

Vitrification and Sinter-Crystallization of Iron-Rich Industrial Wastes

Alexander Karamanov

Institute of Physical Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Block 11, 1113 Sofia, Bulgaria
karama@ipc.bas.bg

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Abstract. Results about the vitrification of several hazardous iron-rich industrial wastes (from productions of Zn and Cu metals, as well as EAFD and MSWA) and the usage of obtained glasses for synthesise of sintered glass-ceramics are summarises. It is shown that the appropriated method of sinter-crystallization mainly depends on the crystallization trend of used glasses. When the parent composition is characterised by formation of a moderate amount of crystal phase low temperature sintering with short crystallization step in the interval 800-900 °C can be used. In addition, attractive granite-like building glass-ceramic can be obtained by mixing fine and coarse glass frits and “free” sintering in refractory moulds at 1000-1050 °C. Contrary, when intensive phase formation carries out the crystallization inhibits the sintering resulting in specimens with scarce degree of densification. However, in some cases a secondary densification process occurs at temperatures near to the eutectic ones, leading to well sintered samples with higher crystallinity and improved mechanical properties. It is also highlighted that the preventing of Fe²⁺ oxidation by using inert atmosphere during the heat-treatments leads to a decreasing of sintering temperature, finer crystalline structure and additional enhancement of the mechanical properties.

Introduction

During the melting of glass batches, based on hazardous industrial wastes, and the following cooling of the melt the harmful elements are chemically bonded in durable amorphous network. For this reason the vitrification is considered as the surest method for immobilization of these streams [1-4]. However, due to its relatively high cost, this tool is justifiable only if materials with commercial value are obtained. From this point of view, the synthesis of quality glass-ceramics seems to be one of the most promising solutions.

The commonly used method for glass-ceramic production is based on bulk nucleation and crystal growth. This technique needs addition of proper nucleation agents, high degree of refining and homogenisation of the parent melt, forming procedure (mainly by casting, rolling or pressing) and two step heat-treatment treatment with duration of several hours [1,4,5].

An alternative technology is the sinter-crystallization (i.e. simultaneous densification and crystallization of glass powders or grains). This technique requires no nucleation agents and no nucleation step, which reduces the batch price and shortens the time of crystallization heat-treatment. Moreover parent glasses with lower degree of homogenization may be used, which significantly decreases the melting time and thus the overall price of vitrification procedure.

The sinter-crystallization seems to be very appropriate for synthesise of glass-ceramics by industrial residues. In fact, several sintered glass-ceramics, obtained by pressing or slip casting of glass powders by different industrial wastes were studied last decade. Composite glass-ceramics and foams were also investigated and characterised [6].

During sinter-crystallisation the densification and the crystalline phase formation take place in the same temperature interval. When the crystallisation trend is low the sintering carries out for a very short time at low temperature while higher temperature and longer time are needed to complete the crystallisation process. However, in the major part of sintered glass-ceramics by industrial wastes the crystallisation process is very intensive, which decreases the sintering rate or even hinders the densification. In this case the sintering can be improved using high heating rates or applying a secondary densification process near the liquids temperatures.

Another promising method of sinter-crystallization is the direct sintering of glass frits, placed loosely in refractory form. This technique was firstly used for the production of famous building marble-like glass-ceramic Neoparies [5,7] and latter for synthesise of different granite-like materials from industrial wastes [8,9].

In case of iron-rich glasses the sinter-crystallization is characterised with some interesting peculiarities, which are summarised in the present work using author's results obtained last 15 years [10-16]. The publication presents data about the chemical durability of glasses from hazardous iron-rich wastes, as well as results about their crystallization and sintering behaviours. Information about the appearance, the micro- structure and the properties of obtained materials is also presented and discussed.

Experimental procedures

In the work are discussed glasses, based on the following industrial wastes: Jarosite (**Jar**) and Goethite (**Goe**) – residues arising from zinc hydrometallurgy, flotation waste from copper production (**Flo**), electric arc furnace dusts (**EAFD**) and municipal solid waste incinerator bottom ash (**MSWA**). From the selected industrial residues only **MSWA** is appropriated for “as it is” vitrification. In the other glass batches, because of low amount of glass formers (i.e. $\text{SiO}_2 + \text{Al}_2\text{O}_3$) in the wastes, inert industrial residues or cheap raw materials (as glass culets, waste from granite sawing, quartz sand, limestone and Na_2CO_3) were added in amounts between 45 and 60 wt %. The chemical analysis of parent wastes (**W**) and corresponding glasses (**G**) were performed by XRF analysis (Spectro-Xepos) and the results are summarized in Table 1.

