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Conversion of blast furnace slag into new glass-ceramic material

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Abstract

The devitrification behavior of different sizes of slag-derived glass was investigated using differential thermal analysis, X-ray diffraction and scanning electron microscopy to determine the possibility of preparing glass-ceramic materials. The crystalline phases were identified as gehlenite, diopside pyroxene and barium aluminium silicate. The degree of crystallization was determined by evaluation the changes of density at different temperatures where a maximum density was achieved at 900 °C. A remarkable difference in the glass-ceramic texture was observed by treating the sample at different crystallization temperatures. Both acicular and dendritic morphology have been identified in the sample heat-treated at 1050 °C. A slight variation in peak crystallization temperature with particle size indicated a bulk crystallization mechanism.

Keywords: Devitrification; Glass ceramics; Slag; Waste material

1. Introduction

Environment and human health effects are intricately linked, therefore the need for wastes recycling is a fact of healthy life today and scientists and technologists alike continue to seek ways to reduce the environmental impact of wastes that is discarded to landfills and enhance the protection of the environment from gaseous and dust emissions as well. Although the economical importance of industry for development and progress and its contribution to the improvement of the quality of life for millions of workers throughout the world as well as realizing their dreams of getting all what they want, it has been a major source of not only air and water pollution but also industrial pollution resulting from solid waste disposal which consequently lead to environmental inconvenience.

Owing to the growing amount of solid waste produced by industrial firms and the enforced environmental regulations as well as the needs to pollution abatement, an increasing interest has been developed to utilize recycling as a means of diverting solid wastes into new glass-ceramic products. Slag is an industrial solid waste generated in the process of iron ore reduction in blast furnace and 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 benefits and offer significant potential for cost savings profit if reintroduced into the industrial process through well planned programs.

Glass-ceramics are materials that are processed and formed as glasses and then converted into a crystalline ceramic by a subsequent heat treatment. Whether a crystalline or glassy phase is formed depends upon many parameters such as constituents, rate of cooling and the presence or absence of nucleating agents. The research activities and efforts carried out by several authors in treating industrial wastes e.g. goethite wastes resulted from the hydrometallurgy of zinc, fly ashes from domiciliary and waste incinerators, coal fly ash and blast furnace slags,[1–8] demonstrate the wide possibilities of using such wastes to resolve environmental problems and contributing to the efforts for waste regulation and pollution prevention. It is believed that the principal usage for blast furnace slag-derived glass is in the form of tiles and pipes for the conveyance and storage of abrasive materials where glass-ceramics are

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much more resistant to abrasion than alternative metals and alloys.[9]

The purpose of this paper which is a continuation of research work carried out by the author, is to conduct a study on crystallization behavior of slag-derived glass by means of differential thermal analysis (DTA), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis.

2. Experimental procedure

The solid waste used for the development of this work is a slag generated in blast furnace (BFS) and provided by the iron and steel company. The chemical composition of the slag, determined using X-ray Fluorescence (XRF) - ARL 72000, was 36.97% SiO_2, 14.79% Al_2O_3, 26.64% CaO, 1.43% Na_2O, 0.33% Fe_2O_3, 6.7% MgO, 3.29%MnO, 1.09% S, 0.65% K_2O, 6.16% BaO. The slag without additives was melted in a platinum crucible at 1350 °C for 1 h, poured onto a preheated steel plate, annealed,ground and screened to different particle sizes of <125 μm, 312–500 μm and 800–1600 μm. The crystallization process was performed by means of Shimadzu DTA-50 technique using 45 mg of slag sample in a flowing atmosphere of nitrogen and air using powdered alumina as a reference material within the temperature range 20–1200 °C at a constant heating rate 20 °C/min.

The thermal expansion was measured up to 700 °C in a Dilatometer (Theta Instruments Inc.—New York—USA) on bar sample having the diameter of 5 mm × height 5 mm × length 15 mm. XRD experiments were performed in a Philips diffractometer (type PW1730). The source is CuK_α, the working voltage and tube current were 40 kV and 40 mA respectively. XRD Analysis has been used to identify the crystalline phases present in the glass-ceramics. The density of the samples was determined by the well-known Archimedes'technique.[10] The microstructure was investigated by Scanning Electron Microscope (SEM) of selected samples mounted on Bakelite, mechanically ground on SiC paper, polished and coated with carbon and observed with a Jeol JSM5410 equipped with energy dispersive X-ray spectrometer (EDS). The erosion behavior of the glass-ceramic material was determined by the weight loss of the bar test specimen after rotating in slurry of 100 g sand in 1000 ml water at room temperature and for times up to 9 h.

