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Evaluation of the Degree of Crystallisation in Glass-ceramics by Density Measurements

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Abstract

A theoretical procedure has been developed with the aim of obtaining an accurate and rapid estimation of the degree of crystallisation in jarosite glasses by measuring the densities of the parent glass and, after the thermal treatment, of the glass-ceramic. Compositions were prepared by mixing jarosite waste with granite scraps and glass cullet, yielding three different glass-batchs, melted at 1450°C, quenched and thermal treated to obtain glass-ceramics with different degrees of crystallisation. Density measurements were carried out by means of a helium displacement pycnometer. The results were compared with the degree of crystallisation as evaluated by XRD and showed a good agreement. The method is applicable if the variation of density connected to the phase transformation is sufficiently large. In the formation of pyroxene and magnetite phases, with large density variation compared to the parent glass, it is precise and easily applicable.

Keywords: glass-ceramics, crystallisation, density, silicate.

1 Introduction

Glass–ceramics are polycrystalline materials prepared by the controlled crystallisation of highly viscous glass-forming melts. Their properties depend on the kind and the percentage of crystal phase formed and on the composition of the residual glass. Therefore, the determination of the degree of crystallisation and the investigation of the transformation of the parent glass in glass-ceramics are very important.

The most usual method for the estimation of the percentage of crystal phase formed in glass-ceramics involves X-ray diffraction (XRD) and electron microscopy.[1–5] This is, however, accompanied by several experimental difficulties and is time consuming. Furthermore, the associated experimental error can be as high as 5–10%.

As a result of the crystallisation process, the parent glass is transformed into a new material with different and sometimes outstanding properties. The property modification depends on the degree of crystallisation in such a way that, in some cases, it can itself indicate the transformation or the degree of crystallisation.

Partridge,[6] as an example, used changes in the apparent viscosity and electrical resistivity for the direct study of nucleation and crystallisation processes. Fraiman and Hench[7] showed that in $Li_2O{\cdot}2SiO_2$, the degree of crystallisation may be estimated from the variation of the thermal expansion coefficient of the material.

Density is another simple property, since it is an additive function of the volume fraction of the glass and crystal phases co-existing in the glass-ceramic. In principle, density variation may reveal the degree of crystallisation, especially when the difference between the densities of the parent glass and of the final material is substantial.

Gutzow has used change in density as a measure of the crystallisation kinetics[8,9] in silicate and non-silicate glasses in which the crystal phase formed and the parent glass have had the same composition. He demonstrated that classical pycnometric measurements in solution can give precise results and that this method even allows investigation of the starting period of crystallisation, when the percentage of crystal phase formed is very low.

In commercial glass-ceramics, however, the parent glass composition is different from that of the crystal phases; the residual glass changes its composition and density as a function of the crystallisation process. This behaviour, which in principle complicates the utilisation of density measurements to monitor crystallisation, may be overcome by

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*To whom correspondence should be addressed assuming that the parent glass is an ideal solution of components which will generate, in the glass-ceramic, the crystal phase or phases and the residual glass, respectively.

The aim of the present study is to evaluate the degree of crystallisation of SiO_2–Fe_2O_3–CaO–Na_2O glass-ceramics, made up of hazardous industrial wastes — i.e. the jarosite arising from the hydrometallugy of zinc ores[10–12] by measuring the density variation as a function of the thermal treatment schedule.

2 Theoretical approach

From a thermodynamic point of view, in a glass-ceramic system, a stable crystal phase has lower free energy and higher density than an unstable amorphous-one with the same composition. When secondary heat-treatment of a supercooled liquid is carried out at temperatures higher than the glass transition temperature, T_g, crystallisation can take place. This is commonly connected with a volume change, which is related to the degree of conversion α where $\alpha = V_\tau / V_{tot}, V_\tau$ is the volume (per mass unit) of the crystal phase at time τ and V_{tot} is the total volume (per mass unit) of crystal phase following complete crystallization. If accurate experimental data are available, the change of density can be used to estimate the degree of crystallisation and to allow kinetic investigations.