Table.1 – Chemical compositions of the studied wastes (**W**) and glasses (**G**)

| | Jar | | Goe | | Flo | | EAFD | | MSWA | |
|------------------------------------|------|------|------|------|------|------|------|------|------|------|
| | W | G | W | G | W | G | W | G | W | G |
| SiO₂ | 3.7 | 53.8 | 7.7 | 42.9 | 24.9 | 56.6 | 4.4 | 50.6 | 32.1 | 34.1 |
| Al₂O₃ | 0.3 | 3.7 | 1.9 | 5.8 | 0.9 | 2.9 | 1.5 | 0.9 | 13.3 | 13.6 |
| Cr₂O₃ | | | | | | | 15.9 | 6.9 | 0.1 | |
| Fe₂O₃ | 49.2 | 21.7 | 45.4 | 25.2 | 67.7 | 19.9 | 24.3 | 10.6 | 10.8 | 11.5 |
| CaO | 0.1 | 8.7 | 5.2 | 9.6 | 0.7 | 10.9 | 20.6 | 11.5 | 20.8 | 22.1 |
| MgO | 0.2 | 0.2 | 0.8 | 0.1 | 0.4 | 0.2 | 9.6 | 5.3 | 2.8 | 3.7 |
| ZnO | 5.6 | 2.4 | 11.0 | 5.6 | 2.8 | 1.1 | 7.6 | 3.3 | 0.8 | 0.7 |
| PbO | 4.0 | 1.5 | 1.2 | 0.7 | 0.2 | 0.1 | 0.5 | 0.2 | 0.1 | |
| MnO | | | 0.5 | 0.2 | 0.3 | 0.1 | 5.2 | 2.2 | 0.1 | 0.2 |
| CuO | 0.1 | | | | 1.0 | 0.4 | 0.3 | 0.2 | 0.7 | 0.8 |
| NiO | | | | | | | 1.8 | 0.8 | | |
| CoO | | | | | 0.2 | 0.1 | | | 0.1 | 0.1 |
| Na₂O | 0.1 | 6.9 | | 6.5 | | 7.1 | 6.6 | 6.8 | 2.0 | 2.2 |
| K₂O | | 1.0 | 0.4 | 2.1 | 0.5 | 0.2 | 1.8 | 0.8 | 1.0 | 1.4 |
| P₂O₅ | | 1.0 | 0.4 | 2.1 | 0.5 | 0.2 | 1.8 | 0.8 | 1.9 | 2.0 |
| LOI | 36.9 | | 19.7 | | 4.2 | | 1.2 | | 13.4 | |

Batches of 0.2-0.5 kg were melted in electric furnace at 1350-1450 °C using corundum crucibles and holding times between 0.5 and 3 h. 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 and after formation of “mirror” surface the melt was quenched in water to obtain glass frits. After crashing or/and milling and sieving different fractions with appropriate granulometry for the subsequent research were prepared.

The melting temperatures were estimated according to the expected viscosity of the melt; the lowest was the melting temperate of **G-Goe** and **G-Jar**, while the highest – one of **G-MSWA**. The melting times mainly depend on the tendency of parent melt to form sulphate foam. This process

started at about 1300 °C and carries out in different manner. In *G-Flo* and *G-EAFD* melts the refining completes after only 10–15 min, while in *G-Jar* and *G-Goe* batches, due to the high amount of SO₃ in parent wastes, the foaming process was very intensive and the formation of “mirror” surface of the melt occurs after 3-4 h melting step. Glasses, obtained by the wastes from hydrometallurgy of zinc and granite mud, were also melted in a pilot-scale melting kiln [4, 12].

The chemical durability of dried wastes and the corresponding glass frits was evaluated by the toxic characteristics leaching procedure (TCLP), created by the US Environmental Protection Agency (EPA). The samples were placed in distilled water and stirred for 24 h at room temperature. During the treatment pH of the solution was kept constant at 5±0.2 by addition of 0.5M acetic acid. Then the extracted liquid phases were analysed by atomic adsorption spectroscopy (Varian Spectra 200) and the obtained concentrations of harmful elements were compared with the maximum allowable limits.

The phase formation and the densification were estimated in non-isothermal conditions by Differential Thermal Analysis and Dilatometry, respectively, and the formed crystal phases were evaluated by XRD analysis.

The methods to obtain sintered glass-ceramics by pressed glass powders and by densification of grains, placed loosely in refractory molds, were studied. The first technique gives possibility to manufacture samples with complicate shapes and high mechanical properties; the second technique elucidates the possibility to produce large granite-like building panels for the modern architecture.

The glass-ceramics by pressed powders were obtained using fractions bellow 75 microns. “Green” samples with dimensions of 50x4x3 mm³ were obtained by mixing the glass powders with 7% PVA solution and by uniaxially pressing at 100 MPa. After drying and 30 min holding at 280 °C (to eliminate the organic binder) the specimens were heat-treated in an electric furnace or in dilatometer. The structures of final glass-ceramic and the morphology of the formed crystal phases were observed by SEM.

