QUANTITATIVE PHASE ANALYSIS IN SINTERED GLASS-CERAMICS OBTAINED FROM INDUSTRIAL WASTES

M.V. Folgueras[*], A.P. Novaes de Oliveira[**], O.E. Alarcón

Universidade do Estado de Santa Catarina - UDESC,
Departamento de Engenharia Mecânica - DEM.
Campus Universitário Avelino Marcante s/n,
Bom Retiro, Joinville SC, dem2mvf@joinville.udesc.br

[*]Universidade do Estado de Santa Catarina - Departamento de Engenharia Mecânica
[**]Universidade Federal de Santa Catarina - Laboratório de Materiais, LabMat

ABSTRACT

In this study, glasses and sintered glass-ceramics were obtained from the combination of blast furnace slags and fly ash, produced by coal combustion in power stations. The glasses were melted at 1350°C and thermal treatment for crystallisation and sintering of the powder compact was carried out in a short cycle with a maximum duration of 60 minutes. The glass-ceramics were produced with the intention of achieving properties similar to those of porcelain tile, for use in ceramic tiles. The identification of appropriate process conditions was based on the determination of crystallisation efficiency, quantifiable by means of the determination of formed crystalline phase volume or residual glassy phase volume. For this, a procedure has been developed in this work for the quantification of the crystalline phases and residual glass volume present in sintered glass-ceramics made from industrial wastes. For this analysis the relation was considered between the intensity of the main diffraction peaks of each phase present in the system and the quantity of the phase present in the composition, the relation being defined by the Chung method. The results showed the possibility of obtaining sintered glass-ceramics using short sintering cycles, which yielded materials with a degree of crystallinity of the order of 70%. The resulting materials presented equal or better mechanical properties than those found in materials such as porcelain tile, the high mechanical strength being particularly noteworthy.

INTRODUCTION

The development of glass-ceramic material from the sintering of glass powder, formulated from waste raw materials, has been studied as an alternative for obtaining new products, while also being a solution for the use of by-products of industrial processes.

The study of the use of industrial by-products as raw materials initially focused on materials for building construction, such as mortars, and for the paving industry. Fly and heavy ash, steel slags and mining wastes have been among the main materials. More recently it has become possible to use these raw materials in making glasses that can be used in glass-ceramics production, which can in turn be employed in ceramic tiles.

Glass-ceramics are materials obtained by controlled crystallisation of glasses. They can be made by crystallisation in monoliths or by crystallisation and sintering of pieces produced by moulding glass in powder form. They are used in different applications; in the ceramic tile industry they can be applied as raw materials in manufacturing products with porcelain tile characteristics, and for use as glass-ceramic glazes. In both cases, the properties of the glass-ceramic, and consequently of the flooring, are strongly influenced by the efficiency of the sintering process, which is reflected in density after sintering, and in the glass crystallisation process, evidenced by the percentage of arising crystalline phase formation.

For the determination of the crystalline phase percentage present in the glass-ceramic, different methods have been put forward, the most important being X-ray diffraction (XRD). This technique allows describing crystallisation behaviour qualitatively and quantitatively.

For the quantitative determination by XRD of the crystalline phases that form during crystallisation, different methods are used. Several of these methods were initially created for the study of polymers and later on adapted for the study of crystallisation in glasses. In this work the Chung method has been used, on being the only one, amongst those that are based on the relation of individual phase with characteristic peak intensity, which allows individual identification of the different phases present.

This method proposes that the fraction by weight of a crystalline phase in the mixture of analysed material and of a reference material relate directly to the intensities of the characteristic diffraction peaks of each phase. Thus, studying mixtures of the material being analysed with defined, known quantities of a reference material, which is generally alumina, enables determining the percentage of each phase present in the material being studied, and also the residual glassy phase content. To achieve this result it is indispensable to have standard samples of each phase to be identified, thus enabling the determination of a proportionality factor used in the method. The accuracy of the obtained results depends on the correct determination of peak intensity, of the match between test material and reference material and of the care in avoiding performing the analysis based on peaks produced by overlapping diffraction lines of more than one phase.

