

Kinetics of Phase Formation in Jarosite Glass-ceramic

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Abstract

The crystallisation behaviour of an iron-rich glass was studied by means of density measurements, Differential Thermal Analysis and X-ray Diffraction. The results highlighted that there is no typical nucleation process in which the number of nuclei is influenced by the thermal treatment and influence the crystallisation process. The kinetics of phase formation was investigated in isothermal and non-isothermal conditions; the Avrami parameter value, 1.5, is indicative of a three dimensional diffusion controlled growth of the pyroxene crystals on a fixed number of nuclei. The activation energy of crystal growth, obtained by the isothermal and non isothermal methods, resulted in being 377 kJ mol⁻¹ and 298 kJ mol⁻¹, respectively. Considering the different temperature range, these values are in fair agreement and consistent with values reported by other authors. Using TEM-EDS analysis the high immiscibility of the initial glass was highlighted; the two liquid phases, one richer in Fe and the other in Si and Ca, promote the formation of magnetite and pyroxene during the thermal treatment, respectively. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

In the past 30 years, a large number of papers, dealing with the kinetics of transformation of the glasses in glass-ceramics have been published. A large part of these works is connected with

isothermal investigations of the nucleation,^{1,2} the crystal growth^{3,4} or with the kinetics of crystallisation.^{4,5} Using the Differential Thermal Analysis technique (DTA), other publications investigate the crystallisation process in non-isothermal conditions.^{6–8}

These studies throw important light on the understanding of the nature of the phase transformation in glasses and clarify some typical aspects of the crystallisation process, such as the nature of the nucleation and the mechanisms of the crystal growth in different glass-forming systems. They also represent an important means for optimizing the heat-treatment regimes of the glass in order to tailor the final properties of the glass-ceramics. Some of these works are related with iron-rich glass compositions, in which the crystallisation process is more complicated due to the high immiscibility tendency of the initial glass and the formations of different crystal phases. The investigations carried out on compositions based on industrial wastes^{9–11} or on basalt rocks^{12–16} belong to this later group of studies.

The aim of the present work is the investigation of the kinetics of phase transformation in iron-rich glass compositions based on jarosite, which is hazardous industrial waste¹⁷ arising from the hydro-metallurgy of zinc-ores to produce the metal. The crystallisation of jarosite-glasses produces two mayor phases: pyroxene and magnetite, being the ratio between these phases influenced by the parent glass composition, the Fe³⁺/Fe²⁺ ratio^{12,18} and the thermal treatment schedule.

In this study, isothermal and non-isothermal investigations of the crystallisation kinetics were carried out by helium-displacement pycnometer and DTA measurements. The Avrami kinetics parameter and the activation energy of crystal growth were determined and the optimal heat-treatment was defined.

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2 Kinetic of Crystallisation Process

To explain the kinetics of bulk crystallisation of supercooled melts the so-called Avrami equation usually is used.³⁻⁵

$$\alpha(\tau) = 1 - \exp(-gI_0U^{n-1}\tau^n) \quad (1)$$

where $\alpha(\tau)$ is degree of transformation at time τ , g is a shape constant, I_0 is the rate of steady-state nucleation, U is the rate of crystal growth and n is a integer number which depends on the growth direction numbers, the mechanisms of nucleation and crystal growth. By taking the logarithms of eqn (1) twice, the value of the Avrami constant, n , may be calculated by the slope of the experimental curve.

In the case of crystals growth from a previously formed constant number of nuclei the Avrami constant only depends on the crystallisation growth. In this case, using isothermal results obtained at different temperatures, the activation energy of crystal growth, E_c , can be evaluated assuming an Arrhenius temperature dependence, i.e. $U = U_0 \exp[-E_c/(RT)]$, eqn (1) can be rewritten as:

$$\ln \tau_\alpha = E_c(RT) - \ln(\text{const}U_0^n) \\ /n - [\ln - \ln(1 - \alpha)]/n \quad (2)$$

where τ_α is the time, corresponding to a certain value of α . If the logarithm of τ_α is plotted against $1/T$, the slope gives E_c/R value.

As previously demonstrated,¹⁹ the degree of the phase transformation can be evaluated by using density measurements, through the following equation:

$$\alpha = [(\rho_{x(\tau)} - \rho_g)\rho_{x(\text{tot})}] / [(\rho_{x(\text{tot})} - \rho_g)\rho_{x(\tau)}] \quad (3)$$

where ρ_g is the density of the initial glass, $\rho_{x(\tau)}$ is the density at time τ and $\rho_{x(\text{tot})}$ is the maximum density at the end of the crystallisation process.

