Chapter

Sintered Iron-Rich Glass-Ceramics and Foams Obtained in Air and Argon

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Abstract

The subsequent synthesis of sintered self-glazed glass-ceramics and/or glass-ceramic foams using metallurgical slag is the topic under discussion. The observed intensive sample expansion can be considered as an autocatalytic process related to the oxygen release due to thermal reduction of Fe$_2$O$_3$ and MnO$_2$ present in the slag. The sintering of the samples is studied by optical dilatometry and the foaming process by hot-stage microscopy, while the structure of the final materials is revealed by 3-D computed tomography and SEM. The phase composition of the glass-ceramic foams is analyzed by XRD. The species are characterized by moderate crystallinity, 80–85 vol.% porosity and fire resistance above 1000°C. The innovative point of this study is the synthesis in argon of sintered glass-ceramic materials where reduction is inhibited, together with a double-stage foam formation in air and argon, leading to lower working temperatures and better material characteristics.

Keywords: industrial waste, glass-ceramics, sintering, foaming

1. Introduction

The development of methods and technologies for the production of glass-ceramic materials and foams, as a particular case of glass-ceramics, has recently revealed an interesting economically grounded field for research in the synthesis of advanced materials with unique properties for application in the civil engineering and in a variety of different industries.

Many industrial streams in the metallurgy provide large amounts of waste raw materials, e.g., in the form of slag, containing the necessary composition making it suitable to be entirely recycled with just minor modifications into new glass-ceramic materials via melting and a subsequent sinter-crystallization treatment [1, 2]. This is especially appropriate when speaking of large-scale production projects.

The most significant producers of iron-rich waste are the iron and steel industries. The different final products (e.g., steel or cast iron) and the different processes used determine the variations in the waste material composition [1]. Blast furnace slag (BF) is easier to be converted to a glass and further to glass-ceramics [3] than the other slags due to the high content of silica and alumina. Other slags like the basic oxygen furnace slag (BOF) and electric arc furnace slag (EAF) are on
the contrary more enriched in iron oxides but far more poor in glass formers. They can be used after a certain composition modification [4]. Zinc hydrometallurgy turns out to be another important source of iron-rich waste raw material. Most recent research refers to iron-rich waste from the nonferrous metallurgy [5, 6].

Recent developments in the field of thermal analytical methods and instrumentation result constantly in cutting-edge machines providing faster and far more reliable laboratory measurements. In particular the high-temperature imaging systems like modern optical dilatometers (ODLT) allow in situ contactless observations of the sintering shrinkage during the synthesis of ceramics and glass-ceramics and technology development on a laboratory scale as well. Among the most significant physical parameters governing the technology of sintered glass-ceramic production are the firing temperatures, the thermal treatment rates, the thermal regimes governing the viscosity of the forming material and, as it turns out, the used atmosphere (air or inert).

An innovative part of the presented research is the synthesis in a dual air/argon environment. The authors have initiated pioneering research in this field of glass-ceramic synthesis starting in the year 2000 with some experimentation with air and inert nitrogen atmosphere [7-9] and a further development recently (started 2017) by N.B. Jordanov and A. Karamanov with argon and dual air/argon atmosphere. This development allows currently the process of synthesis of glass-ceramic samples to be separated and carried out in different stages of controlled environment, thus allowing the effect of redox determined processes to be carefully studied, understood and implemented in the design of new materials. At the same time, the crystallinity of thus obtained materials is considered higher, leading to better properties [1, 10].

The influence of the atmosphere in the particular case of foaming in inert environment of sintered iron-rich pressed powder samples however has not been examined yet and is currently the subject of profound investigations.

The overall theoretical description of effective mechanical properties and structure of cellular solid foam materials was considered and proposed first by Gibson and Ashby in 1982 [11] in terms of their famous original equations.

The theoretic development of Gibson and Ashby on the closed-cell foams however is based generally speaking on the presence of regular shape and size (e.g., cubic or hexagonal) of the closed cells determining the foams. When the case is foam of irregular structure, arbitrary shape and broad cell volume distribution, then the method of 3-D computed tomography is very helpful toward the description and characterization of cellular materials [12, 13].