The sintering ability of the frits was estimated after 30-60 min heat-treatment at various temperatures. After that, selected fractions (or their mixtures) were heat-treated at temperatures and times, ensuring the formation of well sintered samples with smooth surface. The obtained samples were cut, ground and polished. The structures of materials were observed by optical microscopy.

Finally, the properties of some of the final products were evaluated. Young modulus was measured by means of non-destructive resonance frequency technique (Grindosonic) and the bending strength was evaluated by a three point bending test (SINTEC D/10). The coefficients of linear thermal expansion (20-400°C) of glass-ceramics were evaluated by a Differential Dilatometer, the density was evaluated by gas displacement Pycnometer (AccyPyc 1330) and the hardness was estimated by using a WOLPERT apparatus.

Results and Discussions

Viscosity and Chemical durability

The iron-rich glasses are characterized by specific viscosity curves, which are characterized by a relatively high glass-transition temperatures and low melting temperatures. Fig. 1 shows experimentally obtained results for the viscosity of a Jarosite glass [17] and Vogel–Fulcher–Tamman (VFT) curve of a traditional container SiO₂-CaO-MgO-Na₂O glass. It is evident that the viscosity curves are very different. The both compositions have similar glass transition temperatures (T_g) while the Littleton softening point (T_L - 10⁷⁻⁸ dPas) of the iron-rich composition occurs at higher temperature (i.e. the iron-rich melt is “shorter” and needs superior forming temperatures). Contrary, the “melting points” - T_m (i.e. the temperatures corresponding to a viscosity of 10² dPas) in the container glass is at significantly higher temperature (by 200 °C). The substantial viscosity drop of the iron-rich melts at high temperatures is quite anomalous and cannot be explained by the usual methods for prediction of glass viscosity. Probably it is related to significant changes of melt structure with the temperature due to the presence of high amount of iron oxides. It can be assumed that these changes are due to the liquid-liquid immiscibility, which takes place during the melt cooling and/or because of some increasing of the Fe³⁺/Fe²⁺ ratio with the temperature decreasing.

The low melting temperature of the iron-rich glasses is an important advantage, leading to significant decreasing of the price of vitrification procedure. In addition, the tendency for evaporation of heavy metals during the glass melting significantly drops at lower melting temperatures. This is another important benefit when iron-rich hazardous wastes are vitrified.

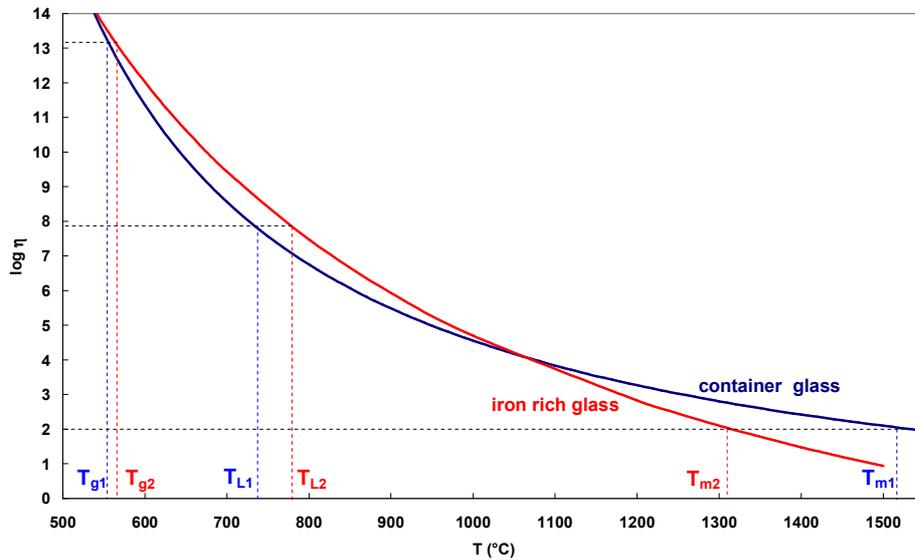


Fig. 1 Viscosity curves of traditional container glass composition (1) and iron-rich melt (2)

At the same time the high glass transition temperatures of iron-rich glasses indicate a good chemical durability. Table 2 summarizes TCLP results for the presented harmful elements in three of studied wastes (i.e. **Jar**, **EAFD** and **Flo**) as well as the values for the corresponding glass frits. The results demonstrate that the concentration of Cr, Pb, Zn and Cu for the residues considerably surpass the applied limits, while all glass frits exhibit high chemical durability corresponding to entirely inert materials. In addition, the subsequent sintering into compact bodies and the crystallization additionally improve the chemical resistance of final glass-ceramics.