X-ray diffractometry is used in this study to identify the crystalline phases, formed during appropriate thermal treatment, in glasses made by combining blast furnace fly

ash and slags. The fraction by weight of each crystalline phase and the residual glassy phase content were determined using the Chung method.

MATERIALS AND METHODS

For this study a combination of blast furnaces slags and fly ash was prepared in a proportion of 70/30 by weight. This composition was selected on the basis of previous studies (01) taking as main criteria the low melting temperature of the mixture and appropriate viscosity of the melt in producing the glass in the form of a frit. The glass was obtained by melting at 1300 °C for two hours, followed by quenching in water. The resulting material was characterised by X-ray diffractometry and differential thermal analysis (DTA).

DTA was used to determine the typical glass/glass-ceramic transformation temperatures (T_g [glass transition temperature], T_c [crystallisation temperature] and T_m [melting temperature of formed crystalline phases]). The test was carried out in air, in alumina crucibles, with a heating rate of 10 °C/min using powder samples.

The amorphous nature of the glass and the crystalline phases produced during the thermal treatments were studied by X-ray diffractometry, using powder samples of the glass obtained initially and of the glass subjected to heat treatment at 1100 °C for 1 h.

Samples of anorthite, gehlenite and diopside supplied by specialised laboratories or sintered in our laboratory were combined with a standard material (alumina) in a proportion of 50/50 by weight, for use as a reference. These mixtures were used to determine the proportionality parameter, Ki, used in the quantitative determination of the phases present. The mixture of the reference phase and reference material was ground in a Y-mill for 30 minutes, the material subsequently being deagglomerated by passing it through a 400 mesh sieve.

Samples of the glasses and glass-ceramics obtained by thermal treatment, under different time and temperature conditions, were prepared for X-ray diffractometry analysis by the following preparation method. Each sample was milled and blended with the reference material (alumina) in a proportion of 80/20 by weight of glass-ceramic and alumina. The sample was prepared by the wet method in an agate mortar, using acetone as a liquid medium. The mixtures, deagglomerated using a 400 mesh sieve, were subjected to X-ray diffractometry tests on a Philips Xpert instrument with copper anode emitter tube.

A second batch of samples of the glasses and glass-ceramics, produced by thermal treatment in different time and temperature conditions, was prepared for X-ray diffractometry analysis by only using the milling and deagglomeration stages. These samples served to obtain X-ray diffractograms used building the TTT glass crystallisation curve.

The microstructural characterisation of the glass and glass-ceramics was carried out using polished samples etched with a 1% HF solution. The images were obtained on a Philips scanning electron microscope (SEM).

RESULTS

The chemical and mineralogical composition of the two raw materials used and of the glass made by melting at 1300°C are detailed in Table 1. Blast furnace slag is mainly made up of glassy phase, depending on the industrial process in which it is formed; during this process quenching occurs which impedes the formation of crystalline structures. In this raw material only one crystalline phase was identified, present in small quantities, as merwinite. Fly ash, in turn, is made up of mullite and quartz, which are characterised as two phases with high melting temperatures.

	Oxide wt%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	MgO
Slag	32,01	14,69	0,3	41,53	1,02	0,4	0,71	9,22
Fly ash	64,05	23,77	4,13	0,98	0,66	3,68	1,19	1,53

Table 1 – Chemical and mineralogical composition of the raw materials used.

In the DTA curve found for the glass in powdered form (Figure 1), the following can be identified: glass transition temperature of 756°C; an exothermal transition in the 930 to 1100°C range with a peak at 981°C, corresponding to glass crystallisation; three endothermal transitions above 1120°C, corresponding to melting of the arising crystalline phases. These results allow stating that glass crystallisation during heating begins between 756 and 930°C, reaching the maximum crystallisation rate at a temperature close to 980°C. In these glasses, the tendency to crystallise should diminish at temperatures exceeding 1000°C, by virtue of the fact that the melting process of the arising crystalline phases begins. Thus, to favour crystallisation the possibility should be considered of conducting heat treatments at temperatures between 800 and 1000°C. In the case of glass powder sintering, this process should be considered to occur in the 756°C to 930°C range, since at lower temperatures, the densificación rate will be low or zero, owing to kinetic factors, while, at temperatures higher than 930°C, the sintering process can be affected when glass crystallisation commences.

