

DEVELOPMENT OF LOW COST GLASS-CERAMIC BASED ON BLAST FURNACE SLAG AND GRANITE ROCK

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The development of low cost glass-ceramic based on various contents of Egyptian blast furnace slag and granite rock has been investigated. The effect of granite / slag replacements on the crystallization characteristics of the glasses and the resulting microstructure, are traced by differential thermal analysis (DTA), x-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Varieties of melilite phase of gehlenite type, wollastonite solid solution and anorthitic plagioclase phases were mostly formed depending on the granite/slag ratios in the glasses. The types of the crystallized phases formed are discussed in relation to the compositional variation of the glasses and thermal treatment applied. SEM micrographs showed that granite/slag replacement promoted a uniform volume crystallization of fine-grained interlocked microstructure, which is achieved by increasing the granite content in the glasses. The addition of LiF as nucleation catalyst enhanced the crystallization characteristics of the glasses. The increase of granite at the expense of slag in the glasses led to improve both the thermal expansion characteristics and the chemical durability of the materials investigated.

INTRODUCTION

In general, glass-ceramics may be defined as polycrystalline solids produced by controlled crystallization of glasses [1]. Slag-based glass-ceramic materials are different in resulting properties than those prepared from elemental technical grade oxide powders. The primary difference is that slag-based glass-ceramic materials are multicomponent systems to start with, whereas glass-ceramics developed from elemental powders are made multicomponent by choice for the purpose of tailoring resulting properties.

Slag is an industrial solid waste generated in the process of iron ore reduction in blast furnace which represent one of the many types of wastes resulting from the industrial metallurgical processes. The major amount of slag produced in Egypt at a rate of 300 000 tons/year is being used as a raw material for the cement industry and in road pavement. The rest is directly discharged in landfills, which consequently can cause environmental problems. So reducing the environmental impact of slag, scrap and dust resulting from iron and steel product will give its product further important benefit and other significant potential for cost savings profit if reintroduced into the industrial process through well planned programs [2]. Knowledge of the atomic scale structure of slags is essentially required in order to discuss various properties of slags [3-4].

Granite is widely distributed in Egypt and occurs in large deposits at Aswan, in the Eastern desert, the Sinai and to a smaller extent in the Western desert. In the

Aswan region the granite deposits consists of both the monumental red and monumental black varieties. The term granite applies to any holocrystalline quartz-bearing plutonic rock, in which quartz makes up 10 to 50 % of the felsic components, the alkali feldspar/total feldspar ratio is between 65 to 90 %, and the modal concentration of mafic minerals is less than 10 % (hornblende, biotite). Grain size of the minerals components generally range from 1 millimeter to many centimeters [5].

Due to the high cost of some of the chemical ingredients e.g. Li_2O , B_2O_3 , Al_2O_3 etc., and the high melting temperatures or special melting conditions, glass-ceramics are relatively expensive materials. The motivation for developing glass-ceramics from metallurgical slags together with granite rock as a raw material instead of using technical grade powders stems from the fact that cheaper production costs would allow higher profits in practical applications such as wall claddings and floor tiles [6].

Glass-ceramic materials have a number of outstanding characteristics in comparison with the traditional ceramics and glasses, which determine their application in advanced technology as well as in electronics and medicine [7].

The aim of the present work is to develop some types of glasses and glass-ceramics based on blast furnace slag - granite rock mixtures and to study their crystallization behaviour, microstructure, and phase relation as well as the thermal expansion and chemical durability of the materials.

EXPERIMENTAL

Local granulated blast furnace slag of the Egyptian Iron and Steel Company and Aswan granite, at Upper Egypt were the main starting materials used in this study. The chemical compositions of slag and granite were chemically analyzed [8]. After drying and pulverizing steps, the slag had the following chemical composition (in wt.%): 34.15 % SiO₂, 46.13 % CaO, 11.33 % Al₂O₃, 2.28 % MgO, 1.10 % MnO₂, 1.65 % Fe₂O₃, 0.84 % FeO, 0.88 % Na₂O, 0.11 % K₂O, 0.09 % P₂O₅, 1.47 % S.

Aswan granite rock had the following chemical composition (in wt.%): 69.91 % SiO₂, 1.91 % CaO, 14.66 % Al₂O₃, 1.40 % MgO, 1.6 % FeO, 0.6 % Fe₂O₃, 3.06 % Na₂O, 6.08 % K₂O, 0.78 % TiO₂. The amount of Fe²⁺/Fe³⁺ was determined by calorimetric analysis [9]. LiF was added in amount of 3 g over 100 g glass oxide constitutions of the batch compositions as a nucleating agent. Details of the batch compositions of the prepared glasses are given in table 1.

The weighed batches were thoroughly mixed and were melted in Pt-2%Rh crucible in an electric heating furnace, with SiC heating elements, at 1400-1450°C for 3 hours duration with occasional stirring to ensure homogeneity. The homogeneous bubble-free melts were cast into rectangular rods (0.5 × 0.5 cm cross section and 1.5 cm length), and as buttons, which were then well annealed at 600°C in a muffle furnace to minimize the strain of the glasses.

The thermal behaviour of the finely powdered (45-75 μm) glass samples was examined using a SETARAM Labsys TMTG-DSC16. The powdered glass was heated in Pt-holder against another Pt-holder containing Al₂O₃ as a reference material. A uniform heating rate of 10°C/min was adopted. Data were recorded using a computer-driven data acquisition system. The results obtained were used as a guide for determining

the required heat-treatment temperatures applied to induce crystallization of the glasses.