The wt% crystal phase formed, x , can be evaluated through the relation:¹⁹

$$x = 100(1/\rho_g - 1/\rho_{gc}) / (1/\rho_{gc} - 1/\rho_c) \quad (4)$$

In this case ρ_{gc} is the density of the glass-ceramic, ρ_c is the density of the crystal phase formed and the $\rho_{g(c)}$ is the density of a glass, having the same composition as the crystal phase formed.

In non-isothermal conditions the kinetics investigations are usually carried out by DTA. The activation energy of crystal growth, E_c , can be estimated by the Kissinger equation,²⁰ using DTA results obtained at different heating rates:

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

Here T_p is the peak temperature of the DTA exotherm and ϕ is the heating rate. A plot of $\ln(\phi/T_p^2)$ versus $1/T_p$ is a line, whose slope corresponds to E_c .

Matusita and Sakka²¹ pointed out that the Kissinger equation gives real results only when there is no nucleation process. In the case of nucleation, when the number of nuclei is influenced by the heating rate, they proposed a modification of the eqn (5) which takes into account this behavior.

The occurrence of a nucleation process is usually indirectly investigated by two-step isothermal heat-treatments. The first step corresponds to a temperature region where the nuclei are formed; the second step is at a higher temperature, where the nucleation rate is negligible and the crystals grow to a measurable size. Then the number of the crystals formed can be estimated by microscopic methods or by comparing the degrees of crystallisation. The results are related to the nucleation heat-treatment regimes.^{1,4,5}

A preliminary indication of the nucleation can be obtained by DTA, comparing the shift of the crystallisation peak in samples with and without the nucleation step.^{22,23} A consistent nuclei formation lowers the peak temperature.

3 Experimental

Jarosite waste was calcined at 800°C for 2 h to eliminate the volatile fraction (NH₃ and SO₂) present in the composition. About 10 kg of calcined jarosite were mixed with glass cullet and granite scraps in the ratio 30:40:30. Mullite crucibles were used to melt the batch; about 3 kg of powder mixture were melted per each fusion. The fusion was carried out in a methane furnace at 1390°C for 7 h to ensure the perfect homogenisation of the components. A final 30 min step was set at 1450°C to obtain the proper viscosity for the pouring. Cooling and forming were carried out in air on preheated stainless steel moulds at 500°C. These conditions were considered sufficient to allow annealing of the glass phase and to release stresses. Several 200 x 200 x 10 mm tiles were obtained and one of them was cut to obtain suitable pieces for the experimental investigations. An Fe³⁺/Fe²⁺ ratio of about 3 was obtained for the initial glass. This value is similar to the equilibrium ratio for iron rich compositions after a long melting time,¹² and is comparable to glass-ceramics obtained by casting molten basalt rocks in the production plants.

Table 1 reports the chemical composition of the 'as it is' jarosite sample used in this study, granite

Table 1. Chemical compositions of the jarosite, granite, glass cullet and parent glass (wt%)

	Jarosite	Granite	Glass cullet	Parent glass
SiO ₂	3.7	70.2	72.5	52.9
Al ₂ O ₃	0.3	12.1	0.5	4.1
Fe ₂ O ₃	49.3	1.6	0.1	24.1
CaO	0.1	5.2	8.7	5.2
MgO	0.2	0.6	4.0	1.8
ZnO	5.6	—	—	2.7
PbO	3.6	—	—	1.7
Na ₂ O	—	2.9	13.4	6.4
K ₂ O	—	3.3	0.2	1.1
L.O.I.	37.2	4.1	—	—

scraps and glass cullet; the last column shows the corresponding glass composition. Iron oxides are presented as Fe₂O₃.

The crystallisation ability of the initial glass was investigated in isothermal conditions by a 1 h thermal treatment in the 560–900°C. The degree of crystallisation was evaluated by density measurements¹⁹ employing a 3–4 bulk sample in a gas displacement AccuPyc 1330 pycnometer. The experimental associated error to our measurements was evaluated as $\pm 0.001 \text{ g cm}^{-3}$.

In order to investigate the nucleation process, the samples, heat treated for 1 h in the temperature range 560–620°C at 20°C steps, were then successively heated at a higher temperature, (680°C), and held for 30 min. The degree of crystallisation was evaluated by density measurements.