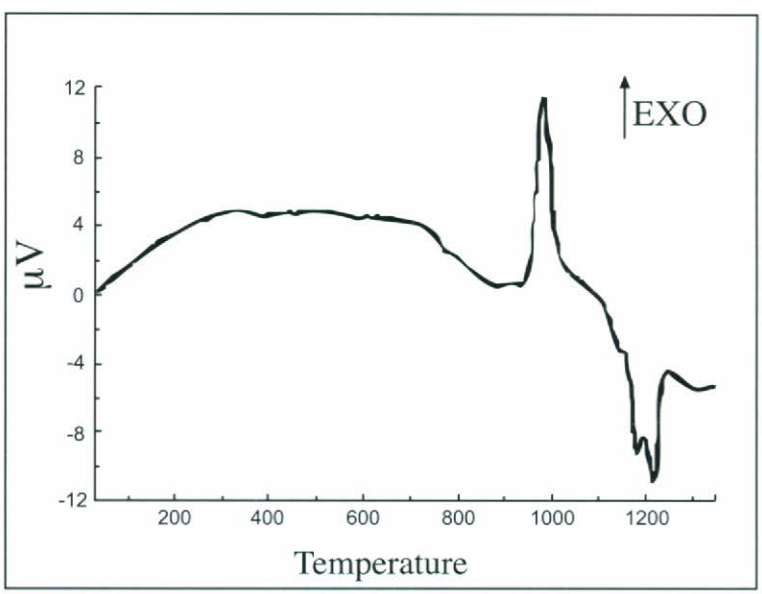

Figure 1 – DTA curves of the glass obtained by combining blast furnace fly ash and slag.

The X-ray diffractogram of the glass after milling the frit (Figure 2) confirms the glassy character of the material, while the diffractogram of the same glass, after the crystallisation thermal treatment, shows the presence of three major crystalline phases (Figure 3).

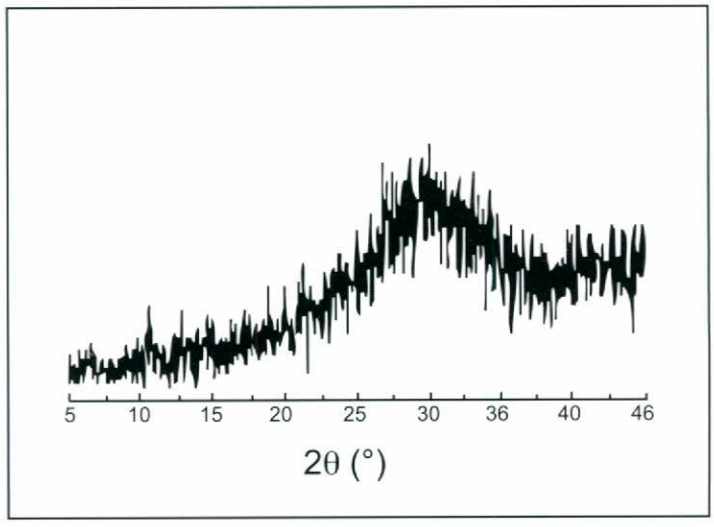

Figure 2 – X-ray diffractogram of the glass powder.

The predominant phase found belongs to the melilite group. This group has gehlenite and akermanite as ends, whose differentiation by X-ray diffractometry encounters some difficulties owing to the structural similarity of the two species. The identified secondary phases were anorthite, which belongs to the plagioclase group, and diopside, which arises as a secondary phase at high temperatures and belongs to the pyroxene group.

Based on this identification of crystallised phases, the process of quantitatively characterising the arising crystalline phases commenced. First, reference samples of anorthite, diopside and gehlenite were prepared. These standard samples were prepared mixing the phase being studied with a reference material, in this case alumina. The mixtures were made in proportions of 50/50 of the phase to be quantified and alumina. The mixture was homogenised in a Y-mill by stirring for 30 minutes. The homogenised material was deagglomerated on a 400 mesh sieve.

