



Optimal thermal cycle for production of glass–ceramic based on wastes from ferronickel manufacture

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Abstract

Hazardous electro-furnace slag (*EFS*), dust (*D*) and converter slag (*CS*) from ferronickel smelting plant were mixed with glass cullet and vitrified. The optimal heat-treatment regime for transformation of obtained glass into glass–ceramic was evaluated using fast alternative methods: the nucleation step was estimated by DTA analysis, while the crystallization step – by pycnometric measurements. Additional kinetics data, attained by non-isothermal heat-treatments at different heating rates, were also analyzed and the formed crystal phases were studied by XRD analysis.

The investigated glass is easily melted (2 h at 1400 °C) and is characterized by a spontaneous tendency for bulk crystallization. In addition, due to the presence of 1.5 wt% Cr₂O₃ in the batch, supplementary nucleation process takes place, which is a premise for formation of fine crystalline structure and improved mechanical properties. The results elucidate that short heat-treatment at low temperatures (45–60 min nucleation at about 650 °C and 30–45 min crystallization at about 750 °C) leads to formation of mono-phase pyroxene glass–ceramic with ~50 wt% crystallinity. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

Last decades intensive research was focused on the possible manufacture of glass–ceramic by various metallurgical wastes [1–3]. This fact is caused by two main reasons. The first one is that the international legislation concerned to waste materials require priority on re-use, recycling, useful components recovery and treatment of waste instead disposal on landfills [4,5]. In addition, the disposal of hazardous residues, containing heavy metals, is completely forbidden. On the other hands several metallurgical wastes contain high amount of SiO₂, CaO and MgO [6,7], which act as regulators of the chemical and physical transformations during the metal production, as well as other metal oxides from the processed ores. Moreover, in many cases the recovery of metals from slags or ashes cannot

be economically efficient or the recovery procedure creates new types of wastes.

When the amount of glass formers (SiO₂, Al₂O₃ and partially Fe₂O₃) is appropriate for glass forming the metallurgical residues can be considered as potential raw material for production of glassy materials. Depending on the composition, with or without additives, the waste-based glass could be transformed into glass–ceramic with properties comparable or better than the commercial ones. In addition, the vitrification of harmful metallurgical solid waste is an effective method for the immobilization of heavy metals, because during glass melting the harmful elements are chemically bonded in a durable amorphous network [8,9].

Many solid wastes, either from ferrous or non-ferrous metallurgical industries, contain high amount of iron oxides. Chinnam et al. [10] in their review highlight the following types of iron-rich waste materials for glass–ceramics manufacture: goethite and jarosite from hydrometallurgical production of zinc, blast furnace

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flue dust from ferrous metallurgy, copper flotation waste from copper metallurgy, nickel leaching residues from hydrometallurgical production of nickel and Pb foundry slag. Generally, the research with iron-rich glasses and glass–ceramics demonstrate their good chemical, physical and mechanical properties, together with lower cost price of the products due to inferior melting temperature and shorter crystallization cycles [10–12].

The evaluation of appropriated thermal schedule is very important for the successful transformation of parent glass into fine crystalline glass–ceramic with optimal properties. Usually the times and the temperatures of nucleation and crystallization steps are evaluated by complex microscopic examinations coupled with XRD quantitative analysis [13–15], which are time consuming and expensive. However, alternative techniques also might be applied. The nucleation step effectively can be estimated by non-isothermal DTA analysis [16–18], which in addition give kinetics information for the activation energies of crystallization and for the expected morphology of formed crystal phase. The variations of amount formed crystal phase, i. e. the efficiency of crystallization step, can be measured by several unconventional techniques (based on viscosity, chromatography separation, thermal expansion, density, dielectric properties, etc.) [19–25]. The relevance of used method depends on the variation of measured property with the crystallinity. In the case of iron rich compositions, where the crystallization volume change is extremely high, it was demonstrated that the density measurements are very appropriate [19].

