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Preparation and properties of glass-ceramic materials obtained by recycling goethite industrial waste

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The recycling of toxic goethite waste, originated in the hydrometallurgy of zinc ores, in glass-ceramic matrices has been studied. Oxide compositions suitable to form glasses were prepared by mixing the goethite waste with granite scraps and glass cullet, yielding the following oxide composition (wt%): SiO_2, 44.6; Al_2O_3, 3.3; Fe_2O_3, 25.5; MgO, 1.6; CaO, 4.5; Na_2O, 5.9; PbO, 3.1; ZnO, 6.5; K_2O, 1.0; TiO_2, 2.0; other 2.0. By proper addition of carbon powder, the initial Fe^{3+}/Fe^{2+} ratio (12) of glasses melted in air at 1450 °C was approximated to the stoichiometric value of magnetite (2) to obtain high nucleation and crystallization rates. The heat treatment of iron supersaturated goethite glasses above 630 °C led to the formation of magnetite nuclei with a high tendency to grow and coalesce with time. The crystallization of pyroxene, occurring on the magnetite crystals above 800 °C, was found to be influenced by the nucleation period, so that the highest crystalline volume fraction, V_f (0.80–0.85), was obtained for 90–120 min nucleation time at 670 °C and 120 min crystallization at 860 °C.

1. Introduction

The production of glass-ceramic (GC) materials made by recycling industrial wastes is a known and consolidated technology: it was begun in the ex-Soviet Union about 30 years ago by Kitalgorodskli and Bondarov [1] and Pavlushkin [2]. These materials, known as slag-sitalls, are still produced. Successively, similar products made of foundry slags appeared in several other East European countries, Czechoslovakia, Hungary, Poland, East Germany [3, 4], as well as in the UK [5, 6] and Japan [7]. In recent years, owing to the increasing quantity of wastes produced by the industrial activities and the new environmental regulations which render difficult and expensive the disposal in landfill sites, there has been an increasing interest in developing new glass-ceramic materials made from industrial wastes.

On considering the present research, it appeared that a great part of the studies was aimed at finding a permanent solution to the fly ashes generated from coal and oil-fired electric power stations and to toxic industrial wastes; the first is due to the enormous quantity of residue which has to be disposed of in landfill sites, and the second is due to environmental and health risks.

The large production of fly-ash from coal and oil combustion is recycled, together with other additives such as furnace slags, clays and glass cullets [8–12]. In particular, in China, because of the several hundred million tons produced each year by coal combustion [13], fly-ash recycling has been widely investigated, the additives usually employed being slags from the chemical fertilizer industry, gangue, clay and glass cullet [14, 15].

The recycling of oil shale residues has been considered [16–18] where this waste is produced in large quantities; a vitrifiable composition is being sought, together with fly ash and furnace slags. A consistent number of studies deal with the recycling of industrial residues, such as those from the quartz purification plant [19] and phosphorus production [20]. The recycling of flotation plants residue, constituted by feldspar, biotite, quartz and amphipole, has been the subject of other studies [21, 22]. Wall-covering materials with a granite-like appearance were obtained by vitrifying a mixture of residues from the copper industry, blast-furnace slag and ash from coal combustion. The glass frit was then sintered, crystallized and polished to yield a high-quality artificial granite [23]. Black wall-covering panels and tiles for external applications were obtained by recycling large quantities (up to 60%) of toxic waste from the hydrometallurgy of zinc together with other industrial and civil residues [24].

In the present work, the recycling of this toxic waste, together with other industrial wastes or raw materials and these additives, were sought near the waste-production plant, in order to reduce

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transportation expenses. The composition is designed to maximize the amount of waste in the batch in order to achieve the highest environmental benefit. The final properties are tailored to favour commercial exploitation of the products – bricks, tiles and wall-covering panels – in the large market of the construction industry, and to compete in quality and cost with the already existing products. In this regard, the economical aspects of the GC production process play an important role [17].

Typical industrial toxic wastes are the residues of the roasting-leaching-electrowining process to produce metallic zinc [25]. Iron is precipitated in the form of jarosite, $MFe_3(SiO_4)_2(OH)_6$, goethite, α-FeOOH, or haematite, α-Fe_2O_3, depending on the type of treatment used. The precipitate from the leaching process contains various iron oxides and hydroxides, lower amounts of sulphates of lead, zinc, calcium and other metals such as cadmium, arsenic, copper, nickel, etc. All three processes cause serious environmental problems owing to the large quantity of waste produced (about 750 000 t in the European Union) and the risk of heavy metals being released into the environment.