3. Results and discussion

The preliminary data generated using the DTA technique on an as-quenched sample is shown in Fig. 1 where a slope change at ~719 °C indicating a glass transition temperature Tg followed by two exothermic peaks, a shoulder one covering the range 872–927 °C and well defined one at 1012 °C. An endothermic dip ending at 1114 °C indicating the melting of the crystallized phases and consisting also of stairs-like shape implying the closing-by of the melting point of the phases. With the aim of investigating the influence of the particle size <125, 312–500 and 800–1600 μm on the crystallization behavior of the parent slag-derived glass when heat treated in different atmosphere, DTA was carried out at a constant heating rate 20 °C/min within the temperature range 20–1100 °C Fig. 2. The DTA highlights that the exothermic crystallization peak of the size <125 μm is not well defined and as sharp as those of 800–1600 and 312–500 μm under N_2 and air atmosphere. The slight variation in peak crystallization temperature as a function of the glass particle size reflects that bulk crystallization mechanism is the predominant one. If surface crystallization predominates, a strong dependence of crystallization peak temperature on particle size would have been observed. This result is in consistent with the assumption developed by Ozawa[11] which reports that for a constant heating rate, a broad crystallization peak indicates surface crystallization while a sharp peak signifies a bulk crystallization. It might be claimed that surface crystallization is predominant in the sample prepared from particle size <125 μm while bulk crystallization is predominant in sample of coarse particle size 312–500 and 800–1600 μm.

To investigate the crystalline phases developed during the DTA runs, the samples were finely ground and analyzed by XRD after heat treatment at 900 and 1100 °C Fig. 3, where three different crystallines phases belonging to gehlenite $Ca_2Al_2SiO_7$, $BaAl_2Si_2O_8$ and diopside pyroxene $Ca(Mg,Al)(Si,Al)_2O_6$ were observed at 900 °C. A melting state is beginning to appear at 1100 °C leading to the complete disappearance of $BaAl_2Si_2O_8$ crystalline phase together with the appreciable decrease in the intensity of the other phases. This is in consistent with the deflection started at 1100 °C on DTA which have a stair-like shape indicating the starting-up of melting state of more than one phase, while the hollow endothermic dip observed at 1114 °C may be due to the melting of both pyroxene and gehlenite. It should also be mentioned that the diffraction lines attributed mainly to diopside pyroxene and gehlenite are in consistent with a previous work carried out on the crystallization in glass derived from the system $CaO.MgO.Al_2O_3.SiO_2$.[12–13]

The XRD diffraction patterns in Fig. 4 of heat treated powder samples at 900 °C for different periods up to 4 h shows the same crystalline phases $Ca_2Al_2SiO_7$, $BaAl_2Si_2O_8$ and $Ca(Mg,Al)(Si,Al)_2O_6$ but the crystallization of slag after heat treatment for 1 h is more pronounced. SEM micrograph of polished samples of the BFS-derived