In this work a glass, obtained by vitrification of high amount of iron-rich wastes from ferronickel production mixed with glass cullet, is used. The preliminary TCLP (toxic characterization leaching procedure) test highlight that the used residues can be characterized as hazardous wastes, while the resulting glass is an inert material, appropriated for glass–ceramic manufacture [26]. The aim of this study is to evaluate the optimal two step heat-treatment for transformation of parent glass into glass–ceramic with enhanced properties using alternative methods: the optimal nucleation step is estimated by DTA analysis, while the crystallization step – by pycnometric measurements.

2. Experimental

In this research electro-furnace slag (*EFS*), dust (*D*) and converter slag (*CS*) from ferronickel smelting plant in R. Macedonia were used as raw materials. The annual production of these residues is estimated as 1. 135, 000 tons *EFS*, 102, 000 tons *D* and 109, 000 tons *CS*, respectively [26]. The preliminary leaching tests demonstrate that these residues can be classified as hazardous materials [26] which means that their inertization or re-using is obligatory. Since two of wastes (*EFS* and *D*) are characterized with elevate amount of SiO₂ and iron oxides a potential route for their inertization could be the vitrification procedure. Because of high cost this tool is justifiable when materials with commercial value are obtained. From this point of view, the synthesis of glass–ceramics is considered as one of the most promising solutions. In addition,

Table 1

Chemical composition (wt%) of slag from electro-furnace (*EFS*), dust (*D*), converter slag (*CS*), waste mixture (*WM*) glass cullet (*GC*) and studied glass (*WG*).

Item	<i>EFS</i>	<i>D</i>	<i>CS</i>	<i>WM</i>	<i>GC</i>	<i>WG</i>
Wt%	56	7	7	70	30	100
SiO ₂	53	37.5	1.9	47.8	71.4	55
Al ₂ O ₃	2	1.8	0.3	1.9	0.6	1.5
MgO	16.9	14.5	6.2	15.9	3.3	12.1
CaO	2.4	2.3	15.9	3.5	9.8	5.4
Cr ₂ O ₃	2.5	1	0.7	2.2		1.5
CoO	0.1	0.1	0.1	0.1		0.1
NiO	0.1	2.7	0.45	0.3		0.2
Fe ₂ O ₃	14	30	60	19		19.8 ^a
FeO	9		19	8.8		
Na ₂ O					13.3	4
K ₂ O					1.3	0.4

^aIron oxides are presented as Fe₂O₃.

the iron-rich glass–ceramics are of particular interest due to lower melting temperatures and shorter crystallization cycles.

In order to evaluate the possibility for entire simultaneous usage of these streams they were mixed in ratio *EFS/D/CS* = 10/1/1 (similar to the production one) and homogenized. The chemical composition of wastes, determined by X-ray fluorescence (XRF) spectrometer (Model XRF ARL 9900), and the composition of their mix (labeled *WM*) are reported in Table 1.

Due to elevate percentage of MgO, iron oxides and Cr₂O₃, the direct vitrification of main waste *EFS* or *WM* can lead to formation of melts with extremely high crystallization trend, which are not appropriate for controlled crystallization.

For this reason 70% *WM* was mixed with 30% cullet from container glass (labeled *CG*). Thus obtained batch of 300 g was melted in 200 ml corundum crucible using lift superkanthal furnace. A part of the batch was put in the crucible at room temperature, while the remaining part was added during a step at about 1200 °C. Then the temperature was increased up to 1400 °C. Notwithstanding of the high amount of different wastes in the batch, after 1–1.5 holding time the formation of “mirror” surface of the melt was observed, which highlights no serious problems with the refining and the homogenization. After 2 h holding time the resulting melt was quenched in copper casting mold.

A little part of the glass was crushed into 10–15 mg bulk samples for DTA analysis, while the main part was annealed at chamber furnace at 600 ± 5 °C for 30 min. and after that cut into appropriated forms for different studies.

The chemical composition of *CG*, the composition of new waste glass (labeled *WG*) and the percentages of each component in batch also are reported in Table 1

WG composition is characterized with a decreasing of amounts of MgO and iron oxides, some increasing of percentages of SiO₂ and CaO as well as with presence of about 4.5% alkali oxides. These variations can lead to some decreasing of the viscosity [27] as well to the reduced trend for spontaneous uncontrolled crystallization.

