating rates.

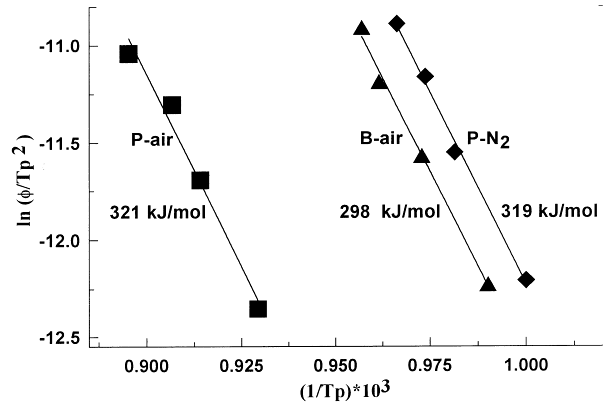

Fig. 4. Activation energy of crystal growth, E_C, for P-air, P-N_2 and B-air samples, obtained by Kissinger equation.

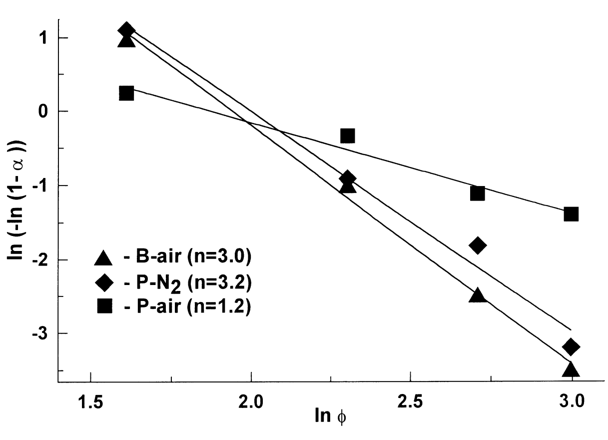

Fig. 5. Avrami parameter, n, for P-air, P-N_2 and B-air samples, obtained by Ozawa equation.

Table 1
Values of the Avrami parameter, n, obtained by Augis and Bennett method

	Heating rate (°C/min)				
	5	10	15	20	Average
P-air	1.2	1.3	1.1	1.1	1.2
P-N2	3.1	3.0	2.6	2.7	2.9
B-air	3.1	2.8	2.9	2.7	2.9

Table 2
Percentages of crystal phases formed in samples P and B, heat-treated in different experimental conditions

		Crystal phase (wt%)	Magnetite (wt%)	Pyroxene (wt%)	P/M[a]
P-N_2	30 min at 730°C	43–44	8–10	33–35	3.6
P-Air	30 min at 730°C	12–13	4–6	5–7	1.2
P-Air	60 min at 810°C	36–37	5–7	29–31	5.1
B-air	30 min at 740°C	44–45	9–11	34–36	3.5

[a] P/M, pyroxene/magnetite ratio.

Augis and Bennett method ([Eq. (4)] for each of the experimental exotherms. The results are summarised in Table 1 and are in good agreement with the ones obtained by the Ozawa equation.

For P-N_2 and B-air samples, the Avrami parameter value is near 3, which can be related to a three dimensional time independent growth on a fixed number of nuclei. In P-air sample the value of the Avrami parameter is near 1 corresponding to two dimensional parabolic growth or, alternatively, to one direction time independent growth.

The differences of the n values can be related to changes of the crystal growth mechanism and morphology.[4,7] As noted by Uhlman,[4] by increasing the undercooling, crystal morphology changes from faced or fibrillar to dendritic or spherolithic. Similar results are reported for an iron rich composition, in which three dimensional growth was observed near T_g and two dimensional at higher temperatures.[23]

XRD spectra were carried out after thermal treatments at different temperatures and atmospheres on the crystallised glasses. The results are shown in Fig. 6 while in Table 2 the experimental conditions, the percentage of crystal phase formed and the ratio between magnetite and pyroxene are reported. The reported heat-treatment times yield the maximum degree of crystallisation for each of the experimental temperatures.

Spectrum a and b were carried out on powder, heat treated in the same conditions but in different atmospheres. The comparison shows that the P-N_2 sample is crystallised with 43–44 wt% crystal phase, while in P-air the pyroxene formation has just started. The full crystallisation of P-air (36–37 wt%) is obtained at 810°C for 1 h, as shown in the spectrum c.

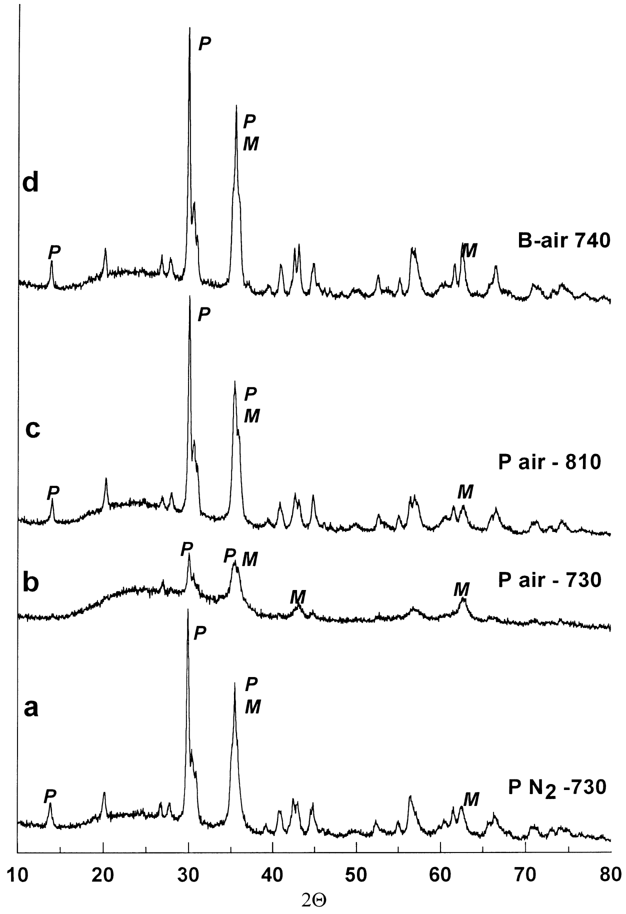

Fig. 6. XRD spectra of P and B samples, heat-treated in different experimental conditions. (P, pyroxene; M, magnetite).

Finally, by comparing P-N_2 and B-air spectra, it happens that the two samples have similar crystallisation behaviour as supported by the same activation energy and reaction order obtained by DTA.

5. Conclusions

The results of this study throw some light on the understanding of the crystallisation phenomena in iron-rich compositions, which are typical of glasses made up of metallurgical industrial wastes.

For the investigated composition and experimental conditions, crystallisation always begins with magnetite formation; then the magnetite crystals become nuclei for the pyroxene precipitation, so the crystallisation kinetics can be explained as pyroxene formation on a fixed number of nuclei. The activation energy of crystal growth on the surface and in the bulk are similar in air and nitrogen atmospheres, which is an indication of a similar diffusion process, associated with the pyroxene formation.

The surface oxidation process of Fe^{2+} into Fe^{3+} inhibits the crystallisation of glass-powder, decreases the amount of crystal phase formed and changes the reaction order, n.

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