The progress of crystallization in the glasses was followed by using double stage heat-treatment regimes. The glasses were first heated according to the DTA results at the endothermic peak temperature for 5 h, which was followed by another thermal treatment at the exothermic peak temperature for 10 h.

Crystal phases were identified by the x-ray diffraction (XRD) analysis using a Philips type diffractometer (P.W. 1730) with Ni-filtered Cu-Kα radiation. The crystallization characteristics and internal microstructures of the resultant materials were examined by using scanning electron microscopy (SEM), where representative electron micrographs were obtained using Jeol, JXA-840 A Electron Probe Microanalyzer.

The thermal expansion characteristics of the investigated glasses and glass-ceramics were carried out on (0.5 × 0.5 cm cross section and 1.5 cm length) rods using a Linseis L76/1250 automatic recording multiplier dilatometer with a heating rate of 5°C/min. The coefficients of thermal expansion (α-values) of the investigated glasses were measured from room temperature up to 300°C while the glass-ceramics were measured up to 600°C. The linear thermal expansion coefficient (α) was automatically calculated using the general equation:

$$\alpha = (\Delta L/L) \times (1/\Delta T) \quad (1)$$

where (ΔL) is the increase in length, (ΔT) is the temperature interval over which the sample is heated and (L) is the original length of the specimen.

The chemical durability of the glass-ceramics in acidic medium was determined. The samples were crushed in an agate mortar and then sieved using BS sieves to obtain the fraction with granulation range 0.32 mm 0.63 mm. The grains were washed several times with ether, dried at 110°C for 2 hrs and then transferred to weighing bottles and cooled in a desiccator.

Table 1. Composition of the glasses (wt.%).

oxides	G ₁		G ₂		G ₃		G ₄	
	slag 80	granite 20	slag 60	granite 40	slag 50	granite 50	slag 40	granite 60
SiO ₂	41.3		48.45		52.04		55.61	
CaO	37.28		28.44		24.02		19.60	
Al ₂ O ₃	11.99		12.66		12.99		13.33	
Fe ₂ O ₃	1.44		1.23		1.13		1.02	
FeO	1.00		1.15		1.22		1.30	
MgO	2.1		1.93		1.84		1.75	
MnO ₂	0.86		0.65		0.54		0.43	
Na ₂ O	1.32		1.75		1.98		2.19	
K ₂ O	1.31		2.50		3.10		3.69	
P ₂ O ₅	0.07		0.05		0.04		0.03	
S	1.17		0.88		0.71		0.58	
TiO ₂	0.16		0.31		0.39		0.47	
granite/slag ratio	0.25		0.67		1.0		1.5	

One gram of the sample grains was accurately weighed in a G_4 -sintered glass crucible and then placed in a 400 ml polyethylene beaker. The sample was subjected to the static action of 200 ml of 0.1N HCl for 1, 3 and 7 hrs at 95°C using a contact thermometer water bath. The polyethylene beaker with its content was covered by a polyethylene cover to reduce evaporation. The volume of the leaching solution was made large enough relative to the weight of the sample grains in order to avoid formation of saturated solutions, which might prevent further leaching of grains. The reproducibility of the results for representative duplicate samples was better than 5 %. The percentage weight loss was taken as a measure of the relative magnitude of the leaching rate.

RESULTS

The DTA data of the glasses (figure 1) showed endothermic peaks in the 730-750°C temperature range. These endothermic peaks are to be attributed to the nucleation processes, at which the atoms begin to arrange themselves in preliminary structural elements subsequent to crystallization. Two exothermic peaks are detected in each glass, indicating crystallization reaction in the glasses. However, the heat-treatment was carried out using the higher exothermic peak temperature to attain the most stable phases in the crystalline glasses (G_1 - G_4).

The progress of crystallization in the glasses, the type and proportions of the crystalline phases formed were markedly dependent on the variation of the granite/slag ratios in the glass and the effect of thermal treatment as well as the role of the nucleating agent added.

The DTA data (figure 1) revealed that the endothermic dips as well as the onset of crystallization were shifted to higher temperature values with increasing the granite contents in the glass at the expense of the slag.

SEM micrographs of fracture surfaces of selected crystalline samples C_1 and C_4 demonstrate the effect of increasing granite content at the expense of slag on the microstructure formed. Granite promoted volume crystallization of the glass to form holocrystalline mass without deformation by thermal treatment. For example SEM micrograph of C_1 (with 20 % granite) clearly showed that numerous aggregates of crystals were formed (figure 2). However, at 60 % granite, C_4 , fine interlocked growths was formed giving rise to network-like microstructure (figure 3).

The phases developed in glass-ceramics (C_1 - C_4) over the investigated 980-1030°C temperature range as indicated by the X-ray diffraction analysis (figure 4) were melilite phase of gehlenite type, anorthitic plagioclase phase and wollastonite solid solution.

At low granite / slag ratio (0.25) i.e., G_1 heated at 730°C/5 h - 980°C/10 h led to the formation of melilite of gehlenite- $Ca_2Al_2SiO_7$ type (lines 5.07, 3.72, 3.47, 2.86, 2.40..., PDF No. 20-199) [10] as well as wollastonite ss phase (pattern I). The XRD analysis clearly indicated the diffraction lines of the solid solution formed i.e. (7.62, 3.80, 3.49, 3.28, 3.01, 2.95...) were identical, with a slight shift, to those of wollastonite- $CaSiO_3$ (PDF No. 29-372) [10].