In the case of cellular solid mechanics, Gibson and Ashby provide equations of the effective Young modulus of foams of closed porosity based on wide experimental data. Here the 3-D computed tomography aid is highly welcome. Actually a certain restriction here is the assumption that all closed cells are filled with a fluid. In the particular case of iron-rich glass-ceramic foams however, the inner cellular space is filled with gas. If one assumes that the pressure inside the cells is comparable to the atmospheric pressure, we can write the following equation of Young modulus [14]:

\[
\frac{E^*}{E_V} = C_1 \varphi^2 \left( \frac{\rho^*}{\rho_V} \right) + C_2 (1 - \varphi) \frac{\rho^*}{\rho_V} \tag{1}
\]

where \( E^* \) is the effective modulus of the foam, \( E_V \) is the volume modulus, \( \varphi \) is the ratio of cell edge to the whole solid part, \( \rho^* \) is the effective density of the foam, \( \rho_V \) is the volume density, and \( C_1 \) and \( C_2 \) are geometry shape constants.

The successful synthesis in the presented investigation of glass-ceramic foams from simultaneously iron-rich and manganese-rich waste slag is crucially
determined besides by the thermal treatment, by the redox couple ratio equilibria of Fe(II) ↔ Fe(III) and Mn(III) ↔ Mn(IV) [15]. The state of these redox couples is of greatest importance since it is entirely responsible for the foaming process to proceed successfully. The latter is being realized by the release of gas molecules in the bulk of the sample in the form of oxygen microbubbles determining the porosity. This is possible due to the reversible thermal partial reduction of the manganese and iron oxides of higher oxidation state into lower states, taking place during thermal foam formation. This process is vastly influenced by the environment. Recently it has been shown by the authors and other research teams as well that not only carrying out the thermal synthesis in atmospheric air but also separating the synthesis to subsequent stages in air and in inert gas environment (e.g., argon) can lead to very surprising results. Materials with different structure and properties could be thus obtained. The conditions of synthesis are also technologically favored this way using different environments.

Having already synthesized the sintered glass-ceramic material with appropriately formulated composition, one has obtained a partially crystalline and densified final product with more than satisfactory industrial features obtained at economically favorable conditions (compared to the expensive production of classic ceramic materials). Thus obtained materials from iron-rich industrial slag are ready for implementation in a number of engineering projects as well. They can be (and are actually ready to be) however further processed in terms of just a well-engineered additional thermal exposure scan at temperatures generally speaking higher than the temperature of sintering. This can be realized either isothermally or by a linear thermal scan.

The use of the novel applied method of sinter-crystallization developed experimentally in the last two decades and still being subject to theoretical progress can lead to very promising results mainly due to the relatively moderate treatment temperatures required for simultaneous sintering and crystallization of the samples. Just for the reference of the reader, the foaming process is taking place at higher temperatures after completion of the sintering and the phase formation. Glass-ceramic foams are a particular case of the general division of the so-called cellular glasses possessing high surface area, low density, low specific heat, high thermal and acoustic insulation and high chemical resistance [10]. When most of the cells are closed, the material is referred as foam.

The synthesis of sintered glass-ceramics depends on the relationship between viscous flow sintering and crystallization, while the production of glass-ceramic foams depends on the balance between apparent viscous flow sintering and gas evolution [1].

The gas release usually depends on the oxidation or decomposition reactions with the modifying compounds in glass-ceramic foaming. Oxidation reactions are associated with the release of CO$_x$ gas from carbon-containing compounds like carbon black, graphite, silicon carbide (SiC) and organics reacting with the oxygen in the atmosphere. Typical decomposition reactions are such with carbonates or sulfates leading to the release of CO$_2$ or SO$_x$ [1, 10]. A special case is when the parent glass contains intermediate oxides (called conditional glass formers) either iron oxides or manganese oxides undergoing transition from higher to lower oxidation state, connected to the release of oxygen gas. This is the actual case here which is the subject of investigation in the presented research.