The results of a study of the crystallization behaviour of a glass composition made by mixing goethite waste together with granite scraps (residues of ornamental stone production) and glass cullet from civil wastes are presented. The goethite was sampled in the Italian zinc-plant located on Sardinia; the granite scraps are generated near the zinc plant in Sardinia, which is one of the main granite producers in the world.

2. Experimental procedure

The particle-size analysis of the dried goethite waste was performed using a Malvern 2600 Diffraction Laser. Goethite is composed of fine particles, 90% of which have a diameter less than 30 μm. The specific area ($23.3\ m^2\ g^{-1}$) of the as-received goethite was measured by the nitrogen-adsorption Micromeritics Asap 2000 BET technique. Its density was measured as $3.64\ g\,cm^{-3}$ by the Micromeritics Accupyc 1330. Further details pertaining to the characterization and preliminary treatments of the goethite redmud were extensively discussed elsewhere [26–28].

The waste was mixed with raw materials and civil and industrial residues to obtain a glass with adequate properties. The following materials were employed: granite scraps, limestone, glass cullet. Table I reports the chemical analysis of the goethite waste, granite scraps and glass cullet obtained using Perkin–Elmer 5000 ICP. The composition with 25 wt% Fe_2O_3 was obtained by mixing 37.2% calcined goethite, 23.0% granite, 37.8% glass cullet and 2.0% titanium oxide, yielding the following oxide composition (wt%): SiO_2, 44.6; Al_2O_3, 3.3; Fe_2O_3, 25.5; MgO, 1.6; CaO, 4.5; Na_2O, 5.9; PbO, 3.1; ZnO, 6.5; K_2O, 1.0; TiO_2, 2.0; other 2.0. Fusion was carried out at 1450 °C using an electric furnace, or in a semi-reduced atmosphere by using a propane gas furnace. For each fusion, 100–500 g powder mixture were utilized.

TABLE I Oxide composition (wt %) of goethite, granite and glass cullet employed in this study

Oxide	Goethite	Granite	Glass
SiO_2	2.2	70.2	72.5
Fe_2O_3	51.3	1.6	0.1
Al_2O_3	0.7	12.1	0.5
MgO	–	0.6	4.0
CaO	0.1	5.2	8.7
Na_2O	0.1	2.9	13.4
K_2O	–	3.3	0.2
ZnO	13.3	–	–
PbO	6.3	–	–
CuO	0.5	–	–
As_2O_3	0.8	–	–
NiO	0.4	–	–
CdO	0.4	–	–
Loss on ignition	23.9	4.1	–

Because high iron-content glasses are corrosive to crucibles during melting, zircon, mullite and alumina–silica crucibles were tested, as well as platinum. After melting, air cooling and cutting the crucible perpendicular in the centre, several areas of the melt–crucible interface were analysed using a Philips 505-Link AN10/50 SEM–EDX. The results showed that the chemical interaction between the zircon crucible and the melt was consistent, and important quantities of ZrO_2 were solved in the glass batch. When employing mullite and alumina–silica crucibles, less corrosion appeared at the interface crucible–melt and minor additions of SiO_2 and Al_2O_3 (compared to zirconia) were seen in the glass batch. In particular, the alumina–silica crucible showed the best behaviour when melting high iron-content glasses. The melt was quenched in stainless steel. A Philips PW 1400 X-ray fluorescence (XRF) spectrometer was employed to determine if appreciable modifications occurred in the glass composition during the melting operation. The glasses were annealed at 600 °C for 30 min, and then analysed by XRD to ensure that no crystallization occurred during quenching and annealing.

The crystalline fraction developed in the GC, as a function of the thermal-treatment time, was calculated from the XRD spectra using a modification of the Alexander–Klug method [29]. Several standard solutions were prepared by mixing goethite glass, magnetite and pyroxene standard minerals in different ratios. A calibration curve has been constructed by XRD analysis of the 100% glass and crystalline content and various mixtures of the two. The magnetite/pyroxene ratio in the crystalline content was considered to be 2 : 3. The crystalline volume fraction, V_f, of a GC sample was obtained by comparing the areas of the amorphous phase and those of the major peak of magnetite and pyroxenes with the calibration curve. All the calculations were carried out by computer through dedicated software. This method is, in theory, more time-consuming than that adopted by Klug and Alexander and recently reviewed by Kim *et al.* [30] but ensures an accurate quantification of the crystalline/amorphous ratio because the entire spectrum of two reference phases (magnetite and pyroxene) is