Table.2 – TCLP results (ppm) of the studied wastes (**W**) and the corresponding glass frits (**G**)

| Elements | Jar | | Flo | | EAFD | | Applied Limits |
|-----------|-------|---------|-------|--------|-------|---------|----------------|
| | W | G | W | G | W | G | |
| Cr | | | | | 23.1 | <0.005 | 2 |
| Pb | 67.1 | 0.062 | 7.2 | <0.001 | 0.018 | <0.001 | 0.2 |
| Cu | 1.6 | < 0.005 | 94.9 | 0.008 | 0.42 | < 0.005 | 0.1 |
| Zn | 132.4 | 0.024 | 114.4 | 0.098 | 5.3 | 0.12 | 0.5 |

3.2 Crystallization trend and sinter-ability

The difference in the crystallization trends of used glasses were estimated by DTA results of powder samples treated in air at heating rate of 10 °C/min. In Table 3 are summarised results for the glass transition temperatures, T_g , the crystallization peak temperatures, T_p , and the meting temperature, T_m , as well as the calculated values of the ratio T_g/T_m and the Hruby parameter, $K_H = (T_p - T_g)/(T_m - T_p)$.

For the traditional glass forming system the ratio T_g/T_m can be $\sim 2/3$ and its decreasing is a clear indication for a reduced possibility to form a stable glass. The Hruby parameter is an empirical rule which gives a possibility to compare the crystallization trends of glasses from similar systems: lower is K_H - higher is the crystallization trend.

Since the variations of T_g/T_m ratio are not significant the main reason for decreasing of K_H value is related to the shift of crystallization temperature toward the glass transition range, which means that at elevate crystallization trend the phase formation starts at higher viscosities. In this case, the crystallization rapidly increases the apparent viscosity of sinter-crystallising system, resulting in

insufficient time for sintering. Contrary, in compositions with a high K_H the phase formation starts at low viscosity and after the end of sintering, so that the heat-treatment depends only from the crystallization. In other words, the value of the Hrubí parameter might be also used as indicator for the sinter-ability of glass-powders.

In **G-EAFD** composition, due to high amount of Cr_2O_3 , uncontrolled spontaneous crystallization of Cr-spinel carries out during the melt cooling. Then, at heating the formed spinels lead to very fast pyroxene precipitation. As a result, the crystallization peak of this composition occurs at lowest temperature and K_H has an extremely low value of 0.6. In addition, T_g/T_m ratio also has the lowest value, which elucidates the difficulty to obtain a stable glass.

In similar composition significant phase formation carries out yet at viscosities of 10^8 - 10^9 dPas and sintering of glass powders is practically impossible. In fact, the pressed **G-EAFD** glass powders are characterised with a negligible linear shrinkage even after long thermal treatments at temperatures higher than 1100 °C.

In the glasses, obtained from Goethite and MSWA, the crystallization ability is not extremely high. As a consequence, some sintering carries out before the beginning of crystallization and near the liquids temperature a secondary densification process is possible.

Finally, in the glasses from Jarosite and Flotation wastes, where the crystallization ability is low, the main part of the sintering completes before the formation of significant percentage of crystal phase.

Table.3 – DTA results of the studied glasses powder (<75 microns) in air.

| | T_g | T_p | T_m | K_H | T_g/T_m |
|---------------|-------|-------|-------|------------|-------------|
| G-Flo | 590 | 940 | 1050 | 3.1 | 0.65 |
| G-Jar | 575 | 885 | 1060 | 1.8 | 0.64 |
| G-Goe | 600 | 850 | 1120 | 1.1 | 0.63 |
| G-MSWA | 650 | 900 | 1150 | 1.0 | 0.64 |
| G-EAFD | 580 | 780 | 1140 | 0.6 | 0.60 |

The differences in sinter-crystallization trend were confirmed by the XRD results. Lowest amounts of crystal phase are formed in **G-Jar** and **G-Flo** and highest - in **G-MSWA** and **G-EAFD**. In the compositions from Jarosite and Gehlenite, similarly to **G-EAFD**, are formed magnetite (i.e. spinel) and pyroxenes. In the glass from Flotation waste, due to higher CaO and lower Fe_2O_3 percentages, the pyroxene amount decreases and formation of some wollastonite s.s. is observed. Finally, in **G-MSWA**, where a part of SiO_2 is substituted by Al_2O_3 and percentage of CaO reaches 20 wt %, together with pyroxenes are formed gehlenite solid solutions.

3.3 Sintering, crystallization and structure of materials obtained by press powders

By using **G-Jar** and **G-Flo** glass powders can be obtained glass-ceramics, where the densification process is not seriously inhibited by crystallization. In similar compositions the optimal heat-treatment is based on heating to the crystallization range (i.e. 850-950 °C) and holding of 0.5-1 h. Sometimes, in order to avoid pore coalescence or deformation of the samples, low heating rate can be used. Unfortunately, because of low amount of crystal phase (30-40 %), the obtained materials are characterized with moderate mechanical properties: Young modulus of 55-65 GPa, bending strength of 65-75 MPa and Vickers hardness of 3.5-4.5 GPa.

In order to increase the properties the crystallinity can be raised and compositions as **G-MSWA** or **G-Goe** can be used. However, in similar glass-ceramics the low temperature sintering is inhibited and the densification process can be loaded in a narrow temperature interval near the liquids temperature.