The kinetics of phase transformation, the Avrami parameter and the activation energy of crystal growth were investigated by isothermal treatments carried out at 620, 640 and 660°C for different times. In performing these experiments, the glass samples were placed in the oven at the experimental temperature for times ranging from 10 to 2500 min, quenched on a metallic surface and the corresponding densities measured.

The crystallisation was also investigated in non-isothermal conditions, by DTA technique. About 120 mg of coarse particles, used to minimise surface iron oxidation effect,¹⁰ were heat treated in air, at 5, 10, 15 and 20°C min⁻¹ heating rates. DTA was also employed to investigate the nucleation process.

The crystalline phases formed during all series of crystallisation experiments were determined by XRD technique, using a Philips-1830 apparatus and CuK α radiation. The crystalline fraction developed during the thermal treatment was estimated by comparing the areas of amorphous and crystalline phases in the XRD spectra (24). The ratio between different phases has been obtained by comparing the intensities of the major peaks of each-one.

Transmission Electron Microscopy (a Philips CM 200 operating at 200 keV + EDS) was

employed to investigate the phase formation. For these studies samples were thermally treated at different temperatures and times and then crushed and sieved to obtain a very fine fraction and deposited on a copper-carbon grid; TEM image was used to identify and photograph particles with well defined crystalline formation. The EDS analyses highlighted the variation of composition of the amorphous and crystalline phases during the thermal treatment.

4 Results and Discussion

4.1 Nucleation and crystallisation

Figure 1 shows the density variation of a glass sample heat treated for 1 h at different temperatures. The density does not vary appreciably before 620°C, highlighting that no crystallisation occurs; the density variation starts to be evaluable at 620°C and reaches its maximum at 700°C. By treating the glass at 800 and 900°C the density decreases, showing that the degree of crystallisation decreases at a heat treatment temperature above 700–720°C. Similar results were obtained in other studies with pyroxene crystallisation.^{15,25} The density at 800 and 900°C was repeatedly measured for times up to 10 h and no sensible variation was detected; therefore, the values shown in the figure can be considered the maximum degree of crystallisation obtainable at these temperatures, respectively.

The nucleation process was investigated in two different series of experiments. In the first series, which is summarised in Table 2, glass samples were treated for 1 h, at 20°C steps, in the 560–620°C temperature range. The density was measured and is reported in the first row of the table. Then the samples were treated at 680°C for 30 min each to allow crystallisation. The density values after this second treatment are reported in the second row of the table. A parent glass sample (with 2.799 cm³

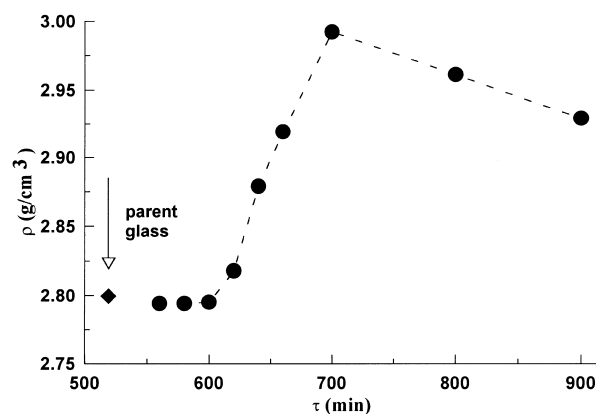


Fig. 1. The variation of the density after 1 h heat-treatment at different temperatures.

initial density) was directly treated at 680°C for 30 min. The results, expressed as density difference, highlight that no sensible variation of density is induced by the nucleation heat treatments compared to the direct crystallisation of the parent glass. It can be concluded that in the investigated temperature range, no nucleation takes place.

In the second series of experiments, bulk glass samples were placed in the DTA and treated for 1 h at 600, 620 and 640°C. Then the temperature was erased, at 15°C min⁻¹ heating rate, and the positions of the crystallisation peak were detected. In the three investigated samples, the position of the crystallisation peak resulted in being the same as the non-nucleated sample, treated with the same heating rate. These results confirm that the nucleation process is negligible. In similar experiments carried out on Li₂O·2SiO₂²² and Na₂O·2CaO·3SiO₂ glasses²³ a 15–20°C shift of the peak was detected as a consequence of the nucleation process.