In additions, the reduction of Cr₂O₃ can favor the control on the nucleation process. Since this oxide is characterized with a

limited solubility in silicate melts its usage as nucleation agent is recommended in concentrations below 1.5–2.0 wt% [13].

An indication for the efficiency of nucleation process could be obtained by DTA technique because the formation of a consistent number of new nuclei accelerates the crystallization rate and leads to a shift of the exothermal crystallization peak, T_p , toward lower temperatures [16–18]. Therefore a qualitative evaluation of the nucleation can be measured by comparing the positions of crystallization peak in samples nucleated at different thermal schedules.

The nucleation and the crystallization processes of WG glass were investigated by DTA technique using PerkinElmer-Diamond apparatus. In order to estimate the optimal temperature for nucleation diverse little bulk samples with weight of 10–15 mg were hold for 1 h at different temperatures and then heated at 20 °C/min up to 1000 °C. The efficiency of nucleation treatments was evaluated by temperature difference, ΔT , between T_p of non-nucleated and nucleated samples (see Fig. 1). In similar way, by changing the holding time was also estimated the optimal nucleation time.

In addition, by using nucleated and non-nucleated samples and DTA runs at different heating rates (5, 10, 15, 20 and 40 °C/min) the activation energies of crystallization, E_c , were calculated. In this case, preliminary kinetic results obtained by the equations of Kissinger [28] and Matusita and Sakka [29] are compared and discussed.

The activation energy of crystallization, E_c , at non-isothermal crystallization usually is estimated by the Kissinger equation [28]:

$$\ln\left(\frac{\phi}{T_p^2}\right) = -\frac{E_c}{R \cdot T_p} + \text{const.} \quad (1)$$

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

When surface crystallization or phase formation on fixed number of nuclei carries out the value of E_c , obtained by Eq. (1) corresponds to the activation energy of crystal growth, E_G . However when nucleation process carries out during the DTA runs the number of nuclei is influenced by the heating rate (i.e. lower is the rate, bigger is the number of formed during the heating nuclei). As a result the estimated by Eq. (1) E_c has inferior value compared to ones of E_G . In order to avoid this problem Matusita and Sakka [29] proposed the following modification of the Kissinger equation:

$$\ln\left(\frac{\phi^m}{T_p^2}\right) = -\frac{n \cdot E_g}{R \cdot T_p} + \text{const.} \quad (2)$$

where m is the Avrami parameter, while n is a number, depending on the directions of crystal growth. When intensive nucleation carries out it can be assumed that $m=n+1$; contrary when no nucleation carries out $m=n$.

The optimal crystallization temperature and time were estimated measuring the density increasing due to the crystallization [19]. In these experiments nucleated and non-nucleated bulk samples with weight of 2–3 g were heat-treated at

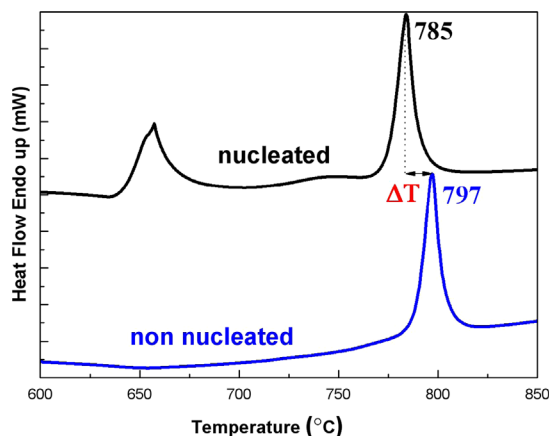


Fig. 1. DTA curves at 20 °C/min of non-nucleated and nucleated (1 h at 650 °C) samples.

different temperatures for diverse times. The density of each bulk sample were measured before the thermal treatments, after the nucleation step and finally after the crystallization step. For this set of measurements, an AccyPyc 1330 Ar displacement pycnometer was employed. Experimental error of $\pm 0.005 \text{ g/cm}^3$ was determined in these density measurements. The method is very attractive when phases with high density variation between amorphous and crystal structures are formed. Typical examples are the pyroxenes, which are the main crystal phase in similar glass–ceramics.