Typical sintering curve of **G-MSWA**, obtained with optical contactless dilatometer, is shown in Fig. 2. The traces confirm the glass transition temperature at 640-650 °C and show that the densification starts at about 700 °C. After the beginning of crystallization (at 830-850 °C) the sintering rate starts to decrease, becoming zero at 880-900 °C and at shrinkage of only 1.5 %.

Then, up to ~ 1050 °C the sintering process remains inhibited by the formed crystal phase, so that high heating rate might be used. After that, due to partial melting [16] and decreasing of the viscosity starts a secondary sintering process, which rate significantly rises with the temperature. The sintering experiments in the interval 1050-1150 °C highlight that minor is the heating rate, higher is the final shrinkage and lower is the closed porosity. Therefore in this temperature interval low heating rate was suggested. The sintering completes after 40-80 min at 1120-1130 °C and the final samples are characterised with $\sim 65\%$ crystallinity, zero water absorption, ~ 9 vol % closed porosity and apparent density of ~ 2.65 g/cm³. It can be noted that a completed sintering cannot be obtained at 1100-1110 °C (even after very long holding times), while at 1140-1150 °C starts overfiring and deformation.

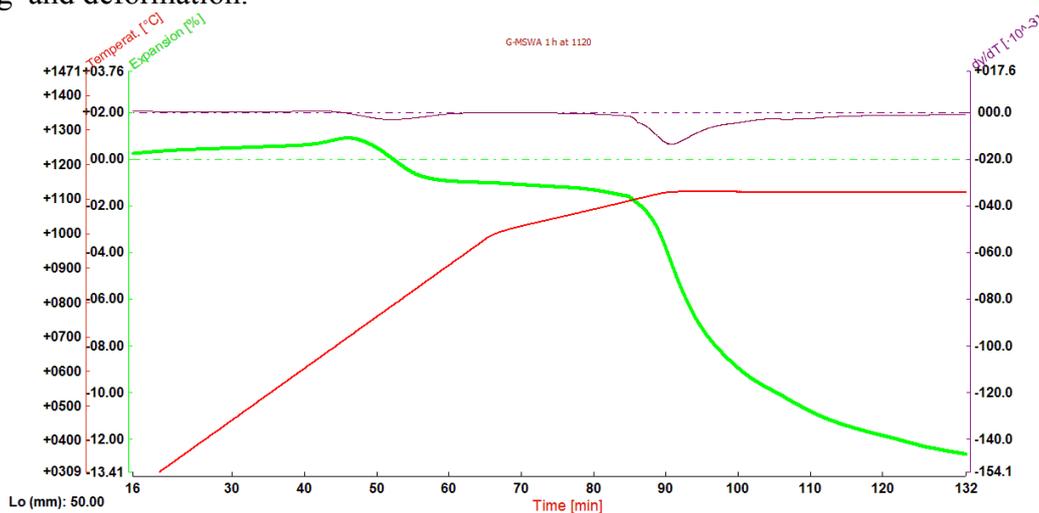


Fig. 2 Dilatometric densification curve of powder sintered glass-ceramic by MSWA

Other important feature of the sintered iron-rich glass-ceramics is the improvement of sinter-crystallization in inert atmosphere [13,16]. This peculiarity is elucidated in Fig 3, where are presented DTA results (solid lines) and sintering curves with contact dilatometer (dashed lined) of **G-Goe** in air and nitrogen atmospheres.

DTA traces in air highlight that in the interval 650-800°C (i.e. instantly after the glass transition range) a wide exo-effect with low intensity is observed. This exo-therm is related to ~ 0.7 % weight gain and can be related to oxidation of ~ 8 % FeO into Fe₂O₃. In fact, the parent Fe³⁺/Fe²⁺ ratio is formed during the glass melting (where 20-30 % of the iron is in Fe²⁺ state), while at 600-900 °C the equilibrium ratio Fe³⁺/Fe²⁺ is significantly higher, which leads to a spontaneous oxidation process. After the oxidation exo-therm crystallization exo-effect with peak temperature at 850 °C is observed. The DTA-TG traces in nitrogen atmosphere show no oxidation and sharper crystallization exo-effect with peak temperature at 770 °C. The huge shift of the crystallization temperature cannot be explained only with lower viscosity due to the presence of FeO; it also indicates that spontaneous bulk crystallization carries out [11]. The DTA results also elucidate a significant decreasing of the melting temperature in inert atmosphere.

The dilatometric results highlight that the low temperature sintering is inhibited by crystallization in both atmospheres. In air, where the phase formation is not so intensive the sintering is blocked at shrinkage of 7 %, while in N₂ - at shrinkage of only 3 %. Similarly to **G-MSWA**, the densification starts again with the increasing of temperatures. Well sintered samples with zero water absorption and firing linear shrinkage of 11-12 % were obtained after 30-60 min holding at 960-970 °C in N₂ and at 1040-1050 °C and air. The lower sintering temperature in inert atmosphere is due to inferior viscosity and lower liquids temperature.