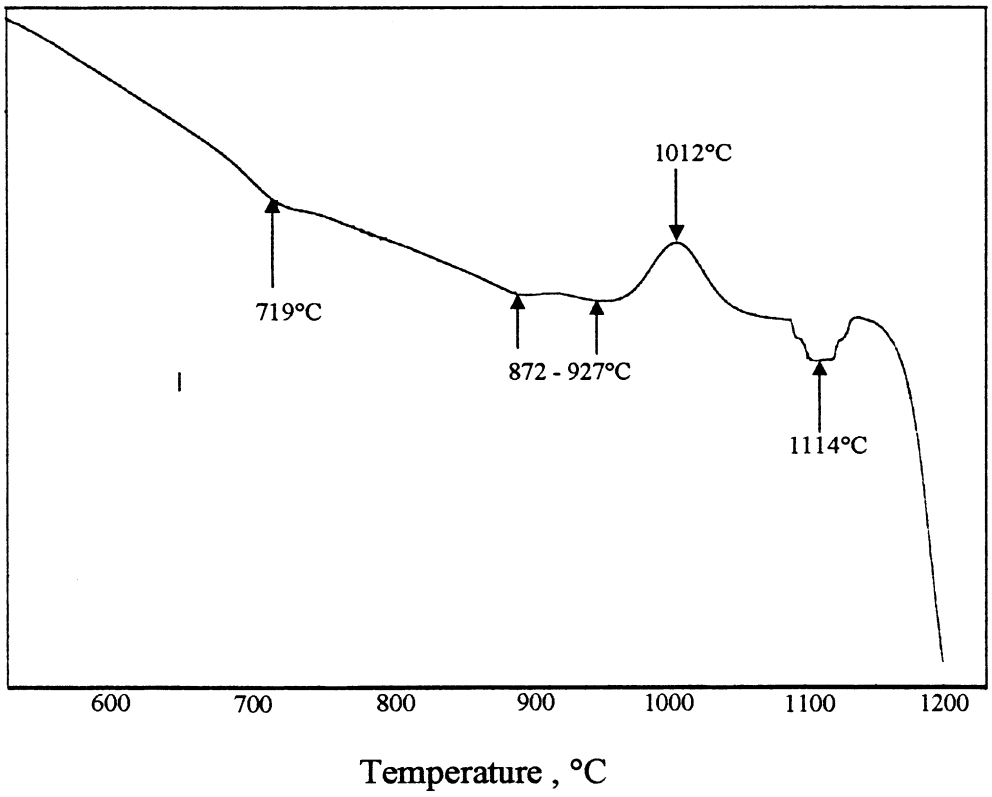

Fig. 1. DTA plot of the slag-derived glass sample.

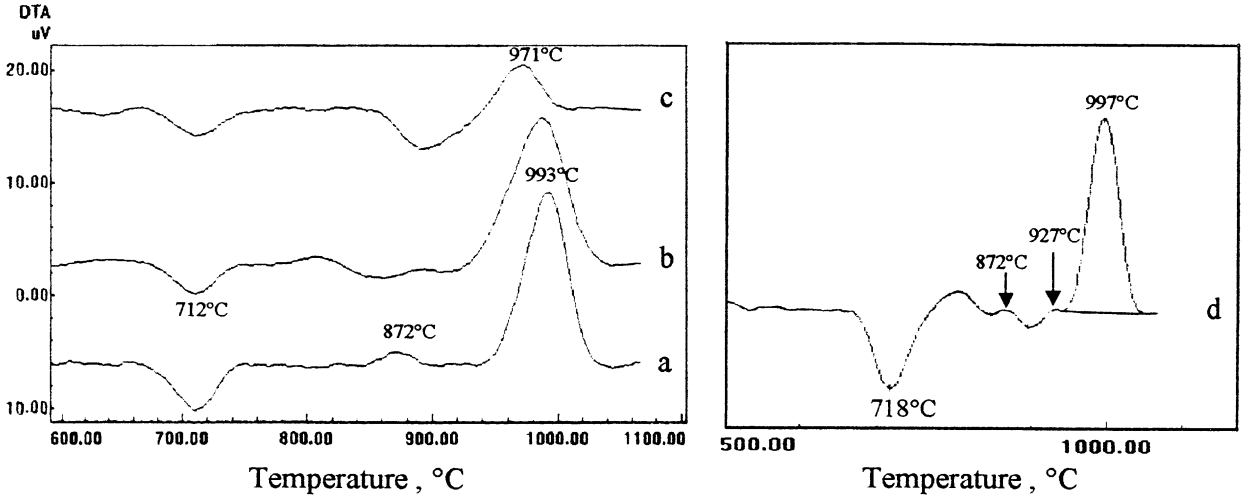

Fig. 2. DTA plot of slag-derived glass of particle size (a) 312–500 μm under N_2 (b) 312–500 μm under air (c) <125 μm under N_2 (d) 800–1600 μm.

glass heat treated at 900, 1050 and 1100 °C Fig. 5, revealed a remarkable difference in the glass-ceramic texture. The heat treated sample at 900 °C exhibits a texture with a needle-like crystals. However closer examination of the sample heat treated at 1050 °C indicates a growth of rod-like shaped crystal (white phase which consists of both gehlenite and $BaAl_2Si_2O_8$) reaching a range of diameter of 0.005–0.11 μm and a length range of 4–9.4 μm with a crystallized dendritic crystals (light gray) of pyroxene phase distributed throughout the glass matrix and directed towards euhedral morphology. EDX analyses collected in spots on glass-ceramic sample heat treated at 1050 °C show that the rod-like shaped crystal is enriched in SiO_2, CaO Al_2O_3 and BaO whereas the dendritic crystals and the glassy matrix are enriched in SiO_2, CaO, Al_2O_3, MnO, MgO, Na_2O and K_2O. The thermal expansion of the sample indicates a medium value of 8.1×10^{-6}/K (20–630 °C) which is consistent with the coefficient of thermal expansion (CTE) of diopside phase and slagsitall.[14]