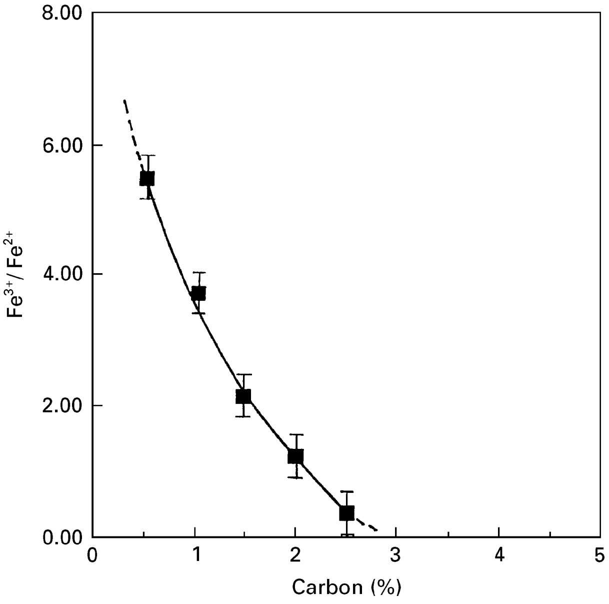

Figure 1 The Fe^{3+}/Fe^{2+} ratio as a function of the percentage of carbon in the glass batch GC_1 25.

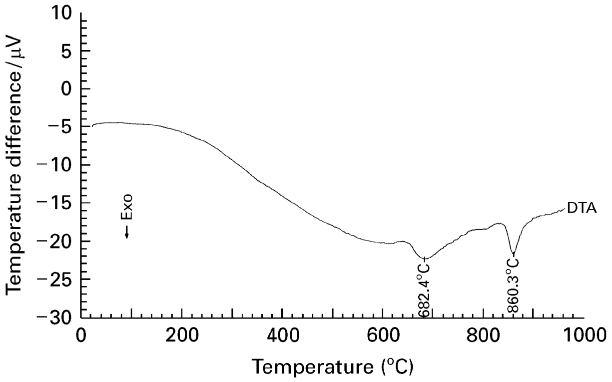

Figure 2 DTA traces of the GC25 glass composition at 10 °C min^{-1} heating rate.

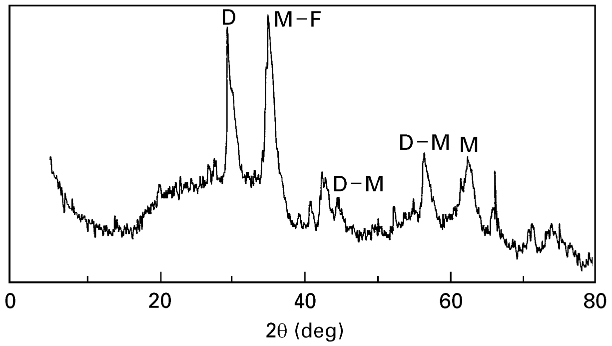

Figure 3 XRD spectrum of the glass nucleated at 670 °C for 4 h. Crystalline phases: D = diopside; M = magnetite; F = franklinite.

considered in the evaluation and comparison of the areas.

The XRD analyses were carried out by using K_α radiation of a copper tube operating at 35 kV and 40 mA with 10 s scanning time on a Philips PW3710 diffractometer. A graphite crystal monochromator was used.

It had been previously demonstrated [31, 32] that the oxidation state of iron plays an important role in the nucleation and crystallization of basalt-type glass compositions because the Fe_3O_4 precipitating above 630 °C, acts as a nucleating phase. In these glasses, melted in air at 1450 °C, the Fe^{3+}/Fe^{2+} ratio was measured as 12. The chemical method [33] was employed to determine the Fe^{3+}/Fe^{2+} ratio.

In order to reduce the ratio to the stoichiometric value of 2, different percentages of carbon powder were added to the glass composition. Carbon was preferred to other reducing substances, such as sugar [31, 34], because it produces a reducing action up to high temperatures and is suitable for industrial application. In these experiments, samples were maintained at 1450 °C for 5 h in an electric furnace. The resulting Fe^{3+}/Fe^{2+} ratios, obtained as a function of carbon weight per cent in the "as-batched" composition, are depicted in Fig. 1.