The XRD spectra of a nucleated glass sample and final glass–ceramic, confirming the pyroxene formation, were obtained by a Philips PW 1050 diffractometer, equipped with Cu $K\alpha$ tube and scintillation detector. X-ray powder diffraction patterns were recorded in the angle interval 10–70° (2θ) at steps of 0.03° (2θ) and counting time of 3 s/step.

3. Results and discussion

DTA traces at 20 °C/min of non-nucleated and nucleated for 1 h at 650 °C samples are plotted in Fig. 1. The results for non-nucleated sample elucidate glass transition temperature at about 610 °C and sharp crystallization exo-effect with T_p at low temperature of 797 °C, which demonstrates that the studied glass has a high trend for bulk crystallization even without nucleation step. This result is typical for several iron-rich glasses and can be related to a tendency for liquid–liquid immiscibility at high temperature. This feature leads to separation of iron-rich phase during cooling of the melt and their fast transformation into magnetite spinel nuclei [11,15]. Usually, the number of thus formed nuclei does not change during subsequent nucleation heat-treatment so that similar iron-rich glass–ceramics can be synthesized by single crystallization step.

However, when Cr_2O_3 is also presented additional nucleation process carries out [18]. At high temperatures, near the liquidus, a part of Cr_2O_3 participate in formation of “preliminary” Cr containing spinel, while other part precipitate as “secondary” Cr-spinel at low temperatures [1,30]. This

peculiarity is a premise for additional nucleation heat-treatment, which can lead to more fine crystalline structure and better mechanical properties. Due to this supplementary nucleation, as it is shown in Fig. 1, a significant shift of T_p is observed in DTA curve of the nucleated sample.

The optimal nucleation temperature was evaluated with similar DTA experiments at 20 °C/min using samples heat-treated at different temperatures in the typical nucleation range ($T_g - 20$ °C)–($T_g + 50$ °C) for 1 h. The efficiency of nucleation is estimated by the difference ΔT between peak temperature of the non-nucleated sample and T_p of the nucleated sample; higher is ΔT , higher is the number of formed nuclei. The variations of ΔT as a function of the nucleation temperature are plotted in Fig. 2 and elucidate that the optimal nucleation temperature of investigated WG glass is at about 650 °C.

In similar manner the optimal nucleation time was evaluated. It was determined by plotting ΔT as a function of the holding times at nucleation temperature of 650 °C. The results of these experiments are shown in Fig. 3 and highlight that a treatment of 45–60 min is sufficient for optimal nucleation.

In order to estimate the efficiency of the nucleation process and to obtain some information for the crystallization kinetics additional DTA runs at different heating rates (5, 10, 15, 20 and 40 °C/min) were made. Results for the activation energies for non-nucleated samples and nucleated samples (45 min at 650 °C), obtained by the equation of Kissinger are presented in Fig. 4.

The big difference between both activation energies is additional indication for an intensive nucleation process. Assuming that three dimensional crystal growth carries out (which is typical for the pyroxene crystallization in similar compositions) the data for non-nucleated samples was settled by Eq. (2) using values of $m=4$ and $n=3$. The results are shown in Fig. 5 and highlight that thus obtained value of E_C is similar to one of the nucleated samples obtained by Eq. (1). At the same time, extremely high and non-realistic values for activation energies of about 640 kJ/mol and 490 kJ/mol were obtained assuming

values of $m=2$ and $n=1$ or $m=3$ and $n=2$, respectively. These results confirm that three dimensional crystal growth can be expected, as well as that the used holding time of 45 min is sufficient to complete the nucleation process.