Glass–ceramics may be considered as composite materials made up of different crystal phases ci and of a residual glass g. The volume of a glass-ceramic, Vgc, is practically an additive function of the volumes of the vitreous and crystal phases present.

$$V_{gc} = \Sigma V_{ci} + V_g \tag{1}$$

As a consequence, the density of the glass-ceramic can be related to the percentage and densities of the different phases by the formula:

$$\frac{100}{\rho_{gc}} = \Sigma \frac{x_{ci}}{\rho_{ci}} + \frac{(100 - \Sigma x_{ci})}{\rho_g} \tag{2}$$

where ρ_{gc} is the density of the glass-ceramic, ρ_g is the density of the residual glass phase and x_{ci} and ρ_{ci} are the wt% and the density of the crystal phase i, respectively.

In the simple case in which the parent glass has the same composition as the crystal phase formed, the relation between the wt% of the crystal phase formed x at the time τ the densities ρ_g and ρ_c and the density ρ_t at the time τ is the following

$$\frac{100}{\rho_\tau} = \frac{100 - x}{\rho_g} + \frac{x}{\rho_c} \tag{3}$$

$$x = 100 \frac{\frac{1}{\rho_g} - \frac{1}{\rho_\tau}}{\frac{1}{\rho_g} - \frac{1}{\rho_c}} \tag{3a}$$

With $V_\tau = x/\rho_c$ and $V_{tot} = 100/\rho_c$, a similar relation can be written for the estimation of the degree of transformation α:

$$\alpha = \frac{(\rho_\tau - \rho_g)\rho_c}{(\rho_c - \rho_g)\rho_\tau} \tag{3b}$$

The values of ρ_τ and ρ_g may be experimentally determined, while the ρ_c value can be found in the literature.[1,2,13]

In the real conditions arising in the crystallisation of glasses, the residual glass g_r, has a composition different from the parent; therefore, in order to evaluate the degree of crystallisation by density measurement, some assumptions must be made.

Since only a portion of the parent glass is transformed to a crystal phase, it is assumed that the volume of the parent glass, V_g, consists of two parts: V_{g_t} with the same composition as the crystal phase which is going to be formed and V_{g_r} with the composition of the residual glass. As a result of the crystallisation process, the fraction V_{g_r} does not change but V_{g_t} is transformed into a crystal phase with smaller volume V_c; the glass-ceramic material acquires a volume V_{gc}.

From a theoretical point of view, this assumption is acceptable only if the fractions g_t and g_r form an ideal solution, i.e. there is no volume change as a result of mixing. This approach however is accepted in glass science and the concept of additive properties of the glass as a function of composition is widely employed.[14,15]

If only one crystal phase is formed in the glass-ceramic, the relation between the wt% of the crystal phase formed x and the densities ρ_{gc}, ρ_{g_r} and ρ_c becomes:

$$\frac{100}{\rho_{gc}} = \frac{100 - x}{\rho_{g_r}} + \frac{x}{\rho_c} \tag{4}$$

A similar relation also applies for the parent glass:

$$\frac{100}{\rho_g} = \frac{100 - x}{\rho_{g_r}} + \frac{x}{\rho_{g_t}} \tag{4a}$$

By combining eqns (4) and (4a), ρ_{g_r} is eliminated and the percentage crystal phase (x) can be obtained through the relation:

$$x = 100 \frac{\frac{1}{\rho_g} - \frac{1}{\rho_{gc}}}{\frac{1}{\rho_{g_t}} - \frac{1}{\rho_c}} \tag{5}$$

In eqn (5), ρ_g is experimentally determined before crystallisation, ρ_{gc} is experimentally determined at the end of the thermal treatment,[14,15] ρ_c is available in the literature when, by XRD analyses, the crystal phase formed during the secondary thermal treatment is known and ρ_{g_t} is available in the literature[16] or can be evaluated using methods for the prediction of glass properties.