3. Results

3.1. Analysis of the crystalline phases

Depending on the heating rate, differential thermal analysis (DTA) of goethite glasses highlighted the presence of two exothermic peaks: the first one occurring in the 650–700 °C temperature range, and the second in the 830–900 °C temperature range. Fig. 2 reports the DTA trace of the GC25 sample, performed at 10 °C min^{-1} heating rate on 125 μm powdered samples.

Hot-stage XRD highlighted the formation of two main crystalline phases: magnetite, in the 650–700 °C range and pyroxene above 830 °C. In a second series of experiments, GC25 glass samples were heat treated at 670 °C for times ranging from 20–240 min; they developed crystalline phases identified by XRD as magnetite Fe_3O_4, and titano-magnetite $TiFe_2O_4$; peaks of franklinite $ZnFe_2O_4$, were also identified. At the longest nucleation times, 150–240 min, peaks of diopside were clearly noticed in the XRD spectrum. Fig. 3 shows the XRD spectrum of a GC25 sample after 240 min nucleation at 670 °C.

After crystallization at 860 °C, pyroxenes became the major crystalline phases in GC, i.e. a solid solution between diopside ($CaFeSi_2O_6$) and tschermakite ($CaAlSi_2O_6$). Rhombic pyroxene was also present and very similar to hyperstene ($MgFeSi_2O_6$) [35].

The morphology of the crystalline phase is composed of dendritic networks forming a fully ordered microcrystalline mosaic; it is mainly made up of magnetite and pyroxene; the glass phase is high in silica content. In Fig. 4, scanning electron micrographs of the GC microstructure show the precipitated phases (a), the radial dendritic crystallization of magnetite (b), and the residual glassy phase (c).

3.2. The crystallization process of the glasses

The crystallization process plays an important role in defining the final properties of the GC materials. In a recent study [34], the Fractional Factorial Design (FFD) has been applied to goethite glasses in order to evaluate the influence of the nucleation and crystallization time and temperature and the presence of a

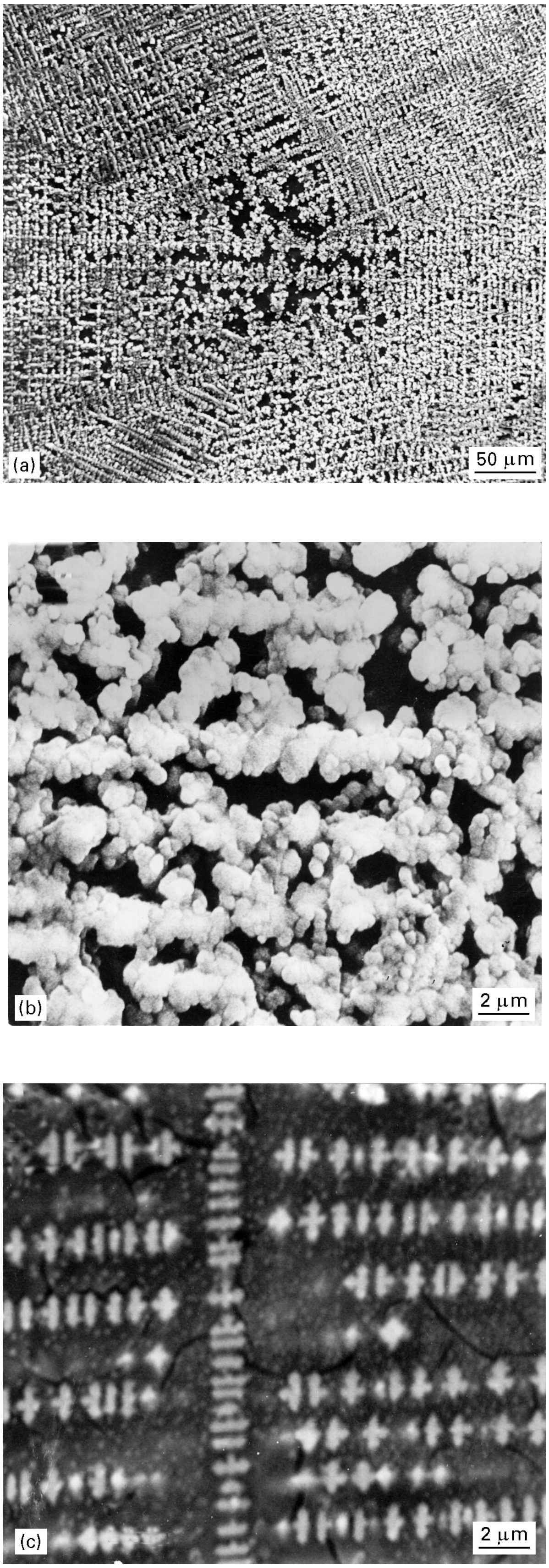

Figure 4 (a–c) Scanning electron micrographs of pyroxene grains.