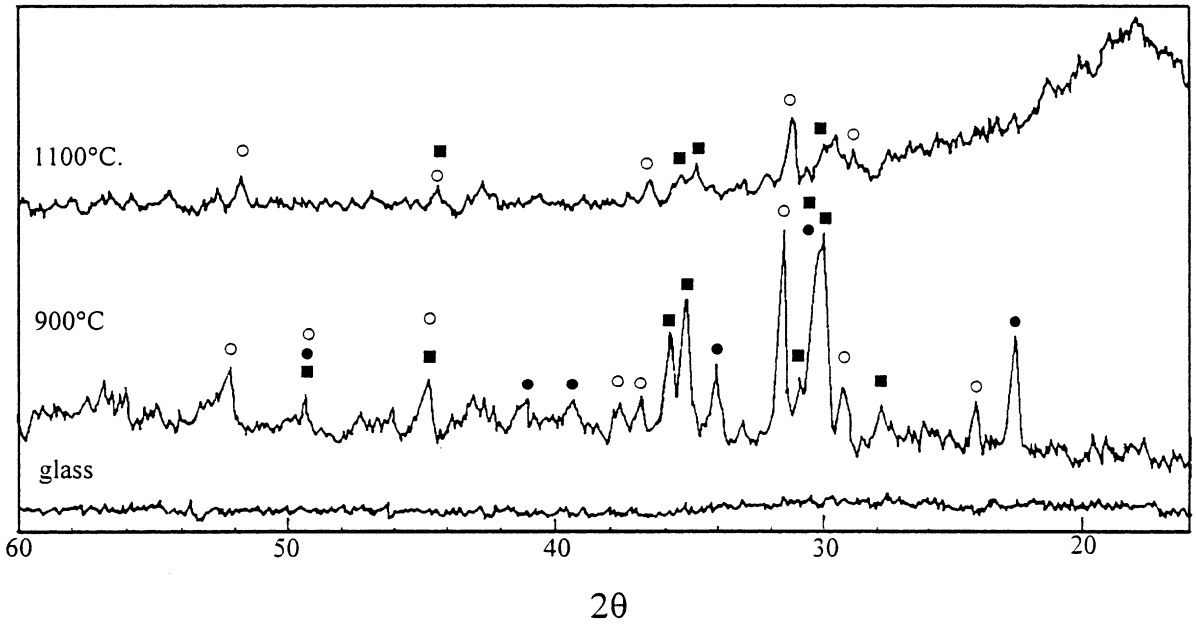

Fig. 3. XRD of thermal treated sample at 900 and 1100 °C for 2 h. The peaks are labeled as • $BaAl_2Si_2O_8$, ○ gehlenite and ■ pyroxene.