The addition of LiF in glass G_1 resulted in enhanced crystallization of melilite of gehlenite type and wollastonite ss phases as indicated from the increase of the intensity of the d-spacing lines characteristics of these phases as indicated in the x-ray diffraction pattern of the glass-ceramic C_1 (figure 4, pattern II).

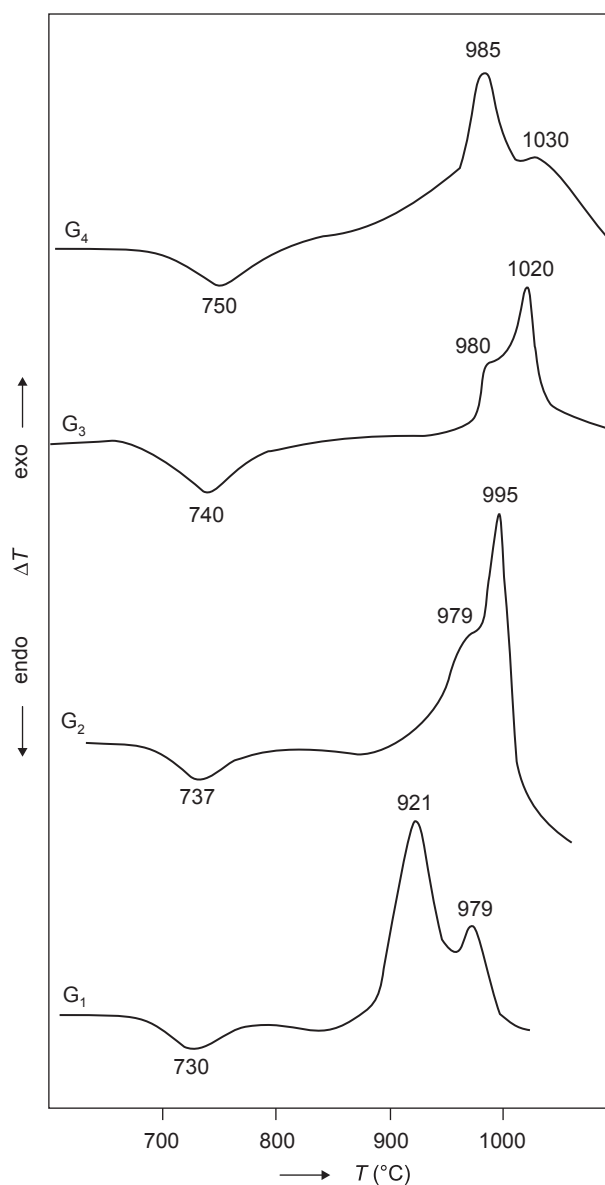


Figure 1. DTA data of the studied glasses.

On increasing the granite/slag ratios (up to 0.67, 1.0 and 1.5) i.e., G₂, G₃ and G₄ respectively, the XRD analysis (figure 4, patterns III-V) revealed that the thermal treatment of these glasses at 735°C/5 h - 995°C/10 h, 740°C/5 h - 1020°C/10 h, and 750°C/5 h - 1030°C/10 h, respectively, led to the formation of plagioclase phase of anorthite–CaAl₂Si₂O₈ type (lines 3.71, 3.28, 3.21, 3.12, 2.51, 1.82..., PDF No. 12-301)[10] (major) and wollastonite ss phase. The addition of LiF to glass G₄, as nucleating agent, led to the formation of the same phases with the increase of the intensity of their characteristics d-spacing lines as indicated from XRD analysis (figure 4, pattern VI).

The thermal expansion data of the glasses and their respective crystalline solids as a function of the granite/slag ratios are shown in figures 5 and 6.

Figure 5 and table 2 revealed that the thermal expansion coefficients of the glasses as well as their T_g and T_s values are greatly dependent upon the base glass composition. With successive increase of granite contents at the expense of slag in the glasses, the expansion coefficients decreased (figure 5). While, both the dilato-

metric T_g and softening T_s temperatures of the glasses were increased. Lithium fluoride has a great influence on increasing the expansion coefficients of the studied glasses and decreasing their dilatometric T_g and softening T_s temperatures (table 2).

The expansion coefficient values of the glass-ceramics are decreased by additions of granite at the expense of slag (C₁-C₄, figure 6). The addition of LiF as nucleating agent led to increase of the expansion coefficient of glass-ceramics, table 2.

Adding the granite at the expense of slag led to improve chemical durability of the glass-ceramics (C₁-C₄) i.e., increasing the granite content in the glasses led to a remarkable decrease in the leachability of the corresponding glass-ceramics. Applying the long-term action of acid, figure (7) indicated that the glass-ceramic with granite/slag ratios > unity, i.e. 1.5, C₄ was the most durable sample, while that with the lowest granite/ slag ratio i.e. 0.25, C₁ was the least durable one. Table 2 revealed that the chemical durability glass-ceramics C₁ and C₄ was decreased by addition of the LiF.

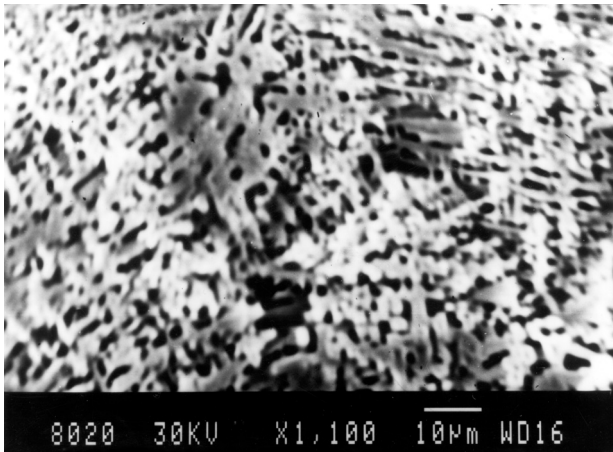


Figure 2. SEM micrograph of fracture surface of C₁ crystallized at 730°C/5h - 980°C/10h showing volume crystallization of coarse interlocked structure.