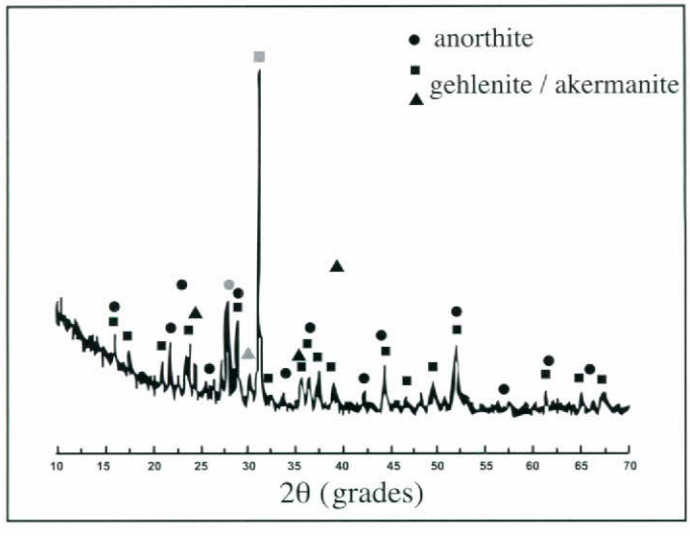

Figure 3 - Diffractogram of the glass-ceramic obtained by crystallisation of the monolithic glass at 1100°C for 1 h.

The diffractograms found of the mixtures anorthite/alumina, diopside/alumina and gehlenite/alumina (Figure 4) allowed determining the proportionality parameter Ki given by the relation:

$$K_i = (X_c / X_i)(I_i / I_c)$$

where

X_i = fraction by weight of component i

X_c = fraction by weight of alumina

I_i = intensity relative to a plane (*hkl*) representative of phase i

I_i = intensity relative to a plane (*hkl*) representative of alumina

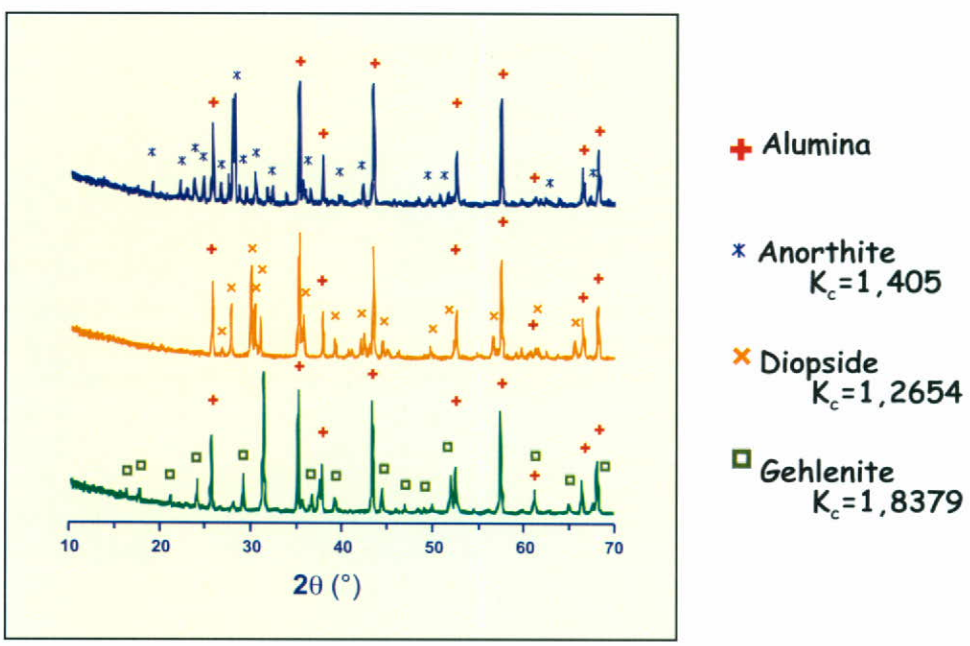

Figure 4 – X-ray diffractograms of the reference samples of anorthite, diopside and gehlenite, combined with alumina.

The values obtained for Ki were 1.838, 1.405 and 1.265 for gehlenite, anorthite and diopside, respectively. These values can be considered appropriate when they are analysed comparatively with values presented by Marsigli (), who determined values of proportionality for different phases belonging to the plagioclase, anorthite and melilite groups.

