Journal of the European Ceramic Society 18 (1998) 161–168

PII: S0955-2219(97)00094-0
0955-2219/98/$19.00 + 0.00

Microstructural Characterization and Physical Properties of a Slag-based Glass-ceramic Crystallized at 950 and 1100°C

M. L. Öveçoğlu

Department of Metallurgical Engineering, Faculty of Chemistry-Metallurgy, Istanbul Technical University, Maslak 80626, Istanbul, Turkey

(Received 2 January 1997; revised version received 7 March 1997; accepted 17 March 1997)

Abstract

Glass-ceramic materials were developed from Turkish blast-furnace slags mixed with 3 and 5 wt% titania (TiO_2). On the basis of the DTA and the dilatometry analyses, nucleation experiments were carried out at 725°C and crystallization was performed at 950 and at 1100°C. DTA and X-ray diffraction studies conducted on the glass samples devitrified at 950°C revealed glassy regions and small amounts of gehlenite ($Ca_2Al_2SiO_7$) and merwinite ($Ca_3MgSi_2O_8$) phases whereas complete transformation to melilite solid solution of akermanite ($Ca_2MgSi_2O_7$) and gehlenite phases occurred for those crystallized at 1100°C. Optical microscopy and SEM investigations on the slag glass-ceramic crystallized at 950°C revealed large crystals due to surface crystallization whereas bulk crystallization was evident for those crystallized at 1100°C. For both cases, the crystalline size decreased with increasing nucleant content. Wear, hardness, fracture toughness and bending properties of the slag based glass-ceramic material were enhanced with the increase in nucleant content and the crystallization temperature. © 1997 Elsevier Science Limited.

1 Introduction

Today environmental and ecological considerations demand the utilization of industrial wastes such as blast-furnace slags produced in the integrated iron and steel works. Commercial exploitation of blast furnace slags for the manufacture of glass-ceramic materials has been underway for more than three decades,[1–4] initiated by Klemantaski et. al.[1] who coined the term *Slagceram* for his invention of the slag based glass-ceramic material. Consequently, a substantial amount of research and development work has been conducted in the exploitation of slag-based glass-ceramic materials for large-scale production of ordinary commercial products.[5–8] Slag-based glass-ceramics have been used as exterior and interior claddings, roof coverings, and as heat and voltage insulators in the former Soviet Union.[9–13]

In general, glass-ceramics may be defined as polycrystalline solids produced by controlled crystallization of glasses.[14–16] 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 resultant properties. The motivation for developing glass-ceramics from metallurgical slags 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. As pointed out by McMillan[14] and Beall and Duke,[17] when used in amounts in ranging typically from 2 to 10 wt%, titania (TiO_2) is an excellent nucleating agent in aluminosilicate-based glass-ceramic systems. As a result, TiO_2 is used as the primary nucleant in most slag-based glass-ceramics.

The primary aim of the present study is to determine the experimental conditions for the development and optimization of glass-ceramics from waste metallurgical slags intended for possible cladding and tiling applications. For this purpose, microstructural characterization and mechanical property investigations were carried out on glass-ceramic materials developed from waste blast furnace slags of Karabük integrated iron and steel works. As-received slag doped with 3 and 5wt% titania (TiO_2) added as nucleant was crystallized at 950 and at 1100°C and the resultant glass-ceramics were characterized by Differential Thermal Analysis (DTA), X-ray diffractometry, optical and scanning electron microscopy (SEM) techniques.[18] In addition, microhardnes, wear and friction, 3-point bending and fracture toughness properties of the resultant slag-based materials were determined. The results indicated overall increases in mechanical properties with increases in the nucleant content and the crystallization temperature.