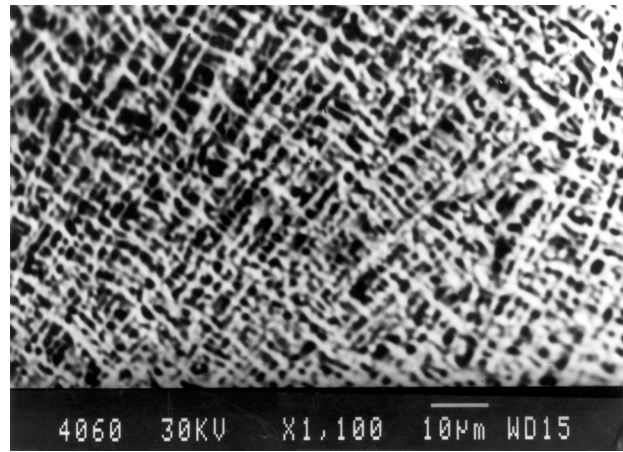


Figure 3. SEM micrograph of fracture surface of C₄ crystallized at 750°C/5h - 1030°C/10h showing volume crystallization of fine interlocked structure.

Table 2. Thermal expansion coefficients and chemical durability data of the LiF-containing glasses and glass-ceramics.

sample no.	expansion coefficients $\alpha \times 10^7$ (°C ⁻¹)					T_g (°C)	T_s (°C)	weight loss (%) in 0.1N HCl at 95°C		
	25-300	25-400	25-500	25-600	25-700			1 h	3 h	7 h
G ₁	87	90	93	94	-	659	710	-	-	-
G ₁ +LiF	97	98	103	-	-	548	580	-	-	-
C ₁	85	89	92	93	94	-	-	1.72	2.34	4.97
C ₁ +LiF	93	94	94	95	96	-	-	5.46	6.74	9.56
G ₄	75	76	77	78	-	690	727	-	-	-
G ₄ +LiF	76	80	86	-	-	559	613	-	-	-
C ₄	42	45	46	47	48	-	-	0.15	0.24	1.39
C ₄ +LiF	67	69	74	80	85	-	-	3.69	4.6	5.89

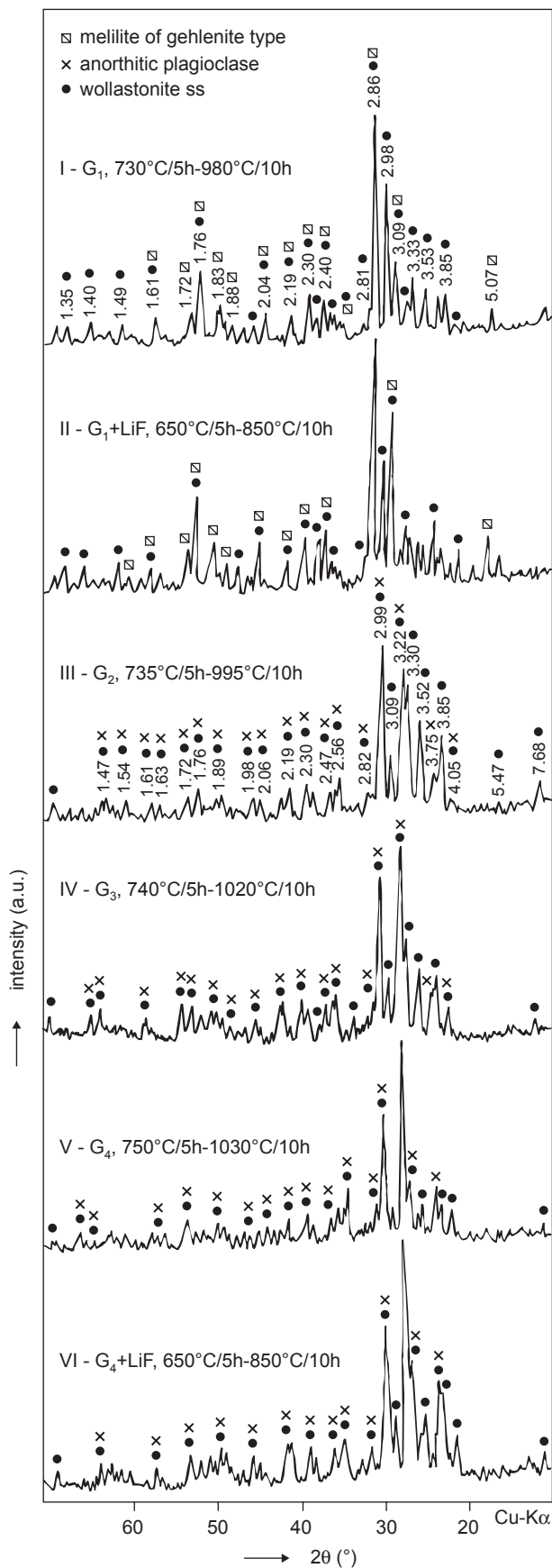


Figure 4. XRD analysis of crystallized glasses.