For the quantitative analysis of the glass-ceramics, samples were prepared consisting of 20 wt% alumina and 80 wt% in glass-ceramic. The samples were homogenised in a Y-mixer and deagglomerated on a 400 mesh sieve. The same procedure was conducted for all the glass-ceramics made.

The homogenised powder was analysed by X-ray diffractometry and the resulting spectrum was used to determine the percentage of each crystalline phase present. For this, characteristic diffraction lines were selected of each phase, taking care to exclude the lines that exhibited overlapping of characteristic peaks of different phases, and selecting the lines located in the 2 θ range between 20 and 45°. After determining the percentage of each crystalline phase present, the percentage of total crystalline phase present was calculated

by summation, and from this value, the residual glassy phase content:

$$X_m = (X_c / K_{im})(I_{im} / I_c)$$

and

$$X_i = X_m / (1-X_c)$$

where

X_i = fraction by weight of phase i in the glass-ceramic

X_{im} = fraction by weight of phase i present in mixture m

X_c = fraction by weight of alumina present in the mixture (in this case, $X_c = 0.2$)

I_{im} = intensity relative to a plane (*hkl*) representative of phase i

I_c = intensity relative to a plane (*hkl*) representative of alumina

The values obtained for the percentage of each crystalline phase and of the residual glassy phase were plotted, showing the variation of the percentage by weight versus heat treatment temperature (Figure 5). In the figure, crystallisation can be observed to begin between 850 and the 900°C, with maximum crystallisation at 960°C. The smaller degree of crystallinity found above this temperature can be explained by the rise in the tendency to form liquid phase by melting of the formed crystals. These results are consistent with the values initially found by DTA. The maximum crystallinity attained was 76%, and hence residual glassy phase content was 24%. This degree of crystallinity can be considered high when compared with values obtained with other similar materials. Of the identified phases, the phase belonging to the melilite group always predominates, while diopside, which is always present in smaller percentage, exhibits greater stability at high temperatures.

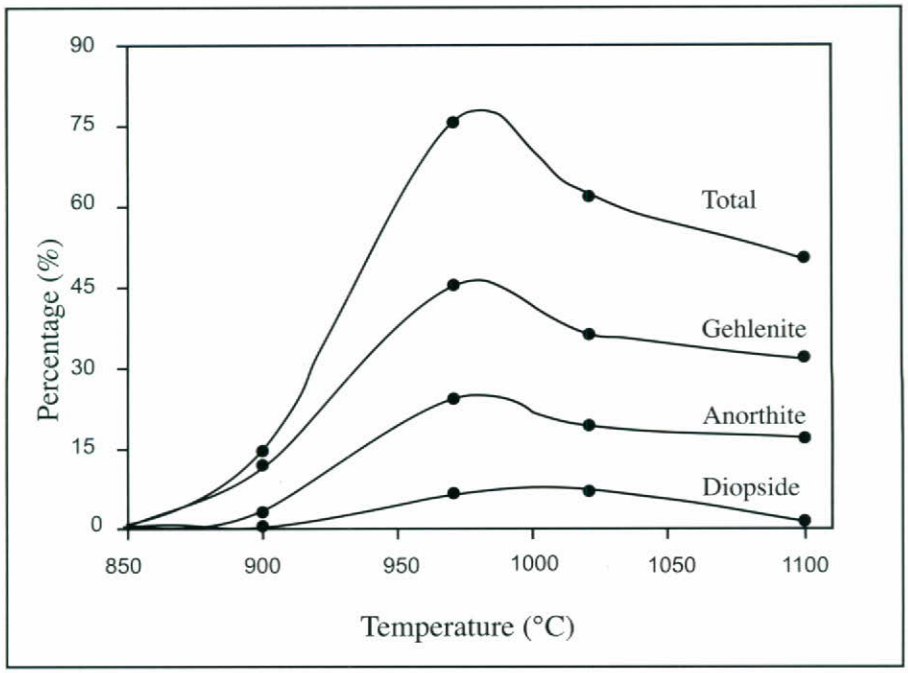

Figure 5 – Plots of the variation of crystallinity with temperature of the sintered glass-ceramics.