4.2 Avrami parameter and activation energy

Figure 2 shows the variation of density as a function of time at different constant temperatures (620, 640 and 660°C). Using eqn (3) and assuming 3.050 g cm⁻³ as the maximum obtainable density value at these temperatures, the degrees of transformation, α , are obtained and plotted as a function of time in Fig. 3

Table 2. Variation of the density as a function of different nucleation heat-treatments

	560°C	580°C	600°C	620°C	Parent glass (2.799 g cm ⁻³)
Density (g cm ⁻³) after 1 h heat-treatment	2.794	2.794	2.796	2.818	—
Density (g cm ⁻³) after second heat-treatment (30 min at 680°C)	2.904	2.912	2.899	2.948	2.912
Density difference	0.110	0.118	0.104	0.130	0.113

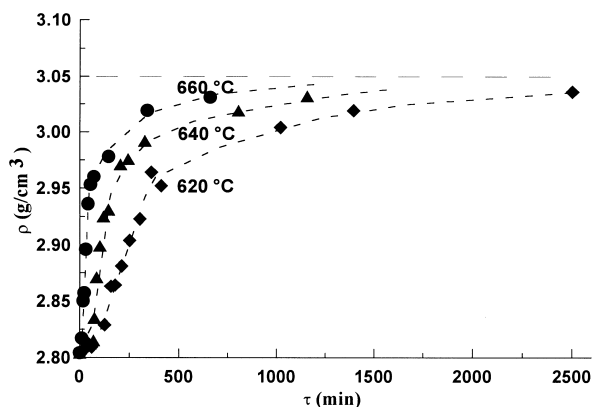


Fig. 2. The variation of the density as a function of time at constant temperatures (620, 640 and 660°C).

By plotting the value of $\ln \ln [1/(1-\alpha)]$ as a function of $\ln \tau$ the Avrami parameter can be obtained from the slope of the experimental linear regression. Figure 4 shows that the n values, relative to the three temperatures investigated, are very close to 1.5. This value corresponds to the diffusion controlled three dimensional growth taking place on the fixed number of nuclei,^{4,5} confirming that no consistent nucleation process takes place in this glasses during the thermal treatment.

By using eqn (2), the activation energy of the crystal growth was obtained as the slope of the line yielded by plotting the $\ln \tau_{0.5}$ as a function of $1/T$, as shown in Fig. 5. The experimental value of the activation energy resulted in being 377 kJ mol⁻¹.

The activation energy of the crystal growth was also evaluated using DTA traces obtained at different heating rates by the Kissinger equations, which applies for non-nucleating glasses. The experimental DTA curves are shown in Fig. 6. Figure 7 reports the plot of $\ln (\phi/T_p^2)$ versus the shift of the peaks ($1/T_p$). The value obtained for the activation energy of crystal growth, using eqn (5) resulted in being 298 kJ mol⁻¹, which is in fair agreement with the previous value obtained at lower temperatures (620–660°C) and in isothermal

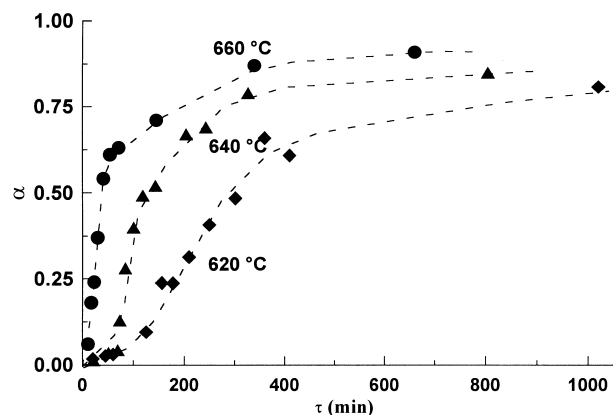


Fig. 3. The degree of transformation, α , as a function of time at 620, 640 and 660°C.

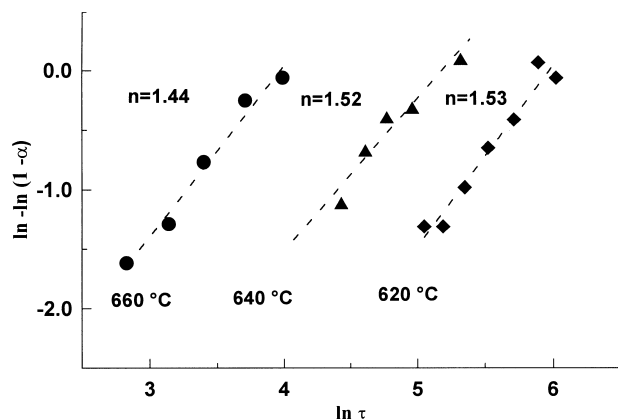


Fig. 4. Avrami parameters evaluated at different temperatures.