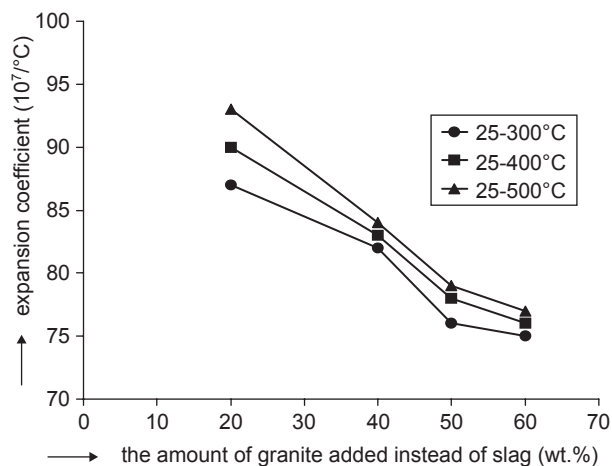


Figure 5. The thermal expansion coefficients of the glasses as a function of the amount of granite added.

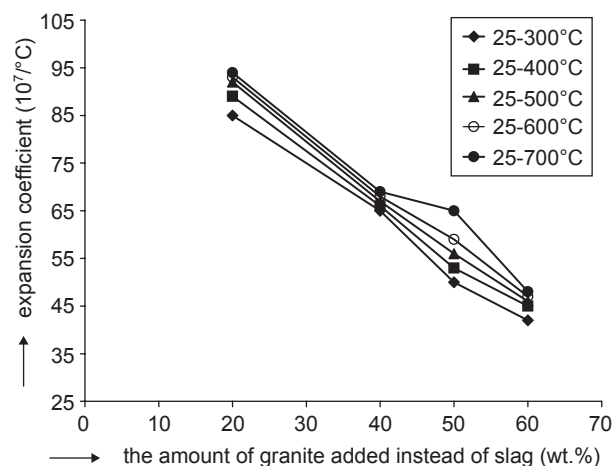


Figure 6. The thermal expansion coefficients of the glass-ceramics as a function of the amount of granite added.

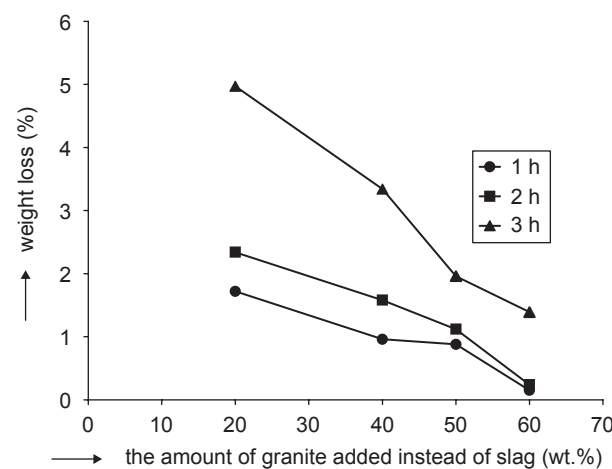


Figure 7. Measured percentage weight loss of glass-ceramic as a function of the amount of granite added.

DISCUSSION

The blast furnace slag is highly susceptible to devitrification to the extent that no monolithic glassy phase could be obtained even through the granulation process. Any composition for a glass-ceramic requires only the ability to form a glass and control its crystallization into the favourable fine-grained microstructure [11]. Therefore, in order to obtain a stable glass from slag, it is necessary to decrease the diffusion rate throughout the slag-based glass by increasing its viscosity. This may reduce either the rate of nucleation or crystallization; or at least minimize the temperature zones of their overlapping. The addition of granite to slag is satisfying these requirements [5].

The DTA data revealed that the addition of granite in the present glasses at the expense of slag had significant effects on the temperatures at which the nucleation and crystallization start. It increases the temperature of both endothermic and exothermic peaks, i.e. more energy is needed to induce crystallization in glasses with higher content of granite. This can be attributed to the role played by Al^{3+} and Si^{4+} ions, which increased as the granite content in the glass was increased. Accordingly, in glasses with high alkaline earth silicate, the Al^{3+} ions being in four-fold coordination form (AlO_4) tetrahedra, which enter the glass network and take part in the formation of a strong aluminium-silicon-oxygen framework [12]. The formation of such closely packed tetrahedral structural groups led to shift both the endo- and exothermic peaks towards high temperatures.

The DTA data revealed also that the sharp crystallization peaks observed at constant heating rate is indicative of the domination of bulk crystallization mechanism. These results are in consistent with the assumption developed by Ozawa [13] who reports that for a constant heating rate, a broad crystallization peak indicates surface crystallization while a sharp peak signifies a bulk crystallization.

The addition of LiF as nucleating agent led to increase the crystallization tendency of the glasses. This can be attributed to the fact that the fluorine ion, with a radius of 1.36 Å, is very close in size to the oxygen ion (radius 1.40 Å) so that a fluorine ion could replace an oxygen ion in the glass network [11]. Since the fluorine ion is monovalent, the overall replacement within the glass must be of two fluorine ions for each oxygen ion in order to ensure electrical neutrality. A general effect of the fluorine would be the replacement of the strong $\equiv Si-O-Si \equiv$ linkages by pair of weaker $\equiv Si-F$ linkages with the result that the glass network structure would be weakened. This led to decrease the viscosity of the glass melts and may result in the subsequent ease of migration and diffusion of different ions and ionic complexes present, therefore an increase in the rate of nucleation and crystallization could be expected.