reducing agent in the batch, on the crystalline volume fraction, V_f. Five different factors, i.e. the nucleation and crystallization temperatures and times and the reducing agent, of each, investigated at minimum and maximum *level* values, were combined through an

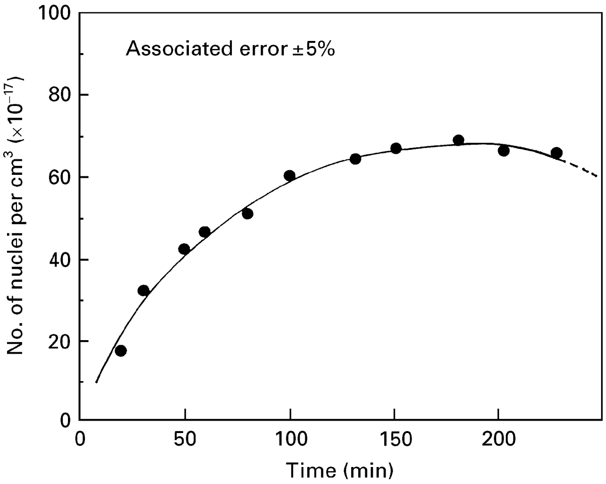

Figure 5 The evolution of the nucleation as function of thermal treatment time at 670 °C.

FFD. The maximum effect on the crystallization of the glass (high V_f) was attained by increasing the nucleation and crystallization temperatures in the investigated *level* range, 630–700 and 800–900 °C, respectively. The effect of the crystallization time was positive (i.e. longer time increases V_f) but with a low significance (85.6%). Increasing the nucleation time (factor *A*) in the level, from 30 min to 240 min, had a negative effect on V_f. In other words, longer nucleation periods seemed to affect adversely the number of sites available for pyroxene crystallization. Moreover, the *interaction*, nucleation time (factor *A*) with nucleation temperature (factor *C*), also generated a negative effect on V_f.

In this study the relation between the nucleation thermal treatment time and the number of magnetite nuclei developed in the glass matrix was investigated. For this purpose, equal samples (in which the stoichiometric Fe^{3+}/Fe^{2+} ratio in the magnetite was approximated by adding 1.5 wt% C powder) were heat treated at 670 °C for different periods from 20–200 min. Each sample was then observed by a Philips 300 kV TEM and the number of nuclei per cubic centimetre was determined by Quantimet 970 Image Analyser technique as a function of the thermal treatment duration. The results, depicted in Fig. 5, show that after 120–150 min, the glass reaches a saturated density of nuclei, and the number of nuclei tends to decrease after about 180 min, thermal treatment.

In a second series of experiments, samples of glasses were heat treated (with identical thermal cycles) at 670 °C, for variable times, followed by 60 min at 830 °C. Fig. 6 shows the behaviour of the measured crystalline volume fraction, V_f as a function of the nucleation time reported on the abscissa. The V_f reaches the maximum value in about 90–120 min heat treatment at 670 °C, and rapidly decreases after 180–240 min treatment. In Figs 5 and 6, the estimated errors associated with each type of measurement, are reported.

A possible interpretation of the results suggests that, due to the high iron content in the glass and the quasi

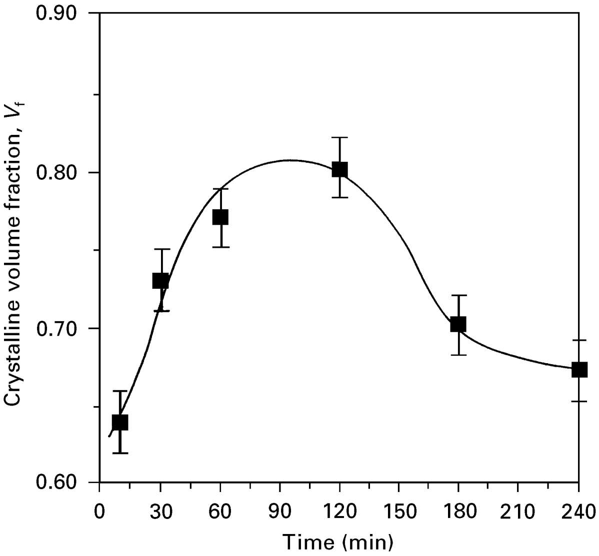

Figure 6 The crystalline volume fraction, V_f, as a function of the nucleation time at 670° C.

stoichiometric Fe^{3+}/Fe^{2+} ratio, a great number of magnetite nuclei are rapidly formed above 630 °C. Furthermore, when prolonging the heat-treatment time, growth of magnetite nuclei occurs and smaller and less-stable crystals are dissolved in the bigger ones, thus reducing the number of sites for pyroxene crystallization.