The XRD results of final **G-Goe** samples show at about 50% and 60% crystallinity, after sintering in air and N₂ atmospheres, respectively. The comparison of both spectra elucidates that the higher percentage for the sample, sintered in N₂, is due to increasing of magnetite phase.

The iron oxidation also produces a change of the colour: after heat-treatment in nitrogen the samples remain black as the parent glasses, while after sintering in air they become red-brown. The

black colour is due to simultaneous presence of Fe^{2+} and Fe^{3+} ions, while the red-brown is due to Fe^{3+} ion. In fact, these colours are typical for magnetite ($\text{FeO}\cdot\text{F}_2\text{O}_3$) and hematite (Fe_2O_3), respectively. Photos of the final *G-Goe* samples, as well as SEM images, demonstrating the degrees of densification (top inserts) and the morphology of formed crystal phases (bottom inserts), are summarised in Fig. 4. Both samples have similar degree of densification but different microstructure. In air the crystallization of main pyroxene phase is surface induced, while in inert atmosphere tiny pyroxene dendrites with 2-4 μm size are formed; in this case the magnetite crystals, which are formed as first crystal phase, act as nuclei for epitaxial bulk pyroxene formation.

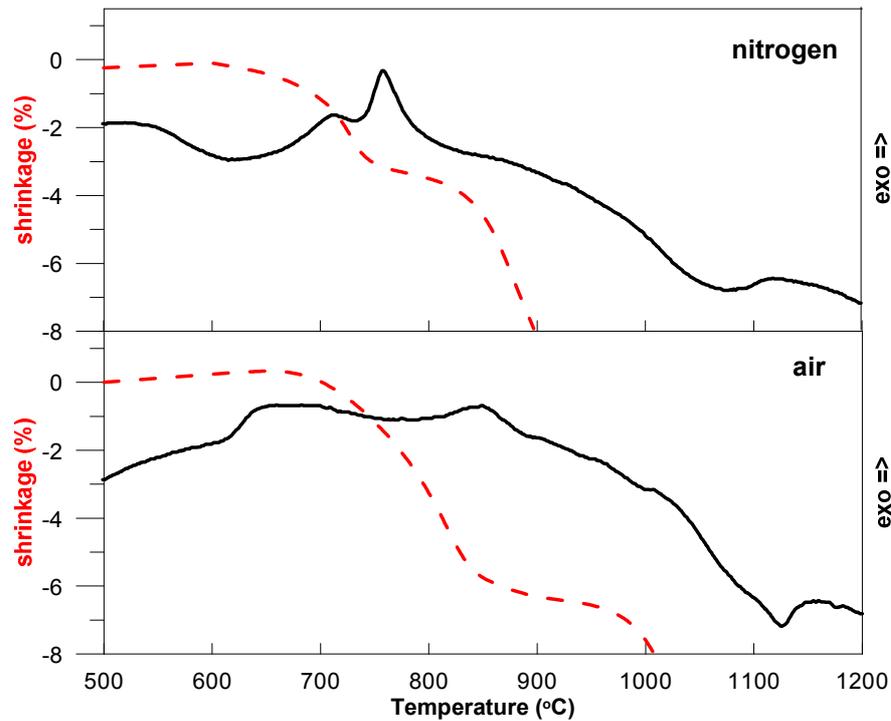


Fig. 3 DTA results and sintering curves of *G-Goe* in air and nitrogen atmospheres