So the production of glass-ceramics from iron-rich metallurgical slag can be terminated at the stage of obtaining just well-sintered glass-ceramics and extended any time further to the stage of glass-ceramic foams (in the particular case of, e.g., iron-rich parent frit).
2. Sinter crystallization and foaming

The sintering of glass-ceramics is a typical example of induced structural densification of a solid sample. The latter is provoked by volume-density variations in the material’s bulk. This is the first step (besides an eventual parallel oxidation process) taking place during new glass-ceramic material formation determined by, e.g., a linear thermal scan. The degree of densification is one of the most important characteristics of sintered glass-ceramics. It is being mainly determined to a great extent by the granulometric composition, the crystallization ability (the crystallization trend) of the parent glass and the rate of heating of the compressed powder sample. At an elevated crystallization trend, the sintering could be blocked because the higher the crystallization trend, the lower the sinter ability and vice versa, respectively. It is well known that the sinterability of a glass-ceramic powder can be significantly improved by using finer glass fractions and/or higher constant linear heating rates [1, 10].

One can thus make the conclusion (and this is actually the case!) that both processes should be carefully balanced in order for a really good material with increased indicators to be successfully produced. This means that both extreme cases of a minimal or a maximal crystallization of the glass-ceramics should be avoided. The crystalline structure determines the stability and durability of the material. On the contrary, a species with higher crystallinity however cannot be sintered.

In the framework of current state of knowledge, it is assumed that both processes of sintering and crystallization are taking place in the same temperature interval. For the sake of a theoretical description however, it is accepted that the sintering stage precedes the crystallization stage. In fact the sintering stops after formation of a critical percentage of crystal phases.

Of crucial importance here is the apparent viscosity of the glass-ceramics. Its value should be maintained in a range, such that the expansion of the structure is possible and the formation and the propagation of open porosity are temporarily unavailable.

The foaming in the studied case is determined by the formation and distribution of a closed porosity population in the bulk of the material due to the release of gas molecules (most often oxygen) during the high-temperature partial reduction of certain oxides from higher to lower oxidation state. These are most often the iron [16] and the manganese [15] oxides. The high-temperature interval of foaming indicates that the mechanism of gas formation is directly related to the oxygen release as a result of the reversible partial Fe(III) and Mn(IV) reduction [15–19]. Moreover when the oxides of the iron and the manganese are naturally present in a sufficient amount in the parent glass frit, this is the most favorable case because there is no need for the process of foaming to be artificially and additionally catalyzed. An inorganic material is thus being formed by autocatalytic foaming.

3. Experimental

For the purpose of current experimentation with sintered materials and foams, a slag from the iron and steel company Helwan, Cairo Governorate, Egypt (with a slag production capacity of 30 kt p.a.), was used for the synthesis of the investigated samples.

This slag is relatively poor in glass formers (SiO₂ and Al₂O₃); that’s why it had to be enriched in silica by mixing 70 wt.% slag and 30 wt.% industrial sand. The
parent batch of 150 g was brought to melting in corundum crucibles using an electric furnace. After an exposure for 2 hours at a temperature of 1450°C, the resulting homogenous melt was quenched in water, and a dark brown-colored glass frit was obtained. Thus obtained glass frit was crushed, grinded several times in a planetary mill FRITSCH (Germany) for 10 minutes and sieved below 75 μm with a digitally programmed sieving machine CISA (Spain).

The investigations were performed by a thermal-optical measuring and imaging system with an ESS HSM-1400 MISURA (Italy). This instrument combines two techniques: a high-precision, high-resolution horizontal contactless optical dilatometer and a hot-stage microscope (HSM). This is an established laboratory method in recent years, since it turns out to be reliable and fast and is used already by many research groups worldwide [2, 20].

The sintering behavior of all glass-ceramic samples was investigated by means of ODLT, a method which allows measurements with very high precision. This is mainly due to the absence of a mechanical push rod in the system, as it is the case with classical contact dilatometer devices. A monochrome optical arrangement employing two video cameras providing high magnification and high resolution is used instead. Typical measurements were performed with holding times of 30 minutes at 950°C in air or argon.

To the sintered glass powder, a small amount of 7 wt.% polyvinyl alcohol (PVA) aqueous solution was added to form a granular mass, which then is mechanically homogenized and placed in a matrix of 50 × 5 × 3 mm. Multiple samples of equal forming are prepared by stuffing loosely the material in a pressing matrix. Then by applying uniaxial pressure at 40 MPa in a hydraulic pressing machine NANNETTI (Italy), samples of almost perfectly equal dimensions and densities, with an increased green strength and a decreased porosity, are produced.