conditions. The decreasing of the value of activation energy by increasing the temperature is consistent with the temperature dependence of the activation energy of the viscous flow.²⁶

4.3 XRD and TEM-EDS analysis

XRD spectra were carried out on the parent glass and after the thermal treatments at 660°C for different times. The initial glass shows an amorphous spectrum with some traces of magnetite formation. After 20 min at 660°C magnetite peaks are evident as the only crystalline phase formed in the sample with about 5–10 wt%. After 3 h of thermal treat-

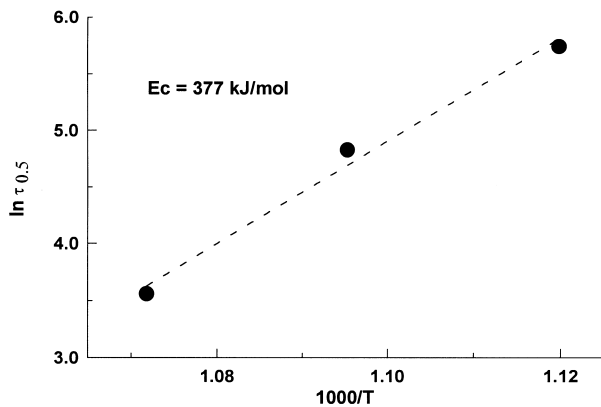


Fig. 5. The activation energy of crystal growth evaluated by isothermal method.

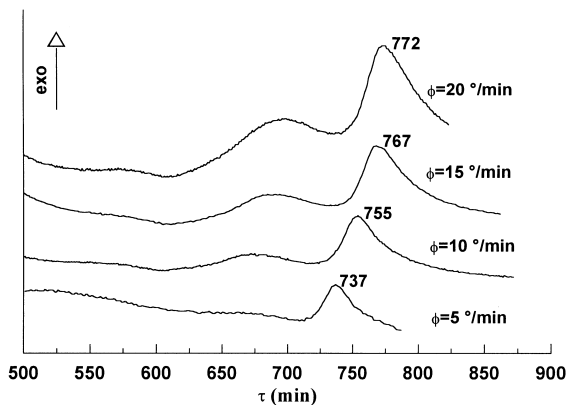


Fig. 6. DTA curves obtained at different heating rates.

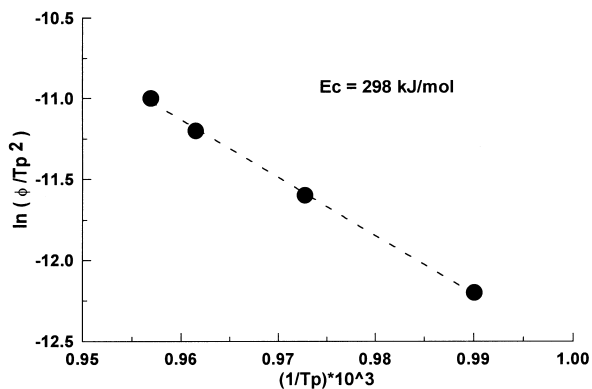


Fig. 7. Activation energy of crystal growth evaluated by non-isothermal method.

ment, pyroxene peaks are present in spectrum and represent the major phase in the glass-ceramic; the magnetite peak intensity is not significantly affected by the prolonged thermal treatment.

The degree of crystallisation was independently measured by XRD and density variation, yielding a maximum degree of crystallisation, after 3 h at 660°C, of 54 and 51% for the two methods respectively.¹⁹

Transmission electron microscopy, TEM-EDS, was employed in this study to highlight the variation of the compositions of the residual glass and crystal phases during the crystallisation process, as well as the evolution of the crystals.