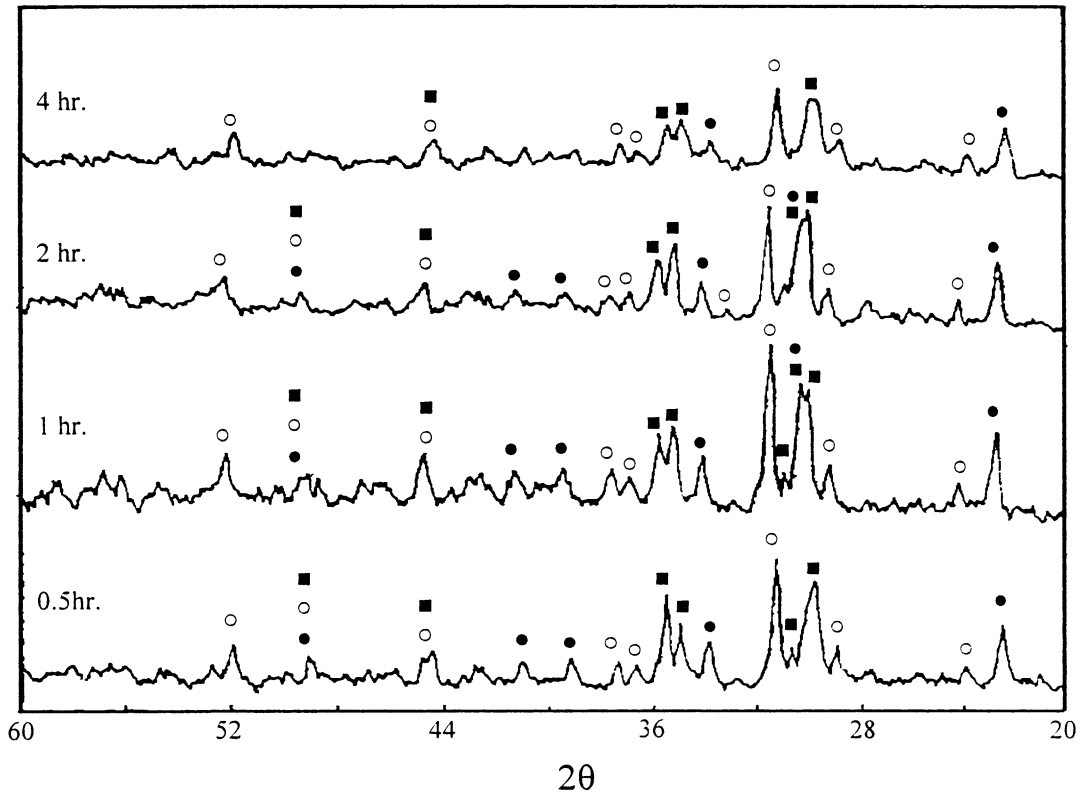

Fig. 4. XRD pattern of thermal treated sample at 900 °C for different periods. The peaks are labeled as •$BaAl_2Si_2O_8$, ○ gehlenite and ■ pyroxene.

Fig. 6 shows the density variation of slag-derived glass sample heated for 1 h at different temperatures. The density of the parent glass measured as 3.095 g/cm^3 did not vary before 800 °C, highlighting that no crystallization occurs. The density starts to be effective at 850 °C and reaches its maximum at 900 °C. By treating the glass at higher temperature, the density decrease indicating that the crystallization decreases. It should be noted that the degree of crystallization followed by density change coincides with XRD determination. The weight loss of the glass-ceramic sample resulted from the erosion test reaches a value of 0.35% for 9 h. The