In the light of microstructural observations, SEM revealed that the combination of crystallization at a high temperature and the progressive increase in the granite contents resulting into a finer grain size and more uniform bulk crystallization. It is clear that the microstructures were changed from numerous aggregates of crystals to fine growths of network microstructure. Strnad [14] revealed that the nucleating agents used for Slagsitall glass-ceramic include the sulphides of the heavy metals (FeS, MnS) in optimal concentrations of 0.2 to 0.4 wt.%. Agarwal et al., [15] studied the crystallization behaviour of cupola slag glass-ceramic and revealed that the heterogeneous nucleation sites for the obtained wollastonite solid solution crystals were Fe-Mn sulphides, which crystallize from dispersed immiscible droplets existing when the glass is quenched. It seemed therefore, that Fe-Mn sulphides present in glass 4 are effective as nucleating agents to induce fine grained bulk crystallization, figure 3.

Effect of granite/slag replacements on the crystalline phases formed

The X-ray diffraction analysis revealed that the base glass G_1 (with granite/slag ratio up to 0.25) crystallized into melilite phase of gehlenite type and wollastonite ss phase. The d-spacing reflections of the wollastonite solid solution formed are similar to those of wollastonite phase. No other phases could be detected. This will lead to an important conclusion that all other elements present in the melt can find place in the wollastonite or melilite of gehlenite type structure [15].

The displacement of the major characteristic d-spacing reflections of the formed wollastonite solid solution phase towards higher 2θ values may support the suggestion that wollastonite could acquire considerable amounts of Fe^{2+} , Mn^{2+} , Mg^{2+} , K^+ ... etc replacing Ca^{2+} and Ti^{4+} replacing Si^{4+} in its structure [15, 16].

Salama [17] found that wollastonite forms extensive series of solid solutions with $MnSiO_3$ extending to about 75 wt. % $MnSiO_3$ and concluded also that varieties of Ca, Mn-silicate solid solutions including Mn-wollastonite ($Ca_{0.75}, Mn_{0.25}SiO_3$), bustamite [$CaMn(SiO_3)_2$] and β -Mn-Silicate ($Mn_{0.25}, Ca_{0.25}SiO_3$) were mostly formed depending on the MnO/CaO ratios in the glasses. Mn-pyroxene ss forming varieties of the probable formula $(Ca_{0.5}, Mn_{0.5})MgSi_2O_6$ and $Ca(Mn_{0.5}, Mg_{0.5})Si_2O_6$ in glass containing Ca^{2+} , Mg^{2+} and Mn^{2+} ions.

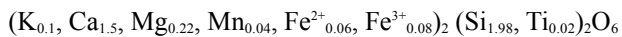
Salama and Salman [18] concluded also that in the presence of mixing of three divalent oxides (i.e. Ca^{2+} , Mg^{2+} and Mn^{2+}), metasilicates of these divalent cations were assumed to be formed i.e. $CaSiO_3$, $MgSiO_3$ and $MnSiO_3$, which go into solid solution to form a pyroxene solid solution series.

Schairer and Bown [19] showed that there is a solid solution between wollastonite and diopside in the CaO–MgO–SiO₂ system with a maximum 22 % of the later at eutectic.

Salman et al. [20] investigated the crystallization behaviour of Li₂O–CaO–MgO–SiO₂ glasses. They pointed out that in Ca-containing glasses, four varieties of Ca, Mg-Silicate phases were identified depending on the CaO/MgO ratio, namely clinopyroxene ss, diopside, wollastonite ss and pure Ca-silicate-wollastonite. They showed that the Ca-Mg-silicate phase formed is a solid solution between diopside and wollastonite. The diopside component in this solid solution amounts to 49.6 %. However, Salman et al., [21] found that wollastonite - diopside solid solution phase containing up to 66 % of diopside could be formed. This Mg-rich wollastonite solid solution which disintegrates ultimately by increasing time or at high temperature of heat-treatment to wollastonite and diopside.

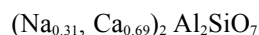
Bowen et al [22] showed that, wollastonite forms an extended series of solid solutions in the system CaSiO₃–FeSiO₃, wollastonite ss being obtained with up to 76 wt.% FeSiO₃ at high temperatures.

Therefore, the theoretical calculation of the glass compositions (G₁–G₄) into normative mineral molecules [23] indicated that the wollastonite solid solution developed in crystalline glass G₁ may had the following probable formula:



Agarwal et al., [15] revealed that the nature of shift in the X-ray peak of wollastonite phase indicates the substitution of a smaller ion for calcium causing the shrinking of lattice.

Gehlenite phase is related to a group of minerals known as melilite. The chemical formula of the melilite group is a solid solution of Al-end member gehlenite–Ca₂Al₂SiO₇ and Mg-end member akermanite–CaMgSi₂O₇ [24]. There is no solid solution in gehlenite–wollastonite system [25]. Goldsmith [26] stated that 15 % Na₂Si₃O₇ enters into solid solution with gehlenite–Ca₂Al₂SiO₇ (with Na₂O content of 3.85 %). Theoretically, [23] it is assumed therefore that the Melilite phase of gehlenite type formed in the glass-ceramic of G₁ has probably the following formula:

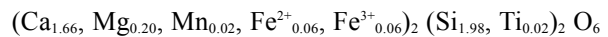


Attempts to synthesize K–melilite have been unsuccessful due to the lack of suitable accommodation in melilite structure for the large K⁺ ion [27].