When several crystal phases are formed in the material and the wt ratio between them is known, eqn (5) can be re-written with the following correction:

$$\frac{1}{\rho_{g_t}} = \sum \frac{b_i}{\rho_{g_t i}}; \frac{1}{\rho_c} = \sum \frac{b_i}{\rho_{ci}} \tag{6}$$

where $b_i = m_{ci}/m_c$. In the last expression m_{ci} is the wt fraction of the crystal phase i and m_c is the total fraction of the crystal phases in the glass-ceramic.

In real glass-ceramics, the estimation of the degree of transformation α can be obtained by the ratio $V_{x_\tau}/V_{x_{tot}}$, where $V_{x_\tau} = x_\tau/\rho_c$ is the crystal volume at time τ and $V_{x_{tot}} = x_{tot}/\rho_c$ is the maximum volume of crystal phase, formed at the end of the process. Using eqn (5) for the calculation of V_{x_τ} and $V_{x_{tot}}$ the following relation is obtained:

$$\alpha = \frac{\left(\rho_{x_\tau} - \rho_g\right)\rho_{x_{tot}}}{\left(\rho_{x_{tot}} - \rho_g\right)\rho_{x_\tau}} \tag{7}$$

The applicability of the above method depends on the difference in density between the crystal and the corresponding amorphous structures and on the accuracy of the density measurements.

In Table 1, the densities of some typical glass-ceramic crystal phases,[2] ρ_c, and the densities of the corresponding glasses, ρ_{g_t}, calculated using Appen's method,[14] are summarised together with the values of the difference $(1/\rho_{g_t} - 1/\rho_c)$. In the table, the densities of some monoclinic pyroxenes, as well as of magnetite and hematite (typical phases in Jarosite glass-ceramics), are also reported for comparison.[13]

Table 1. ρ_{g_c},ρ_c and $(1/\rho_{g_c} - 1/\rho_c)$ for some crystal phases and corresponding glasses

Crystal system	*ρc (g cm^{-3})*	*ρ_{g_t} (g cm^{-3})*	*$1/\rho_{g_t} - 1/\rho_c$*
Wollastonite–$CaO \cdot SiO_2$	2·92	2·87	0·006
Anorthite–$CaO \cdot Al_2O_3 \cdot 2SiO_2$	2·75	2·60	0·021
Litium-disilicate–$Li_2O \cdot 2SiO_2$	2·45	2·42	0·005
Cordierite–$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$	2·53	2·47	0·010
Eucryptite–$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	2·67	2·43	0·037
Hematite–Fe_2O_3	5·26	4·20	0·048
Magnetite–Fe_3O_4	5·18	4·25	0·042
Diopside (D)–$CaO \cdot MgO \cdot 2SiO_2$	3·27	2·75	0·060
Hedenbergite (H)–$CaO \cdot FeO \cdot 2SiO_2$	3·56	2·98	0·057
Pyroxene solid solution–(D + H)	3·55	2·90	0·061
Pyroxene solid solution–Augite	3·41	2·84	0·059

It is important to point out that the monoclinic pyroxenes easily form solid solutions[17] and that an XRD spectrum is not accurate enough to differentiate between the different pyroxenes. On the other hand, as is evident from Table 1, monoclinic pyroxenes with different chemical compositions and different ρ_c and ρ_{g_t} give very similar values for $(1/\rho_{g_t} - 1/\rho_c)$. This allows one to estimate the degree of crystallisation by the above discussed method even when a solid solution of pyroxenes is formed in the glass-ceramic.

3 Experimental

Details pertaining to the characterisation and preliminary treatments of the jarosite red-mud waste have been discussed elsewhere.[10,11] The waste was mixed with selected raw materials and with industrial residues to obtain different glass compositions. The following materials were employed: granite scraps, limestone, sand and glass cullet. Table 2 reports the chemical composition of the glasses utilised in this study.