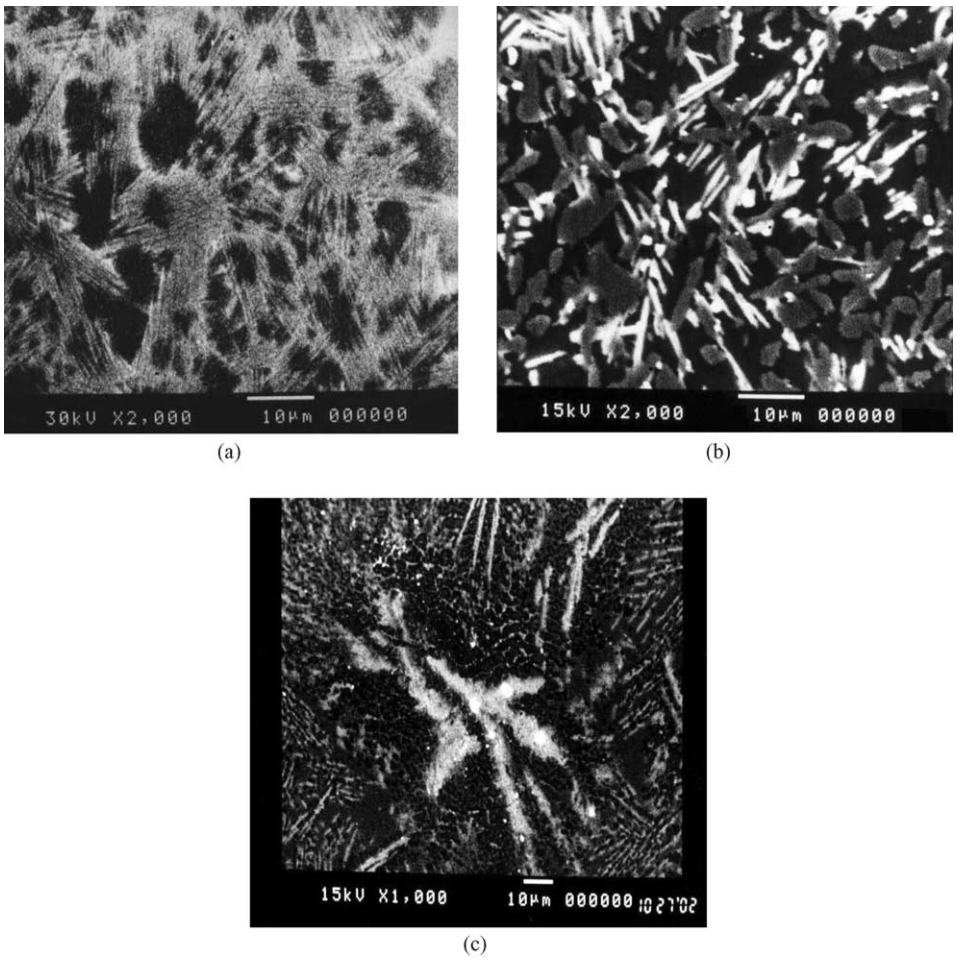

Fig. 5. SEM micrographs of heat treated sample at different temperatures showing (a) 900 °C needle-like shape crystal (b) 1050 °C crystallization of dendritic pyroxene (c) 1100 °C disappearance of the dendritic crystals.

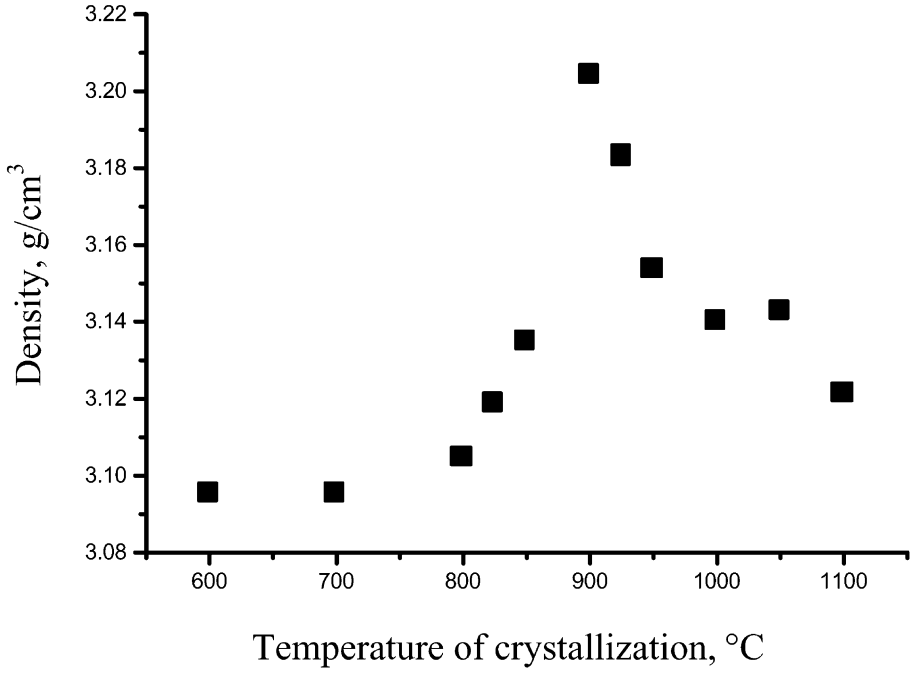

Fig. 6. Variation of density at different temperatures for a constant heat treatment period of 1 h.

chemical resistance of the glass-ceramic samples with size ranging from 312–500 μm was determined for the amount of weight reduction after being kept for 24 h at 25 and 70 °C in a 10% NaOH and 10% HCl solutions. It should be pointed out that the chemical resistance of the glass-ceramic in 10% NaOH at room temperature and at 70 °C is very good, while it is not promising in an acid solution.

4. Conclusion

The glass-ceramic route can be successfully applied to the blast furnace slag with the aim of converting it into useful product. Because we are dealing with a multi-component system more than one crystal phase has been identified and are belonging mainly to the gehlenite and diopside pyroxene phases as well as to $BaAl_2Si_2O_8$. The slight variation of peak temperature with particle size as well as the sharp crystallization peak observed at constant heating rate is indicative of the domination of bulk crystallization mechanism. The morphology of the crystallized samples varied between the rod-liked shape and the three dimensional dendritic shape.

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