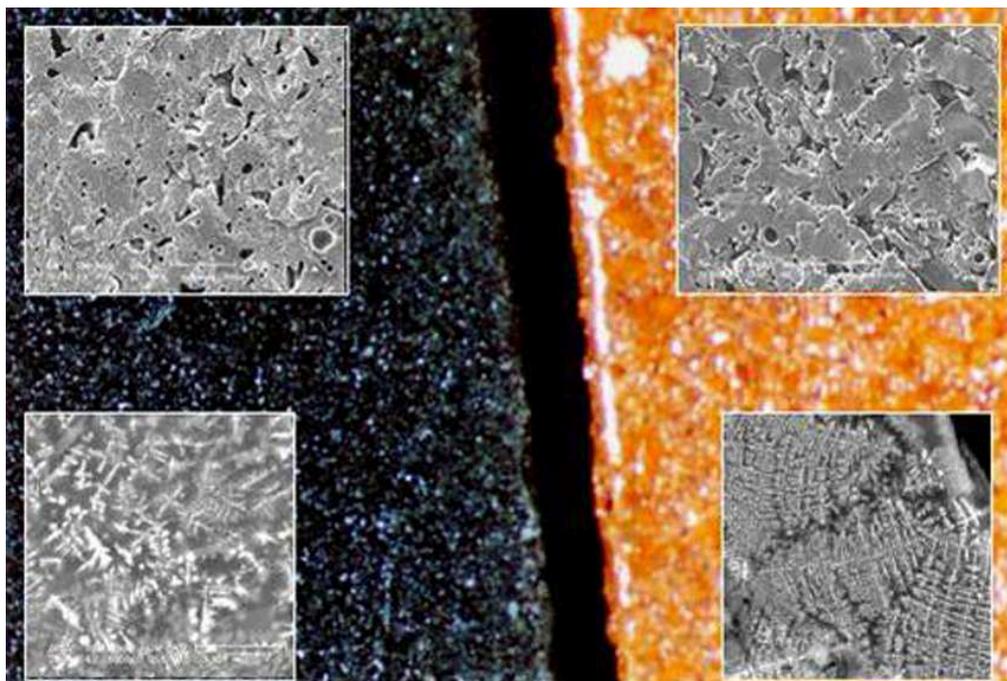


Fig. 4 Appearance and SEM images of *G-Goe* after sintering in N_2 (left) and air (right)

Notwithstanding of the lower sintering temperature the mechanical properties of **G-Goe** samples, sintered in nitrogen (Young modulus of 80 ± 4 GPa, bending strength of 122 ± 6 MPa and Vickers hardness of 6.8 GPa) are better than ones of the samples sintered in air (Young modulus of 77 ± 4 GPa, bending strength of 84 ± 9 MPa and Vickers hardness of 6.5 GPa). These positive results are consequence of the higher crystallinity and the finer crystalline structure.

3.4 Crystallization, sintering and structure of materials, obtained by frits sintering.

The technique of sinter-crystallization of glass granulates has been developed for the production of “Neoparies” in 1974 by “Nippon Electric Glass Co.” [7]. In the original Japanese material fractions between 1 and 7 mm are used and the sintering completes at $950-1000$ °C. The phase formation carries out at $1100-1120$ °C for 1-2 h and leads to a needle-like surface crystallization of ~ 40 % wollastonite ($\text{CaO} \cdot \text{SiO}_2$). As a result, the particles in the sintered tiles become well distinguished (especially after grinding and polishing), resulting in marble-like appearance coupled with good mechanical properties. At the moment hundreds of thousands of square meters of this luxury building materials are produced in Japan and China each year. In 1994 in the Institute of Physical Chemistry – Bulgarian Academy of Sciences was synthesized similar material with diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) surface crystallization [18] and for a first time worldwide was demonstrated that this method may be successfully used for inertization of industrial wastes [8,9].

However, in the iron-rich compositions, due to the spontaneous formation of magnetite in the bulk, surface crystallization is impossible. As a result when large fractions (i.e. $>1-2$ mm) are used the sintered samples have homogeneous unattractive black look. In this case, in order to obtain granite-like appearance another approach, based on the Fe^{2+} oxidation, was developed [10,14].

In the previous part it was elucidated that after sintering in air Fe^{2+} into Fe^{3+} oxidation takes place in the fine iron-rich glass powders, resulting in change of the colour from black into red; in addition, at higher temperatures hematite (Fe_2O_3) is also formed. At the same time, since the oxidation carries out only in a thin surface layer below $50-100$ μm [10, 19], the main crystal phases, formed in bigger grains, remain black magnetite (Fe_3O_4) and dark-green pyroxenes. Therefore, by mixing coarse fractions with fine glass powders in different proportions very attractive chromatic effects can be achieved after grinding and polishing. For example, the coarse particles can be obtained from fractions between 2 and 5 mm, while the fine– after milling of the remaining frits and sieving below $150-200$ μm .

Obviously, this technique can be applied when compositions with reduced crystallization trend and low liquids temperatures are used (i.e. as **G-Jar** and **G-Flo**). The sintering experiments with similar compositions show that the optimal heat-treatment is near the eutectic temperature of coarse fraction. Usually this temperature is lower than the liquids temperature of “oxidized” fine fraction and is similar to one of the fine fraction, treated in inert atmosphere (see Fig.3). Typically, the densification of the mixed fraction and the formation of sample with a smooth surface occur in the interval $990-1030$ °C for 20-30 min.

Notwithstanding of the lower production temperature and shorter thermal cycle the granite-like iron-rich glass-ceramics have higher bending strength ($60-70$ MPa) than the original Japanese material (50 MPa). The other characteristics (density of $2.9-3.1$ g/cm^3 , Young Modulus of $50-55$ GPa, Vickers hardness of $4-4.5$ GPa and thermal expansion of $6.5-7.0 \cdot 10^{-6}$ deg^{-1}) are similar to these of “Neoparies” (density of 2.7 g/cm^3 , Young Modulus of 80 GPa, Vickers hardness of 4.5 GPa and thermal expansion of $6.2 \cdot 10^{-6}$ deg^{-1}) and significantly surpass ones of the natural stones (bending strength of $15-25$ MPa, density of $2.4-2.8$ g/cm^3 , Young Modulus of $30-50$ GPa, Vickers hardness of $2-5$ GPa and thermal expansion of $7.0-15 \cdot 10^{-6}$ deg^{-1}) and the traditional tiling ceramics.