The crystallization time and temperature are evaluated by pycnometric measurements. In these experiments nucleated (1 h at 650 ± 5 °C) and non-nucleated samples with weight of about 2 g, heat-treated at 730 ± 5 °C, 750 ± 5 °C and 770 ± 5 °C for times between 1 and 120 min, were used. The nucleation and crystallization treatments were carried out in electric furnace at heating and cooling rates of 10 °C/min and 20 °C/min, respectively. The densities of each sample were measured before heat-treatment, after nucleation (for nucleated samples) and after crystallization.

The density of parent glass specimens varies in the interval 2.86–2.88 g/cm³. The density increasing after the nucleation heat-treatments was 0.02–0.03 g/cm³, whereas after the crystallization steps – 0.02–0.28 g/cm³. The maximum reached density (after 2 h at 730 °C) was 3.16 g/cm³, which corresponds to the formation of 52 ± 3 wt% pyroxene phase [19].

The variations of density, $\Delta\rho$, of nucleated and non-nucleated samples, treated for different times at 730 °C, are shown in Fig. 6 and highlight that the crystallization is significantly accelerated in the nucleated samples. In both series the phase formation is faster first 20 min and then the rate of crystallization starts to decrease. The maximum density in the nucleated samples is reached after 2 h.

The density variations of nucleated and non-nucleated samples, treated for 5 min at different temperatures, are shown in Fig. 7. The results confirm that $\Delta\rho$ deviations are inferior in non-nucleated samples and elucidate that the increasing of temperature with 20–40 °C significantly raises the crystallization rate. In fact, at 750 and 770 °C the maximum densities for the nucleated samples are reached after 30–40 and 5–10 min, respectively. These highest values, together with the maximum reached density (nucleated sample after 2 h at

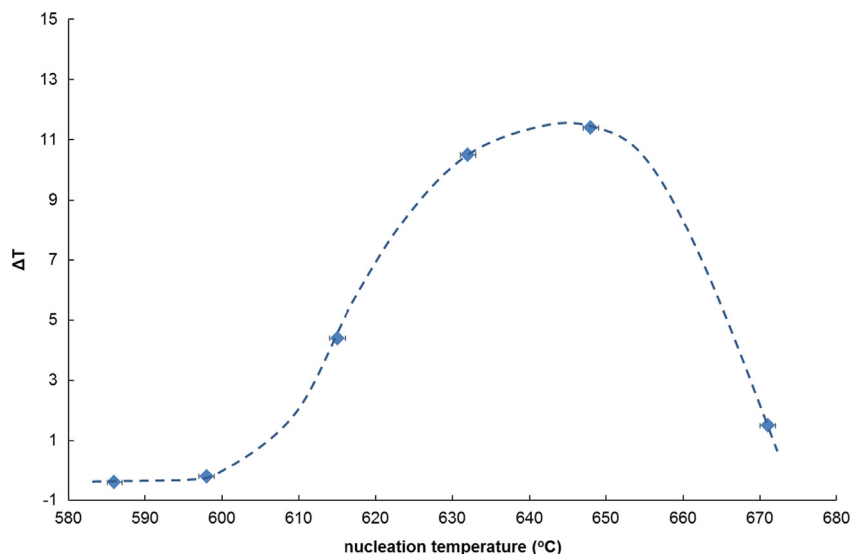


Fig. 2. ΔT as a function of the nucleation temperature at holding time of 1 h.