The X-ray diffractometry study can be supplemented by constructing a TTT crystallisation curve, which not only considers heat treatment temperatures as variables, but also the time of residence at these temperatures. For this study, X-ray diffractometry tests were carried out on sintered glass-ceramics obtained by heat treatments under different conditions of time and temperature. For these tests, the samples were used in powdered form and the resulting diffractograms were divided into three categories, in accordance with the crystalline phase peak intensities and intensity of the amorphous phase band characteristic of the presence of glassy phase. The classification divided the materials into glass-ceramics with a high degree of crystallisation, glass-ceramics with an intermediate degree of crystallisation and non-crystallised glasses. Examples of these diffractograms are given in Figure 6.

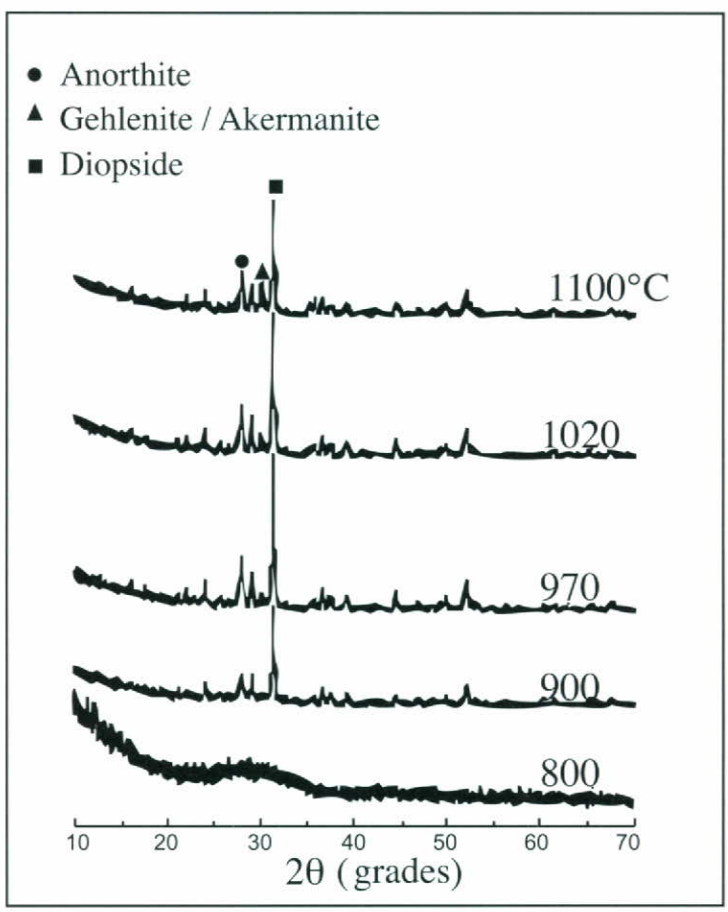

Figure 6 – X-ray diffractograms of the glass-ceramics obtained with different heat treatment at different temperatures with a 60 min hold at the corresponding temperature.

The TTT curve constructed with the results (Figure 7) defines two regions that identify the necessary conditions of time and temperature to favour the crystallisation process. The curve shows that at temperatures close to 850°C, the time of residence at heat treatment temperature can be a fundamental factor in defining the final degree of glass crystallinity, while at higher temperatures, the influence of heat treatment time becomes progressively smaller as temperature rises, which is explained by the high crystallisation rate in the glass. This high crystallisation rate can be beneficial with regard to greater crystallisation in the glass, but can negatively affect the sintering behaviour of the material and lead to glass-ceramics with high porosity, which can be detrimental to its mechanical properties.

The images in Figure 8 represent two micrographs of the glass-ceramics produced by sintering. The images clearly show the influence of varying crystallisation temperature on the final degree of crystallinity of the glass-ceramic.