Fusion was carried out at 1400–1450°C by using an electric furnace and a corundum crucible. The melt was quenched in a stainless steel mould. A Philips PW 1400 X-ray fluorescence (XRF) spectrometer was employed to determine if appreciable modification had occurred in the glass-composition during the melting operation. The glasses were annealed and XRD analysed to ensure that no crystallisation had occurred during quenching and annealing. The T_g temperatures (which are very similar to the upper annealing temperatures), as well as the crystallisation susceptibility of the initial glasses, were determined by Netzsch 409 Simultaneous Thermal Analysis at a heating rate of 10°C min^{-1}.

The densities of the glasses and the corresponding glass-ceramics were measured by AccuPyc 1330 pycnometer. This instrument is a gas displacement pycnometer, which measures the volume of solid

Table 2. Chemical compositions of the parent glasses (wt%)

	GC1	*GC2*	*GC3*
SiO_2	52·9	47·4	53·8
TiO_2	—	2·0	—
Al_2O_3	4·2	3·4	3·7
Fe_2O_3	24·1	29·0	21·7
CaO	5·2	4·7	8·7
MgO	1·8	1·8	0·2
ZnO	2·9	3·3	2·4
PbO	1·7	2·1	1·5
Na_2O	6·4	6·0	6·9
K_2O	1·1	0·9	1·0

objects with regular or irregular shapes as well as of powder samples. The pycnometer determines volume by measuring the change of the pressure of helium in a calibrated volume. The experimental error in the measurements, employing a bulk glass or glass-ceramic sample of about 3–4 g, was evaluated as $\pm 0{\cdot}001\,\mathrm{g\,cm^{-3}}$.

The degree of crystallisation was also evaluated by XRD analysis, carried out with K_α radiation from a Cu tube operating at 35 kV and 40 mA with 10 s scanning time on a Philips PW-1830. A graphite crystal monochromator was used. The crystal fraction developed during the thermal treatment was estimated by comparing the areas of the amorphous halo in the initial glass and in the crystallised sample.[1,3,5] The ratio between different crystal phases was obtained by comparing the intensities of the major peaks of each phase.

4 Results and Discussion

The DTA traces of the three glasses investigated in this study are shown in Fig. 1. They show the glass transition region and the exothermic peak corresponding to the crystallisation process. Such exo-effects are typical for glasses with high crystallisation tendency and also give preliminary guidance for the thermal treatment suited to obtain glass-ceramics.

After additional investigations, the thermal treatments were defined for each composition (Table 3).

After thermal treatment, the samples gave the XRD spectra shown in Fig. 2 in which the different degrees of crystallisation as well as the ratio between the phases are evident. In the GC1 and GC3 compositions, the major crystal phase is pyroxene while in the GC2 composition, due to the higher iron content and the addition of 2% of carbon to obtain a stoichiometric Fe^{3+}/Fe^{2+} ratio,[11] the major precipitating phase is magnetite.

Table 4 reports the experimental results for the parent glass densities, the corresponding glass-ceramic densities and the degree of crystallisation as calculated by eqn (5). In the same table, for comparison purposes, the density of the parent glass as calculated by Appen's method and the degree of crystallisation as calculated by XRD are also shown.