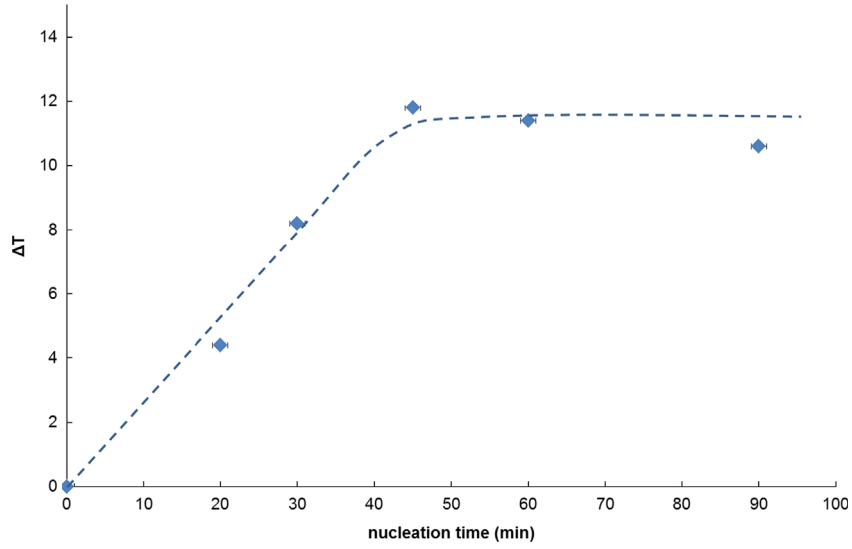


Fig. 3. ΔT as a function of the holding times at nucleation temperature of 650 °C.

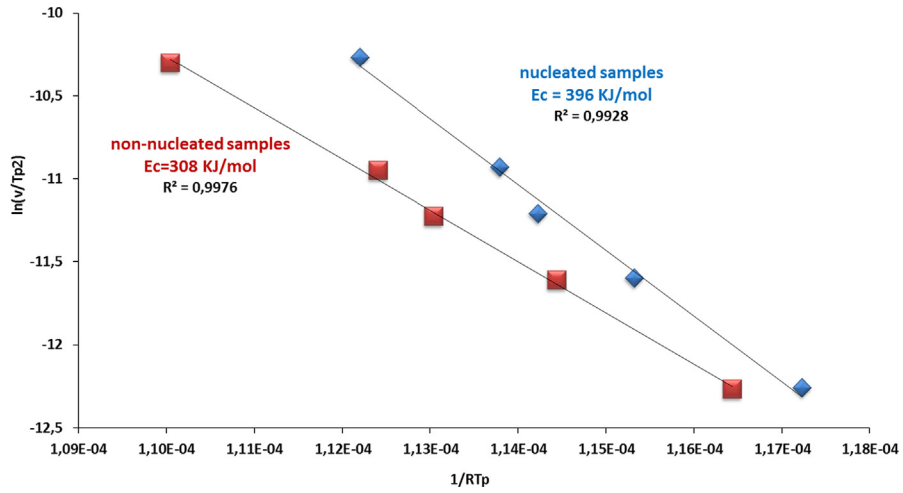


Fig. 4. Activation energy of crystallization of nucleated and non-nucleated bulk samples by the equation of Kissinger.

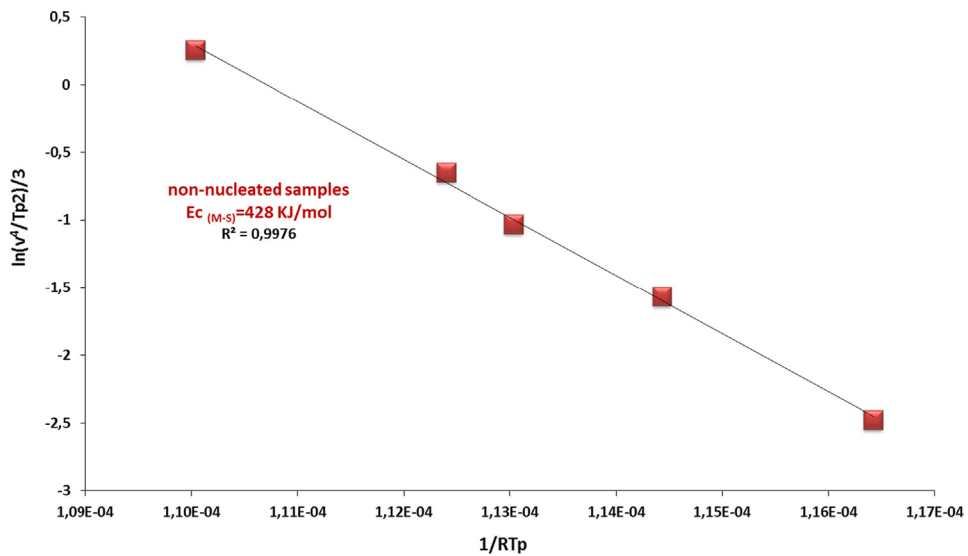


Fig. 5. Activation energy of crystallization of non-nucleated bulk samples by the equation of Matusita and Sakka.