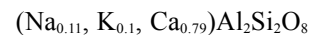
Increasing granite/slag replacements in the glasses G₂–G₄, anorthitic plagioclase (instead of melilite phase of gehlenite type) together with wollastonite ss phases were developed. The SiO₂ and Al₂O₃ contents in these glasses increased while the amount of CaO decreased.

So the formation of plagioclase of anorthite–CaAl₂Si₂O₈ type is more favourable than the melilite phase of gehlenite–Ca₂Al₂SiO₇ type. Anorthite, a triclinic feldspar, has an anionic structure in which Ca²⁺ ions balance the charge on the (Al₂Si₂O₈)₂-tetrahedral units. Anorthite-containing glass-ceramics has been regarded as a potential material in low temperature co-fired ceramic (LTCC). Anorthite crystals have a tendency to coalesce into a huge domain. [27].

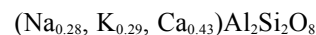
On increasing the granite/slag ratio up to 0.67 i.e., G₂ anorthitic plagioclase and wollastonite ss were formed. The resulting wollastonite solid solution phase may exhibit the following formula:



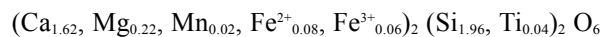
However, the presence of Na₂O or K₂O (in small amounts) may lead to the displacement of some Ca²⁺ ions from the anorthite molecules–CaAl₂Si₂O₈ to form albite–NaAlSi₃O₈ or KAlSi₃O₈ molecules instead, which go into solid solution with the remaining CaAl₂Si₂O₈ molecules [16] during crystallization of the glass G₂, giving rise to plagioclase crystals of varying compositions in the series CaAl₂Si₂O₈–NaAlSi₃O₈–KAlSi₃O₈. Therefore, the anorthitic plagioclase formed may has the following formula:



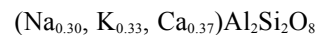
On increasing the granite/slag ratio up to 1.0 i.e., G₃ resulting into increasing appreciable amount of Na₂O and K₂O in the original composition of G₃. This increases the probability of formation of KAlSi₃O₈, NaAlSi₃O₈ in solid solution with anorthite–CaAl₂Si₂O₈, which has the probable formula:



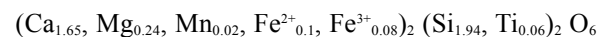
The structure of wollastonite solid solution formed in glass-ceramic G₃ may be had the following formula:



The increase of granite/slag ratio up to 1.5 i.e., G₄, the resulting anorthitic plagioclase may exhibit the following formula:



However, structure of wollastonite ss formed in glass-ceramic G₄ may represent the probable formula:



Thermal expansion

The thermal expansion of the glass is due to anharmonicity of the atomic vibrations. The amplitudes of the thermal vibrations are small when there are many strong bonds present in the network. As a result, the thermal

expansion coefficient decreases as the rigidity of the glass network increases. The change in the thermal expansion coefficient of the glass, which is caused by different additives, is often directly proportional to the amounts of the additives [29].

The addition of granite at the expense of slag led to decrease of the expansion coefficients of the glasses. This can be explained on the basis that the addition of granite increases the rigidity of the glasses due to the increase in the amount of silica, their structure thus being more cross-linked [1]. It was found also that the amount of Al^{3+} ions (found in granite) was increased and forming (AlO_4) tetrahedra, which enter the glass network and take part in the formation of a strong aluminium-silicon-oxygen framework. Thus the amplitudes of the thermal vibrations are small and the expansion coefficients (α) of the glasses are decreased. Consequently, higher T_g and T_s temperatures could be expected on adding granite at the expense of slag.

However, the addition of lithium fluoride led to increase the expansion coefficient values of the glasses. Lithium fluoride may act as network breaker in the glassy anionic structure. This effect is reflected in decreasing the viscosity of the melt (or glass) and consequently led to increase the thermal expansion coefficient of the glass.

The thermal expansion property of the crystalline solids is quite different than that of the parent glasses. The thermal expansion coefficient (α) of the glass-ceramics is a function of the thermal expansion coefficients and elastic properties of all crystalline phases present including residual glass and the resulting microstructure. The contribution of the residual glassy phase, whose composition is altered from that of the parent glass, must be taken into account [11 and 14].

An extremely wide range of thermal expansion coefficients is covered by the different crystal types and the development of these phases in appropriate proportions forming the basis of the production of glass ceramics with controlled thermal expansion coefficients [11].

The crystallization of glasses (G_1 - G_4) generally produces crystal phases such as melilite of gehlenite type, wollastonite ss and anorthitic plagioclase phases with varying expansion coefficients depending on the granite/slag ratios. The contribution of a particular crystal phase to the thermal expansion of a glass ceramic may be also modified if the crystal enters into solid solution with another phase. Gehlenite has high positive expansion of $123 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ (20-1000 $^\circ\text{C}$) [30]. Wollastonite has α -value of $94 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ (100-200 $^\circ\text{C}$) [11, 14]. Anorthite has α -values of $51 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ (25-600 $^\circ\text{C}$) [31] and $64 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ (20-1000 $^\circ\text{C}$) [32].

The glass-ceramics C_1 - C_4 showed that as the amount of granite increased, the coefficients of thermal expansion of the resulting glass-ceramics decreased

(figure 6). Glass-ceramic C_1 has the highest α -values due to the presence of high expanding melilite of gehlenite type together with wollastonite ss phases. However increasing the granite/slag ratios (C_2 - C_4) resulting into the formation of the relatively low expanding anorthitic plagioclase at the expense of the high expanding melilite phase of gehlenite type. Samples C_4 and $C_4 + LiF$ showed the lowest expansion coefficient values.