2 Experimental procedures

2.1 Raw material and glass-ceramic forming

The blast furnace slag used in this investigation was received from the Karabük Iron and Steel Works in the agglomerated form. After drying, pulverizing and demagnetizing steps, the slag had the following chemical composition (in wt%) : 34·8% CaO; 37·7% SiO_2; 14·2% Al_2O_3; 9·22% MgO; 1·75% K_2O; 1·11% S; 0·54% Na_2O; 0·44% TiO_2; 0·24% Fe_2O_3 (all compositions in this study are given in wt%, unless otherwise stated). Since the TiO_2 content in the slag powder batch as a natural nucleant was quite low, appropriate amounts of technical TiO_2 powders were added to the slag-powder batch to constitute 2, 3 and 5% of the total batch. Wet grinding was performed using conventional ball mills for 24 h. After grinding, slag powders with or without the addition of technical TiO_2 powders were melted in air using Pt-crucibles at 1530°C for about 5 h to ensure complete homogenization. Following that, the melt was cast in preheated graphite or steel moulds. To remove thermal residual stresses, the cast glass was placed in a furnace at 500°C for 2 h before nucleation and crystallization experiments.

Density measurements were carried out on as-cast slag material using a Micromeritics® pycnometer. Thermal expansion analyses of as-cast slag and slag with varying TiO_2 amounts were carried out on specimens having dimensions of 5cm × 0·5 cm × 0·5 cm in the range of 25°C–800°C at a heating rate of 5 C min^{-1}. using a Netsch® 402 dilatometer. Differential thermal analysis (DTA) scans of as-cast slag and slag doped with 3 and 5% TiO_2 were carried out in a Perkin-Elmer 7 Series Thermal Analyzer in order to determine the characteristic glass transition temperatures, T_g, and peak crystallization temperatures, T_p. After pulverizing and grinding specimens of as-cast glass to a size of about 30 μm, static non-isothermal experiments were performed by heat-treating 100 mg glass powders in a platinum crucible and using the same amount of Al_2O_3 as the reference in a temperature range between 25 and 1300°C at a heating rate of 20°C min^{-1}. Data for each run were collected directly from the DTA. On the basis of dilatometry and DTA analyses, nucleation experiments were conducted at 725°C at a holding time of 18 h. Following nucleation, the temperature was raised to the desired crystallization temperature (950 or 1100°C) and held for 12 min followed by air cooling. The rationale for choosing the optimum heat-treatment conditions is explained in the Results and Discussion section.

2.2 Microstructural characterization

Microstructural characterizations of the as-cast glass and crystallized glass-ceramic samples were performed using optical and electron microscopy and X-ray diffraction techniques. Optical microscopy investigations were carried out with a Leitz® optical microscope whereas SEM investigations were conducted with a JEOL® SEM operated at 25 kV and linked with an energy dispersive (EDS) attachment. Optical specimens were prepared using standard metallographic techniques followed by chemical etching in a solution of 40 vol% methyl alcohol, 42 vol% distilled water and 2 vol% HF for about 20 s. Some of the etched optical specimens were coated with a thin layer of gold and used during the SEM investigations. The X-ray diffraction investigations were carried out with a Siemens® D-5000 diffractometer using CuKα radiation at 40 kV and 30 mA settings in the 2θ range from 20 to 60° at a scanning speed of 0·03° min^{-1}. The phases were identified by comparing the peak positions and intensities with those listed in the JCPDS (Joint Committee on Powder Diffraction Standards) files.

2.3 Measurements of mechanical properties

The mechanical properties of as-cast slag without titania addition and slag-based glass-ceramics with varying amounts of titania crystallized at different temperatures were determined by microhardness, 3-point bending and wear tests. Vickers and Knoop microhardness tests were conducted in an LL Model Tukon Tester. Optical mounts were prepared using standard metallographic techniques and loads of 100–300 g were used to indent their surfaces. To obtain reliable statistical data, at least 20 indentations were made on each sample. The empirical relation formulated by Ponton and Rawlings[19] which utilizes fracture lines emanating from Vickers diamond indentation was used to determine the fracture toughness values. Three-point bending tests were carried out in an MTS® Universal Tester on specimens having dimensions of 5 cm × 0·5 cm × 0·5 cm machined from as-cast and heat-treated glass-ceramic samples. Friction and wear tests were performed in ambient conditions (about 20% humidity) on optical mounts of glass-ceramic specimens using CSEM® Pin-on-Disc Tribometer with 6 mm diameter WC balls as the abrading pins. A constant perpendicular load of 10 N and a rotational speed of 40 rpm were used throughout the tests. Hardfacing balls and substrate optical mounts were ultrasonically cleaned between each measurements. The frictional force was monitored and recorded with a linear displacement transducer throughout the tests. Wear volume and wear rates were calculated in accordance with the ASTM G 99-90[20] and friction values were read directly from the chart of the transducer. Optical microscopy was used to measure scar thickness. In all wear and friction tests, there was no significant pin wear, namely, no wear on the hardfacing ball.