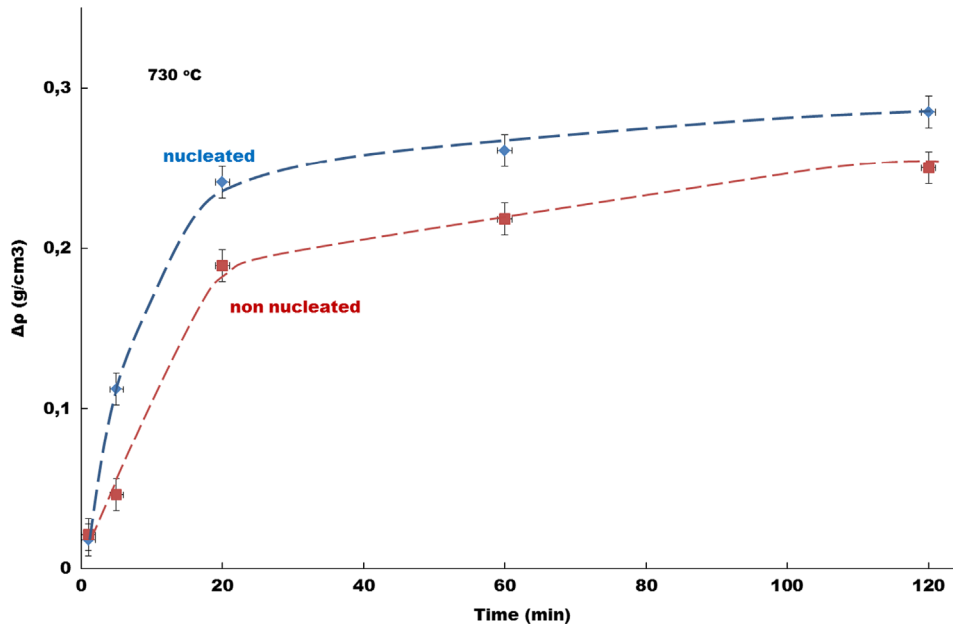


Fig. 6. Density variations of nucleated and non-nucleated samples, treated for different times at 730 °C.

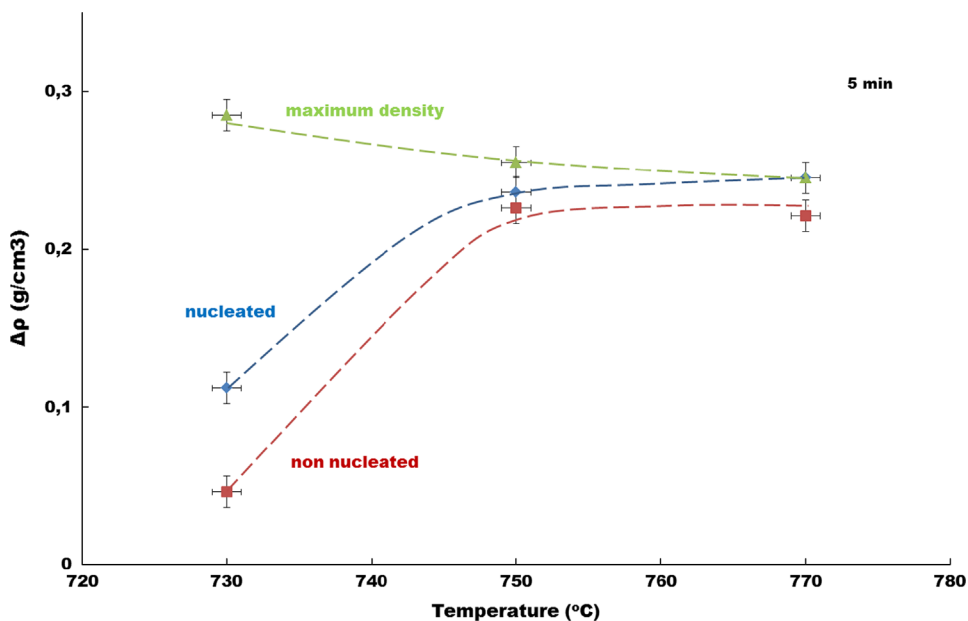


Fig. 7. Density variations of nucleated and non-nucleated samples, treated for 5 min at 730, 750 and 770 °C.