Chemical durability

The powdered test technique was used to assess the chemical durability of the glass and glass-ceramics. The powdered test is sought to yield a true representation of the leaching data of the materials [33]. It provides reliable information about the glasses and glass-ceramics as composite materials and not about the surface, as any effect due to differences in phase composition of the surface relative to the bulk is minimized. The relationship between temperature and time of test has been investigated [33], that one year at room temperature was approximately equivalent to 3 weeks at 50 $^\circ\text{C}$, 2 days at 75 $^\circ\text{C}$, or 7 hours at 95 $^\circ\text{C}$.

Glass-ceramics are multiphase systems with each phase having individual corrosion characteristics and possible unique reactions at the phase boundaries. The multiphase microstructure can be subdivided into two categories: 1) the crystalline phase, and 2) the amorphous phases (or the residual glass phase) [34]. However, the overall durability performance of a glass-ceramic cannot be solely determined by separate phase investigations. It is essential to take the phase boundaries into consideration as well. In this study the indicator of the extent of corrosion is weight loss measurements after corrosion.

In the present work, the addition of granite at the expense of slag improved the chemical durability of the glass-ceramics C_1 - C_4 .

The major factors influencing the overall durability of glass and glass-ceramics appear to be: 1) composition of the crystalline phases as compared with the residual glass, 2) structure and density of the crystalline phase, 3) volume fraction of crystalline phase, and 4) grain size of crystalline phase [34].

The chemical durability data revealed also that sample C_4 exhibited the best durable sample. This can be explained on the basis that the sample C_4 has a fine grain microstructure with small amount of residual glassy matrix as indicated from the SEM micrograph (figure 3). The dense non-porous microstructure of the glass-ceramics makes it possible to count on better chemical stability as compared with porous ceramics, which have a more extensive surface and greater penetrability to liquids and vapours [11].

Alkali metal ions are much more stable in the crystalline phase than in the residual glass phase. Consequently, alkali metal ions are more rapidly removed from the glass phase during the action of leaching solution on glass-ceramic materials [11, 14, 35]. In order that glass-ceramic materials have good chemical resistance, it is thus necessary that the residual glass phase does not contain high concentrations of the oxides of the alkali metals in particular.

However, the solubility of both the formed crystals and the residual glass phase in leaching solution has an almost equally important influence on the stability of glass-ceramics [35-36].

The leaching mechanism may involve the replacement of cations like Na⁺ and K⁺ with hydrogen-bearing ion from the solution leading to the formation of a leached layer, i.e. alkali depleted layer. Therefore, in acid media, the initial stage of the reactions is the diffusion of alkali ions through the glass-ceramic network and across the leached layer into the solution. The diffusion rate of alkali ions gradually slow down as the leached layer becomes thicker [35].

Kay and Doremus [37] stated that the volume of the crystals remains essentially constant with temperature as reflected in its low coefficient of thermal expansion. They suggested that the tendency of the lattice to maintain a constant volume reduces the rate of hydration reaction. This is in agreement with the results reported in the present work that the glass-ceramic C₄ showed a lower α -values and lower leaching rate than that of the other investigated glass-ceramic materials (C₁-C₃). These also can explain why the anorthitic plagioclase-containing glass-ceramics C₄ + LiF is more durable than the melilite phase of gehlenite type-containing glass-ceramic C₁ + LiF.

CONCLUSION

The glass-ceramic route can be successfully applied to the blast furnace slag provided from the Iron and Steel Company and Aswan granite with the goal of converting them into useful products.

The DTA data revealed that the sharp crystallization peaks observed is indicative of the domination of bulk crystallization mechanism. Lithium fluoride enhanced the crystallization of the glasses. Melilite phase of gehlenite type or anorthitic plagioclase together with wollastonite ss phases were mainly detected by XRD analysis depending on the granite/slag ratios. The morphology of the crystallized samples showed uniform volume crystallization of fine-grained network microstructures, which is achieved by increasing the granite/slag ratios in the glasses.

The increase of granite at the expense of slag in the glasses led to improve both the thermal expansion characteristics and the chemical durability of the materials investigated.

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VÝVOJ LEVNÉHO SKLOKERAMICKÉHO MATERIÁLU
NA BÁZI VYSOKOPECNÍ STRUSKY A ŽULY

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Byl zkoumán vývoj levného sklo-keramického materiálu s různým obsahem egyptské vysokopecní strusky a žuly. Vliv náhrady žula/struska na krystalizační charakteristiky skel výslednou mikrostrukturu byl sledován pomocí diferenční termické analýzy (DTA), rentgenové difrakční analýzy (XRD) a skenovací elektronové mikroskopie (SEM). Proměnlivost typů fází melilitu a gehlenitu, tuhého roztoku wollastonitu a anortických plagioklasových fází byla většinou způsobena závislostí na poměrech žula/struska u jednotlivých skel. Typy vzniklých krystalizovaných fází jsou diskutovány ve vztahu k proměnlivosti složení skel a použitému způsobu tepelného zpracování. Mikrosnímky SEM ukazují, že náhrada žula/struska podporuje krystalizaci jednotného objemu jemnozrné propletené mikrostruktury, které se dosáhne zvyšováním obsahu žuly ve sklech. Přídavek LiF jako katalyzátoru nukleace zlepšuje charakteristiky krystalizace skel. Zvýšení obsahu žuly na úkor strusky ve sklech vedlo ke zlepšení jak tepelných expanzních charakteristik, tak chemické odolnosti zkoumaných materiálů.