Subsequently a burnout step at 270°C is required to be carried out before proceeding further with the heat treatment processes in order to remove the binding agent (e.g., PVA). The burnout can be performed in ODLT separately or as an initial programmed step preceding the oxidation, sintering and foaming steps.

The studied thermal behavior in the range up to 1300°C in air and argon of the sintered samples was studied and analyzed by the optical HSM method. As far as the samples used for ODLT measurements have a standard parallelepiped shape (as described above), the samples used for HSM measurements are not the same but represent upright standard cylinders instead.

In addition the foaming trends of the samples were examined by carrying out measurements both isothermally with holding times of 30 minutes (e.g., at 950°C for simultaneous oxidation and sintering and at 1100°C for foaming initiation) and non-isothermally as well (by using constant linear thermal scans). Typically such thermal scans were used with heating rates of 20°C min⁻¹.

During all measurements the ODLT/HSM instrument was mounted in a closed aluminum box (developed and manufactured at the mechanical workshop of IPC-BAS Sofia), allowing measurements in a controlled environment. The box can be purged with dry argon gas on demand. The latter application allows continuous maintenance of an overpressure of ~10 mbar argon to be kept over the entire synthesis and optical measurement of the thermal variation of the structure of the sample. This is achieved by the use of a fine-graded rotameter, Yokogawa (Japan), for manual control of the gas flux in the sample chamber and a high-precision digital manometer with a ceramic membrane, Profimess (Germany), for overall gas pressure monitoring.

According to the current state of knowledge of the authors, such a laboratory experimental setup—a combined ODLT/HSM mounted in a closed vessel for examinations of the sintering and foaming behavior of iron-rich glass-ceramics in
different atmospheres—is unique in Southeastern Europe and even was probably used for the first time in this respect here.

Scanning electron microscopy (SEM) was used to analyze the structure of the sintered glass-ceramics by taking pictures of both fractures and the surfaces of the samples. A JEOL 6390 (Japan) instrument was used. To provide electron conductivity, all samples were metalized with gold by vapor deposition technique.

3-D computed micro-tomography was used for entire bulk scanning of the foam glass-ceramic species. The tomographic measurements were carried out with an X-ray micro-tomograph, Bruker SKYSCAN 1272 (Germany), which uses a white beam with cone geometry. The following setup conditions were applied: X-ray tube voltage 70 kV, current 142 mA and 0.11 mm Cu filter. The voxel (3-D pixel) size was 1 μm and the optical magnification was 7.4. A typical 360° scan took 21 hours and 27 minutes. Reconstruction of the 3-D images was done with the commercial software InstaRecon.

The phase composition of the sintered glass-ceramic foams was determined by X-ray diffraction spectroscopy (XRD) using a Panalytical Empyrean (USA) spectrometer.

4. Summary of results and discussion

As we have already noted, the innovative point of current research is, besides the use of the applied method of sinter-crystallization toward the production of sintered glass-ceramics and/or glass-ceramic foams, the use of a controlled environment during the synthesis of sintered glass-ceramics and in particular extended to the design and production of glass-ceramic foams.

In Figure 1, a comparative graphical representation is presented, together with images at respective temperatures of interest, of the shape alteration during real-time in situ filming of two samples being synthesized in air or in argon atmosphere.

Up to temperatures of about 1050°C, the thermal behavior of both species is quite comparable. Both samples undergo similar densification during the interval of low temperature sintering. At higher temperatures however, iron-rich glass-ceramic materials heated up in different (air or inert) atmosphere reveal a completely different thermal behavior compared to each other when they are subject to a subsequent thermal treatment.

In the case of an argon-sintered sample, further heating of the material leads to sample melting (to, e.g., a hemispheric spill at 1155°C). However, the sample sintered in air starts expanding its volume during heat treatment above 1050°C, and at the same reference temperature of 1155°C, it reveals a maximal value of the structural expansion determined by gas evolution—the foaming in the entire bulk of the newly formed material. This difference in the thermal behavior of both samples is mainly due to differences in the respective material’s viscosity values.