730 °C) also are plotted in Fig. 7 and demonstrate that the obtainable percentage of formed crystal phase decreases with the increasing of temperature. This result is typical for the investigated system [11,15,31] and can be explained with a decreasing of the precipitation with temperature. It can be concluded that the optimal crystallization temperature is at about 750 °C while the crystallization time is below 1 h. At lower temperature the crystallization time increases significantly, whereas at higher temperature a notable decreasing of the crystallinity can be expected. Moreover at very high

crystallization rate problems with the formation of homogeneous crystal structure can be expected due to difficulties with the heat transfer and the latent heat of crystallization.

The XRD spectra of a nucleated sample (1 h at 650 °C) and final glass–ceramic (1 h 650 °C and 1 h at 750 °C) are shown in Fig. 8. The spectrum of nucleated sample shows formation of Cr-Spinel and the beginning of pyroxene formation, while the results of final sample elucidate significant increasing of the pyroxene phase.

Very fine-crystalline structure and the resulting high mechanical properties of glass–ceramic, obtained using the studied in

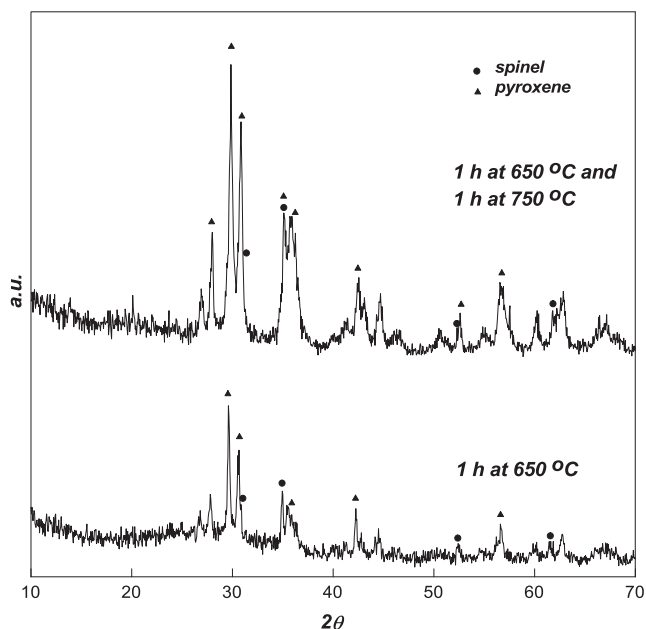


Fig. 8. XRD spectra of a nucleated sample (1 h at 650 °C) and final glass-ceramic (1 h 650 °C and 1 h at 750 °C).

this work optimal heat-treatment schedule, as well as the chemical durability of parent hazardous wastes and resulting stable glass and glass-ceramic will be reported in near future.

4. Conclusions

The investigated glass is obtained using huge amount of industrial wastes from ferronickel production. It is easy melted and is characterized by a spontaneous tendency for bulk crystallization. In addition, due to the presence of 1.5 wt Cr_2O_3 in the batch, supplementary nucleation process takes place.

The optimal heat-treatment for the transformation of parent glass into glass-ceramic was obtained using fast alternative methods: the nucleation step was estimated by DTA analysis, while the crystallization step – by pycnometric measurements. The last technique is possible due to high density difference between glass-ceramic samples and parent glass.

After short heat-treatment at low temperatures (45–60 min nucleation at about 650 °C and 30–45 min crystallization at about 750 °C) mono-phase pyroxene glass-ceramic with ~50 wt% crystallinity was obtained.

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