The phase composition and the resulting appearance, as well as the variations of properties depend on used composition and fractions. For examples, the main phases formed in **G-Jar** coarse particles are pyroxenes and magnetite, while in the powders, where the amount of crystal phase is lower, precipitate pyroxene and hematite. At the same time, the XRD spectra of **G-Flo** samples comprise wollastonite, pyroxene and hematite in the powders and pyroxenes and magnetite in the coarse particles; contrary to **G-Jar** in this composition the crystallinity is superior in powders.

The chromatic effect, due to the combination of fine and coarse fractions was studied by optical microscopy. Fig. 5 presents the appearance of a *G-Goe* sample and the structure of a *G-Flo* specimen, where the red areas of sintered powders, as well as the coarse black particles are well distinguished.

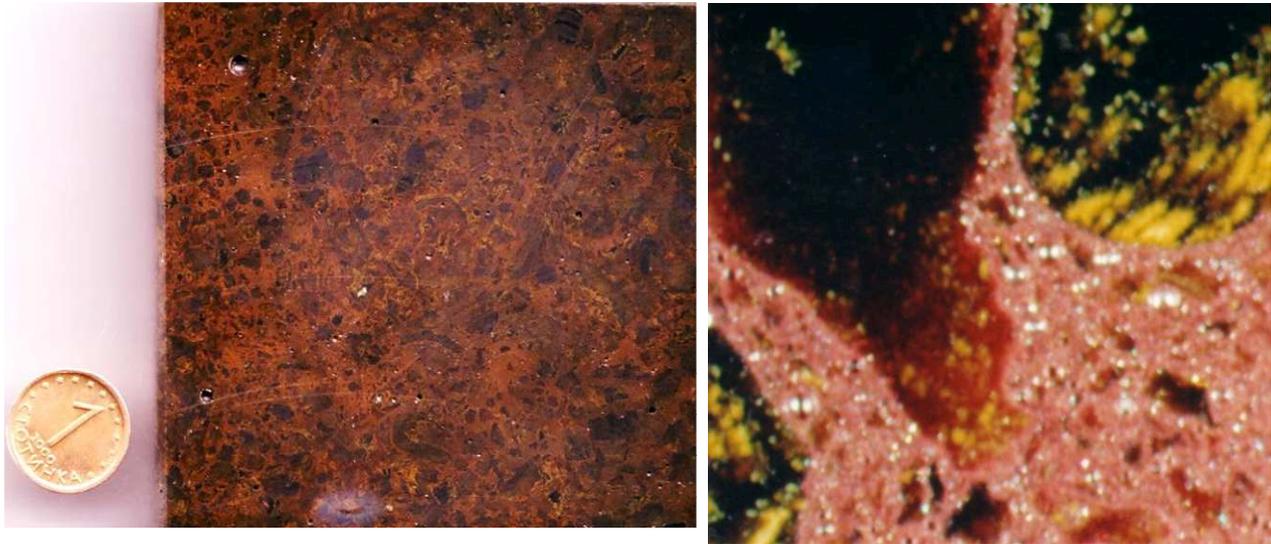


Fig. 5 Appearance and structure of granite-like iron-rich glass-ceramics

Conclusions

The sinter-crystallization methods are very suitable for synthesis of glass-ceramics from vitrified hazardous iron-rich industrial wastes.

In compositions with low crystallization trend the sintering of pressed glass powders completes before the crystallization but the samples are characterised with moderate mechanical properties. However, similar glasses can be used to obtain high quality granite-like panels by mixing fine and coarse fractions, “free” sintering in refractory moulds and subsequent grinding and polishing. In this case, pleasurable chromatic effect is obtained due to combination of red-brown hematite in the oxidised fine fraction and green-black pyroxene and black magnetite in the non-oxidised coarse particles. The obtained building glass-ceramics are characterised with mechanical properties which are 2-3 times higher than ones of the natural stones and traditional ceramics.

When the compositions are characterised with a higher crystallisation trend and formation of 50-70 wt % crystal phase samples by pressed powders can be obtained after a secondary sintering near the liquids temperatures. By heat-treatment in inert atmospheres, due to absence of Fe^{2+} oxidation and lower viscosity, the sinter-crystallization carries out at inferior temperatures. Nevertheless, due to formation of higher amount of crystal phase and finer crystalline structure, the mechanical properties increase, reaching Young modulus of 80 GPa, bending strength of 120 MPa and Vickers hardness of 6.8 GPa.

In the case of spontaneous crystallization the densification remains inhibited even at high temperatures and the sinter-crystallization methods are unappropriated.

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