By observing particles of the initial glass and collecting the fluorescence emission per element, i.e. Si, Fe, Zn, Ca, Na, Pb, a map of the distribution in the glass grain has been obtained. This map showed that Fe and Zn are concentrated in specific areas while the other elements are uniformly distributed in the matrix, suggesting that liquid-liquid separation may occur during the cooling of the melt. Similar behaviour was reported by other authors investigating iron-rich glass composition.^{11,12,16,}

Figure 8 shows a picture of a glass particle heat treated for 20 min at 660°C. The magnetite crystals, indicated by the fluorescence spectrum with Fe and Zn predominant elements, are uniformly distributed throughout the bulk of the glass. After 3 h of thermal treatment at 660°C, the image, reported in Fig. 9 shows the pyroxene dendritic structure. The TEM fluorescence spectrum of the crystalline

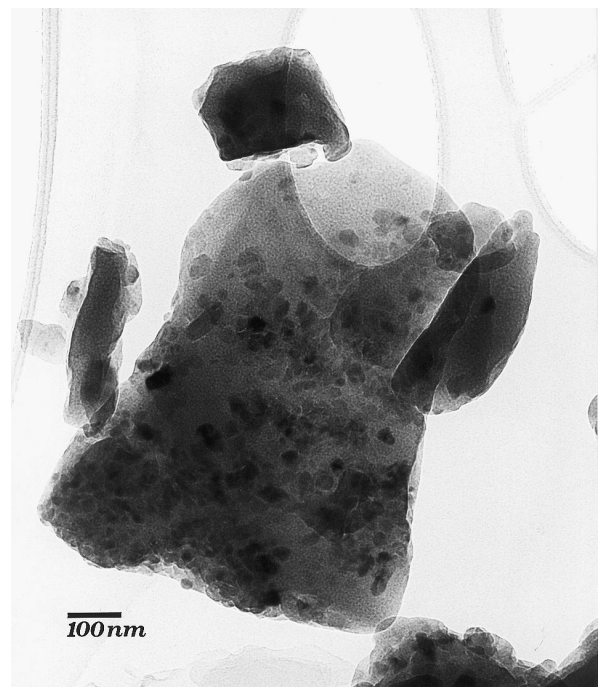


Fig. 8. TEM picture of magnetite grains formed after 20 min heat-treatment at 660°C.

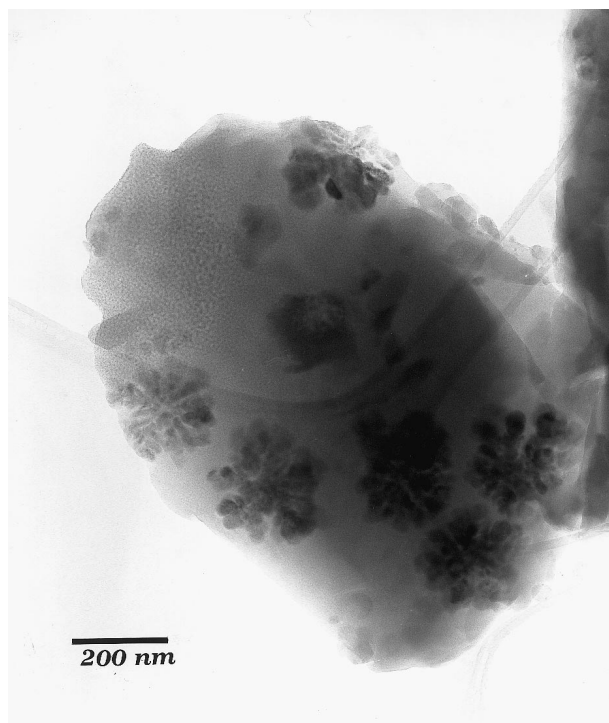


Fig. 9. TEM picture of pyroxene grains formed after 60 min heat-treatment at 660°C.

phase highlighted the typical chemical composition of pyroxene solid solution, i.e. mainly Si, Fe and Ca.

5 Conclusions

The iron rich melts are characterised by a high immiscibility; one of the liquid phases is richer in iron and zinc while the other contains silica and alkalines. The first liquid phase promotes the formation of magnetite as the first crystal phase formed during thermal treatment. By prolonging the thermal treatment, a pyroxene solid solution crystallises and becomes the pre-eminent phase in this jarosite glass-ceramic.

The results of this study highlighted that there is no typical nucleation process in which the number of nuclei is influenced by the thermal treatment and govern the crystallisation process. The activation energy, obtained by the isothermal and non isothermal methods, is in agreement with similar values reported by other authors^{9,11,16} and shows the high crystallisation ability of pyroxene. The Avrami parameter value, 1.5, is indicative of three dimensional diffusion controlled growth of the pyroxene crystals on a fixed number of nuclei.

The results of the present study suggest that the optimum crystallisation thermal treatment for this glass composition could be a single isothermal step at 700–720°C for 60–90 min yielding a 50–55 wt% crystal phase.

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