The GC25 composition with 1.5% C showed high crystallization velocity during pouring, which renders it very difficult to obtain fully glass materials. This behaviour has been attributed to the effect of iron and oxides on the crystallization of pyroxene. It was pointed out [19] that glass compositions with a Fe_2O_3 content between 25% and 30% and an alumina content higher than 3%–5% have a high tendency to crystallize during the pouring of the melt. In the presence of aluminium ions, there is a strong competition between Fe^{3+} and Al^{3+} for oxygen during the formation of the coordination tetrahedra. As a consequence, the quantity of iron that can be assimilated in the glass phase is drastically reduced and creates the conditions for the formation of magnetite.

The crystalline volume fraction of GC25, nucleated and crystallized at various temperatures and times, was found to be between 0.65 and 0.85. The highest crystalline volume fraction, V_f (0.80–0.85) was obtained for 90–120 min nucleation time at 670 °C and 120 min crystallization at 860 °C.

3.3. Glass-ceramic properties

Diopside has been shown to be an ideal crystalline matrix for the immobilization of nuclear or toxic wastes through a combined process of fusion of the waste in oxide mixtures, followed by a controlled cooling of the melt to form a glass-ceramic material [36]. Chick *et al.* [36] reported that the leachability of the basalt GC is 4–10 times lower than the parent glass and the crystalline phase remains intact while the residual glass is dissolved away during leaching.

Because in goethite GC, about 50% of the batch is made up of toxic waste, the chemical resistance in different environments acquires particular importance. It has been previously pointed out [37] that it is the chemical durability of the glassy phase that controls the leaching rate, both in the parent glass and in the GC. However, because the composition of the parent glass is different from that of the residual glassy phase in the GC, the better chemical durability of the GC material might be attributed to the fact that crystallization heat treatment reduces the concentration of alkaline-earth elements in the residual glass, resulting in a chemically more stable structure. The EDX microanalysis, carried out on crystalline grains, has shown the presence of the zinc, lead and copper replacing the iron and calcium between the silicate layers in the pyroxene structure [22], while the elements present in the glass phase, besides silicon, are mainly magnesium, calcium and sodium in the approximate ratio $(MgO + CaO)/Na_2O = 1.5$.

The leachability of the GC powder has been determined in 120 °C distilled water in 5% NaOH, 5% HCl and 0.02 N Na_2CO_3 at 40 and 95 °C constant temperatures. Details of the experimental procedure and results are reported elsewhere [37–38]. In commenting on the results, it must be pointed out that, in the tested conditions, the leachability of the GC in hot water, Na_2CO_3 and NaCl is very good, while the glassy matrix is more easily leached in an acid solution. In any case, the chemical resistance is strongly influenced by the crystalline phases. The higher the crystallinity, the better is the chemical durability and the smaller is the quantity of metals found in the leaching solution.

The toughness is the other remarkable property of the goethite GC material. The K_{IC} has been measured as 1.78 $MPa\,m^{1/2}$. For the same composition, the toughness has been found to be mainly dependent on V_f. This positive behaviour has been attributed to the crack propagation resistance of the microcrystalline structure formed by magnetite crystals inside a dendritic pyroxene matrix [39].

4. Conclusion

It has been proved that toxic industrial waste of a complex composition can be mixed with raw materials and residues, melted and formed into glass and heat-treated to produce glass-ceramic materials.

The glass supersaturation, due to the high iron content, and the quasi-stoichiometric Fe^{3+}/Fe^{2+} ratio, yield high rates of magnetite nucleation; nuclei tend to grow and the small and unstable magnetite aggregates are redissolved into the bigger ones. This combined process of nuclei formation, growth and reaggregation is a function of time at a constant temperature thus resulting in fewer crystallization sites available for pyroxene formation, for prolonged nucleation treatment. Pyroxene, magnetite and zinc ferrite are the main crystalline phases.

The investigated compositions can be formed by conventional glass processing, and tile or panel forms can be obtained for the construction industry. The properties of the GC materials are influenced by the crystalline percentage and show high strength and good chemical resistance.

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