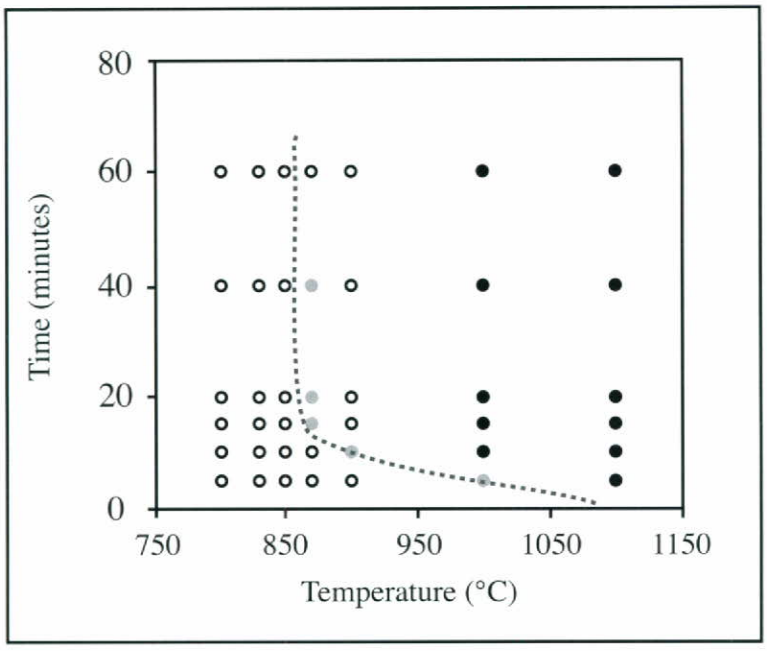

Figure 7 - TTT curve of the glass. Results found for the glass subjected to heat treatments at temperatures between 800 and 1100°C for times between 5 and 60 min.

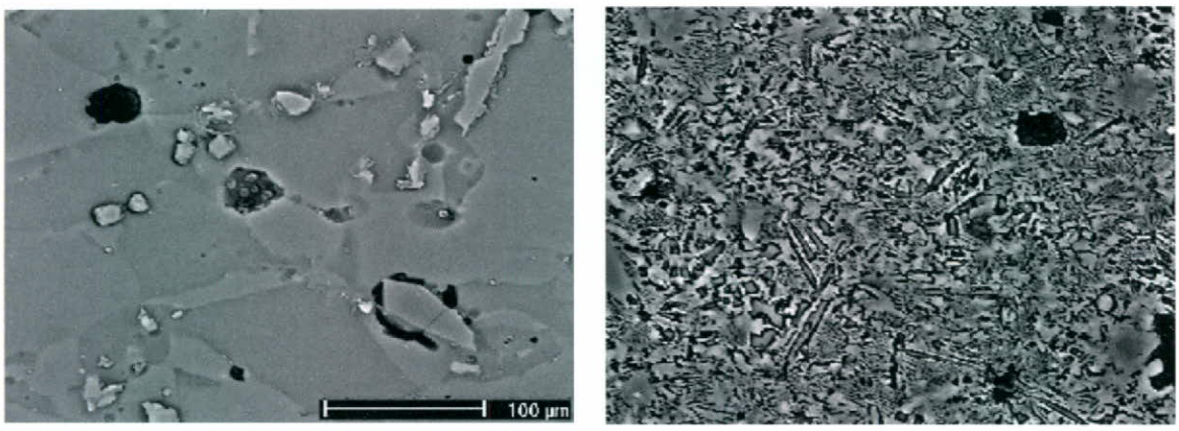

Figure 8 - Micrograph (SEM) of the glass-ceramics produced: (a) heat treatment at 870°C for 15 min; (b) heat treatment at 1100°C for 15 min.

CONCLUSIONS

X-ray diffractometry is a fundamental resource for the study of crystallisation behaviour in glasses. In this study XRD analysis in monoliths provided qualitative information, identifying the crystalline phases present after thermal treatment. At the same time, quantitative analysis by XRD in sintered glass-ceramics allowed identifying the crystalline phases that formed during heat treatment, as well as establishing the fraction by weight of each phase and the residual glassy phase content.

Construction of a TTT curve with the help of X-ray diffractometry data can be considered a semi-quantitative analysis, and is useful in defining the heat treatment conditions required to maximise crystallisation or, depending on the case involved, to avoid this if necessary.

The studied glass-ceramic presented a maximum crystallinity of 76%. It important to highlight that control of heat treatment temperature is fundamental, since low temperatures inhibit crystallisation, while high temperatures favour the melting process.

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