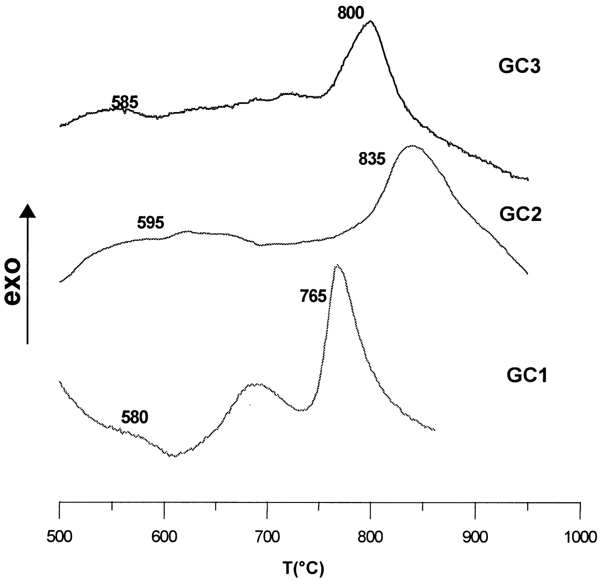

Fig. 1. Differential thermal analysis traces for GC1, GC2 and GC3 compositions.

Table 3. Heat treatment regimes of the glasses

	GC1	*GC2*	*GC3*
Nucleation temperature (°C)	620	660	630
Nucleation time (min)	60	60	60
Crystallisation temperature (°C)	700	820	720
Crystallisation time (min)	120	60	120

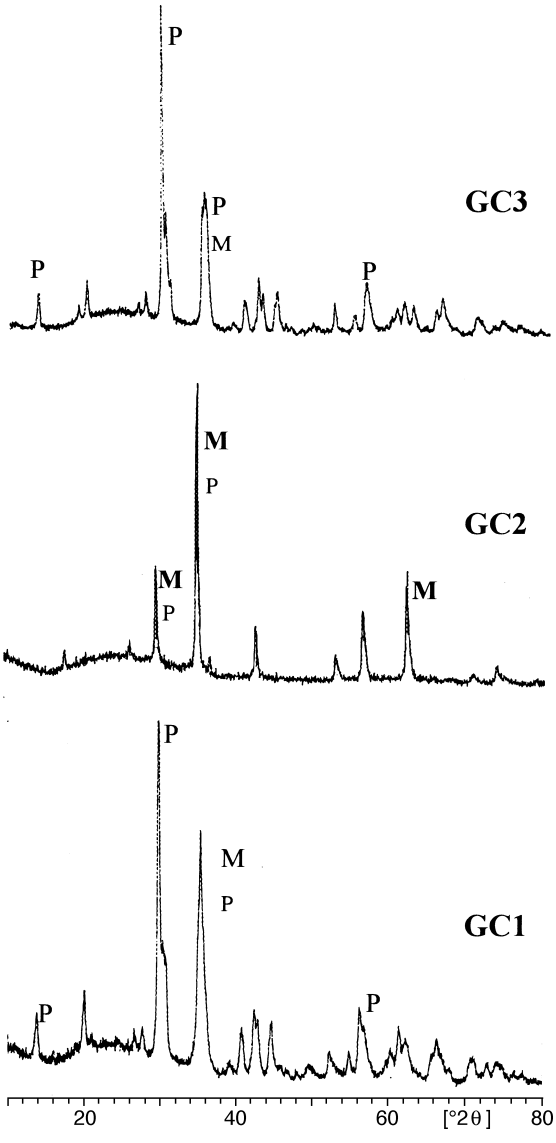

Fig. 2. XRD results for GC1, GC2 and GC3 compositions. (P = pyroxene; M = magnetite).

Table 4. Densities of the parent glass and glass-ceramics. Percentage of the crystal phase (wt%) by density and XRD measurements

Glass composition	*Parent glass density (g cm^{-3})*		*Glass–ceramic density (g cm^{-3}) (experimental)*	*% Crystal phase*	
	(experimental)	*(Appen's)*		*(density method)*	*(XRD method)*
GC1	2·81	2·84	3·05	51	54
GC2	2·84	2·86	3·03	46	44
GC3	2·80	2·83	2·98	39	42

The results reported in the table show that the density of the parent glass as evaluated by Appen's method is similar to the experimental one and that evaluation of the degree of crystallisation by density measurement gives results comparable with those of the XRD method.