The phenomena described above are entirely determined by the state of the redox couple equilibrium Fe(II) ↔ Fe(III) in a sense that an inert environment (e.g., argon) is going to maintain the equilibrium drawn at a maximal extent to the left (oxidation is inhibited [9]), while the air atmosphere is going to keep the ratio Fe(II)/Fe(III) at a minimal value, i.e., the equilibrium is drawn to the right.

In Figure 2a, the sintering curves are presented during an isothermal scan and the respective low temperature behavior of the glass-ceramic samples in air and argon. One can clearly and unambiguously note the effect of the environment on sintering: the onset of the sintering process in argon is shifted to lower temperatures. It starts earlier, and the degree of structural densification is to a certain extent higher than the one in air (14 vs. 12% shrinkage, c.f. again Figure 2a). The shaded area in Figure 2a represents actually the area of temperatures where the glass
transition point, $T_g$, which is the most important physical characteristic of a glass, is to be observed.

In Figure 2a, the shaded area reveals in fact, as it is obvious in Figure 2b, that an ODLT measurement represents certainly a method for truly reliable measurements of the temperature of vitrification, $T_g$, of pressed powder objects as well. It is evident that the glass transition point of the sample sintered in argon is significantly diminished and the difference in $T_g$ between glass-ceramics synthesized in air and argon amounts to $\Delta T = 20^\circ C$.

One can thus summarize that utilizing the ODLT technique for the sake of synthesis of well-sintered glass-ceramic materials is a good approach. It also reveals the possibility for reliable measurements of $T_g$, due to its high precision as a result of lack of mechanical parts, and for exact tuning of the appropriate firing regimes.

XRD spectra of the glass-ceramic foams obtained in air and argon environment are presented in Figure 3. The phase analysis of the samples results in the detection
of pyroxene crystal phases. The crystallinity of the samples is between 30 and 40% as referred also by Strnad [21]. The crystallinity in argon however is higher than that in air. A shift of the peak positions in air to lower theta angles has been observed as well.

The two features described above confirm that the absence of oxidation in argon environment leads unambiguously to higher crystallinity and to some differences in the chemical composition of the pyroxene phases. These differences can hypothetically be due to the facilitated entering of the Fe(II) and Mn(III) ions in the pyroxene structures. Also a change in the lattice interplanar distance is present.

In order for the microstructure of the sintered glass-ceramic species subject to current investigation to be studied, a series of scanning electron microscope images of two sintered glass-ceramic samples are shown in Figure 4. Images have been taken from the surface and from a fracture of both species. Figure 4a and c represents photos of the surface of the air-sintered sample; Figure 4b and d is from the surface of the argon-sintered sample; Figure 4e, g and h is images from a fracture of the air-sintered sample; and Figure 4f is a picture of a fracture of the argon-sintered sample.
Despite the well overall sintering in both atmospheres, it has been found that in argon environment an even better sintering of the sample than that in air is present.
An interesting observation is that on the surface of the argon-sintered glass-ceramics (Figure 4b), the pores reveal a concave morphology. This might be an indication for the formation of these pores in the interval of softening which initiates together with the beginning of the process of high-temperature reduction as well. In both cases of sintering, a large population of small spherical holes on the surface is present, which is almost a certain indication for gas release.

In both cases of sintering, a non-spherical, sharp-edge intergranular porosity is predominant.

The proposed possibility for a selective environment of synthesis of sintered glass-ceramics and glass-ceramic foams provides the option of the synthesis to be carried out and thus to be experimented by using different stages.

Thus after a low temperature sintering stage in air (e.g., see Figure 1), the process of foaming of a pressed glass sample can be carried out in a second stage.
entirely in argon environment. The process of foaming of this sample traced by a HSM measurement is shown in Figure 5. The snapshots in Figure 5 during the run of a thermal scan represent the evolution of structural alteration at characteristic temperatures.

In order for the effect of the atmosphere on the foaming of sintered glass-ceramics to be carefully analyzed, a graphical plot of the structural evolution during foaming in different atmospheres is given in Figure 6. The plot in the expansion-time domain of foaming in air and argon during an isothermal scan at a temperature of 1100°C with 30 minutes holding time (Figure 6) provides a clear and detailed picture on the process under consideration.