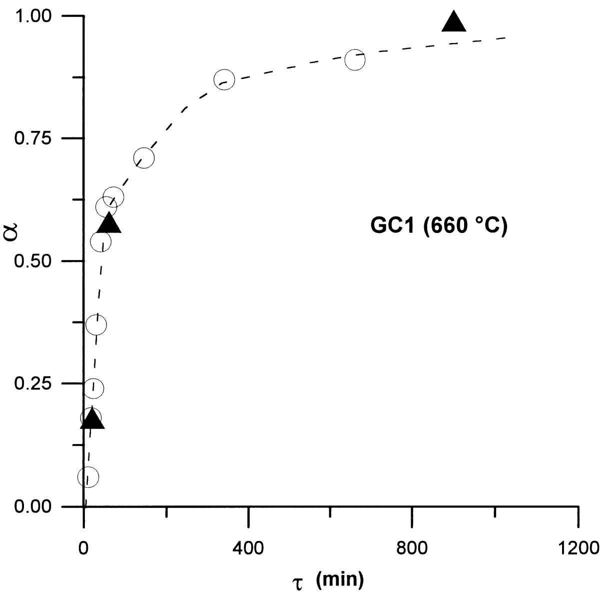

Fig. 3. Kinetic of transformation for GC1 composition. Density results are indicated with circles and XRD-results with black triangles.

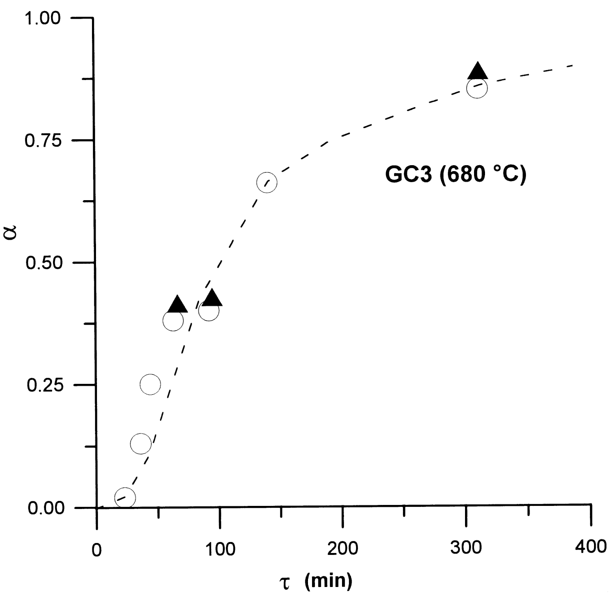

Fig. 4. Kinetic of transformation for GC2 composition. Density results are indicated with circles. and XRD-results with black triangles.

The crystallisation kinetics of the GC1 and GC3 glass compositions, i.e. pyroxene formation as a function of time, were also investigated using density measurement. In these experiments, samples of the same glass were heat treated at the same temperature for different times. By using eqn (7), the degree of transformation was plotted as a function of time, yielding Figs 3 and 4 for the GC1 and GC3 compositions, respectively. For the purpose of comparison, the degree of transformation was also calculated by the XRD method and is reported in the same figures.

The density measurements overlap well with the XRD measurements but it must be pointed out that the former method gives a more precise 'S' curve, due to the experimental simplicity and the accuracy of the technique. Moreover, if the variation of density between the glass and the crystal is high, as in the case of pyroxene and magnetite precipitation in jarosite glasses, density measurements allow evaluation of the beginning of the crystallisation process, when the percentage of crystal phase is lower than 10%.

5 Conclusions

A method has been developed to obtain accurate and rapid estimates of the degree of crystallisation in jarosite glasses; there is practical application of the vitrification and crystallisation process for the recycling of this hazardous waste. The method involves density measurements and is best utilised where the variations of density measurements during transformation are, at least, a factor of 10 larger than the error associated to the technique to be employed.

In this study, the formation of pyroxene and magnetite phases, with large difference in density from the parent glass showed itself to be a suitable system for the application of the method.

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