The expansion of the structure due to the release of oxygen gas and formation of the closed-cell system during high-temperature reduction initiates in both environments (air and inert) in a similar way and almost at the same time as well. The process of foaming in argon however turns to be more effective. The bloating of the material reaches a maximal value of nearly 200%, considerably earlier than the maximal foaming in air (up to 190%); then after a slight volume shrinkage, a stable material with 180% expanded structure is being formed and maintained in the course of the working isotherm.

The entire foam material formation (i.e., the formation of closed porosity population) proceeds relatively quickly with the programmed isotherm in Figure 6. The foaming in argon takes ~5 minutes to complete followed by a small shrinkage and a structural stabilization. The foaming in air takes longer time to complete than argon (15 minutes) and reaches stabilization again. The foam material formation in air and argon atmospheres results in obtaining a new material characterized in both cases generally with fire resistance properties at temperatures of 1100°C.

For the sake of investigation of the entire bulk structure of the newly formed foam material, 3-D X-ray tomographic analysis has been used. In Figure 7a (left), a false-color 3-D reconstruction of the surface is presented and the volume by tomographic scanning of an iron-rich glass-ceramic foam sample synthesized in air. In Figure 7a (right), a selection of three cross sections of the bulk of the same sample is presented. In Figure 7b (left), similar 3-D false-color surface-volume reconstruction of a glass-ceramic foam sample synthesized in argon is presented. In Figure 7b (right), cross-section slices of the material’s bulk are shown, respectively.

![Figure 6](image.png)

*Figure 6.* Temporal evolution of foaming curves in air and argon of sintered glass-ceramic samples.
From visual observations and the performed analysis, one can clearly note that the porosity in the bulk of both samples is predominantly of closed type and amounts to about 80–85% in both species. It is also evident that the walls of the samples are abundant of pores. Another interesting feature is that the closed cells of the species foamed in air are larger than the cells in the volume of the sample foamed in argon. Moreover the thickness of the walls in the sample synthesized in air is on average lower than the wall thickness in the glass-ceramic foam material obtained in argon environment.

5. Conclusions

In current investigation the authors have shown the possibility for carrying out successful synthesis depending on the temperature and the applied atmosphere of well-sintered glass-ceramics and/or glass-ceramic foams.

It was shown that synthesis in inert environment leads to the production of materials with higher degree of sintering.

If properly engineered, the practice and experience show that a glassy-crystalline material with low density and high porosity of about 80% can be obtained, which can be considered as more than a satisfactory result [1, 22]. In addition thus obtained foams are characterized by fire resistance features up to 1100°C as well.

By applying a double-stage heat treatment, first stage, low temperature sintering at 950°C, and second stage, foaming at 1100°C, foam materials with improved properties and differences in the structure have been successfully obtained.

The SEM images from the fractures of both glass-ceramic foam species reveal a well-sintered material. They show a good degree of sintering and total porosity below 10–15%.

Figure 7. X-ray computed tomography, (a) 3-D reconstruction of the surface and the bulk of a glass-ceramic foam synthesized in air (left); volume cross sections (right), and (b) 3-D reconstruction of the surface and the bulk of a glass-ceramic foam synthesized in argon (left); volume cross sections (right).
Inorganic materials obtained by thermal foaming like these subjects of current investigation can be used as modern building materials, as construction materials and as insulation materials in various fields and industries, e.g., as panels or arbitrary shaped.

Inorganic glassy-crystalline foam materials can be considered generally speaking as low-cost thermal insulating, soundproof and fire-resisting low-weight materials.

Acknowledgements

N.B. Jordanov gratefully acknowledges the financial support of the National Program Young Scientists and Post-docs of the Ministry of Education and Science of Republic of Bulgaria under the project “Sintered self-glazed glass-ceramics and foams from iron-rich industrial wastes.” D. Tatchev and A. Karamanov express their gratitude for the support of Project BG05M2OP001-1.002-0019: “Clean technologies for sustainable environment—waters, waste, energy for circular economy.” All authors are thankful for the financial support for realization of the closed experimental setup for measurements in a dual environment of the Bulgarian Science Fund (FNI) under Project DN 19/7 “Theory and application of sinter-crystallization.”

Conflict of interest

The authors declare no conflict of interest.

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