3 Results and Discussions

3.1 Physical properties

Density of the as-cast glass was invariant with temperature in a range between 25 and 800°C and measured as 2·877 g cc^{-1}. This value is very close to the density value reported by Davies *et al.*[4] for the Slagceram, the glass-ceramic material developed from UK blast-furnace slags, having a chemical composition similar to that used in this study. The linear thermal expansion coefficient of the as-cast glass had a negligible variation with temperature in a range between 250 and 800°C and measured as $9{\cdot}1 \times 10^{-6}\,mm^{-1}$. The dilatometry scan conducted on the as-cast glass revealed an average onset temperature of about 710°C in the vicinity where the slope changes slightly. Therefore, this temperature was chosen as the glass-transition, T_g temperature. Glass-ceramics nucleated with titania had similar density and expansion values which changed slightly with the nucleant content but which were invariant with crystallizing temperatures. Due to measured high thermal expansion values of the as-cast slag-based glass and glass-ceramics, they are not suitable for applications requiring low thermal expansion. The dilatometry scan conducted on the as-cast glass revealed an average onset temperature of about 710°C in the vicinity where the slope changes, therefore this temperature was chosen as the glass-transition, T_g temperature.

3.2 Thermal and microstructural characterization

Differential thermal analysis (DTA) investigations were conducted on the as-cast slag and the slag doped with varying amounts of titania. Figures 1(a), (b) and (c) are the respective DTA data of the as-cast slag glass and glass-ceramics doped with 3 and 5% titania scanned between 25 and 1200°C. All DTA scans exhibit a small endothermic peak starting at the onset of 710°C selected as the T_g temperature, in agreement with the dilatometry scan data. Thermal gradient and dilatometry studies can be employed to determine the optimum conditions for two-stage heat-treatment of glass. Davies *et al.*[4] ran DTA and dilatometry measurements on the Slagceram and detected a small endothermic peak around 700°C. Thus, the nucleation rate was very high in the vicinity of 700°C and they recommended a nucleation temperature of 720°C, slightly above the T_g value. Further, they used nucleation times of more than 10 h in order to avoid slumping and coarse crystallization. The work of Davies *et al.*[4] provided the basis for the optimum choice of the nucleation time and temperature in this study. The nucleation temperature was selected as 725°C and some qualitative optical metallographic work was carried out on slag specimens nucleated at times over 10 h to determine the maximum rate of nucleation. Optical samples prepared from slag nucleated at 725°C/18 h displayed the highest amount of visible nuclei which did not increase in number at longer times. Thus, the optimum nucleation temperature and time chosen for this study were 725°C and 18 h, respectively. As for the crystallization heat-treatment conditions, the exothermic peaks in the DTA scans shown in Fig. 1 should be evaluated.

As shown in Fig. 1(a), the as-cast slag sample exhibits three shallow exothermic peaks occurring at 888, 937 and 953°C. The shallow nature of these exothermic peaks and the endothermic peak at 1141°C due to partial melting indicate that surface crystallization is the predominant mechanism for the as-cast slag material. In order to identify the crystallizing phase(s), an X-ray scan was carried out on a specimen of the as-cast glass which had been heat treated up to 955°C followed by air quenching to room temperature. The X-ray analysis revealed the presence of glassy regions and small amounts of crystallizing phases of gehlenite ($Ca_2Al_2SiO_7$)[21] which had a tetragonal structure with lattice parameters a = 0·769 nm and c = 0·507 nm and the monoclinic merwinite ($Ca_3MgSi_2O_8$) phase[22] with lattice parameters a = 1·325 nm, b = 0·529 nm, c = 0·933 nm and $\beta = 91{\cdot}9°$. This observation partially agrees with the results of Orsini[23] and Orsini *et al.*[24], who evidenced that the devitrification of melilite glasses (where CaO and SiO_2 content comprise about 80 wt%) involves the crystallization of the merwinite phase with a composition different from the

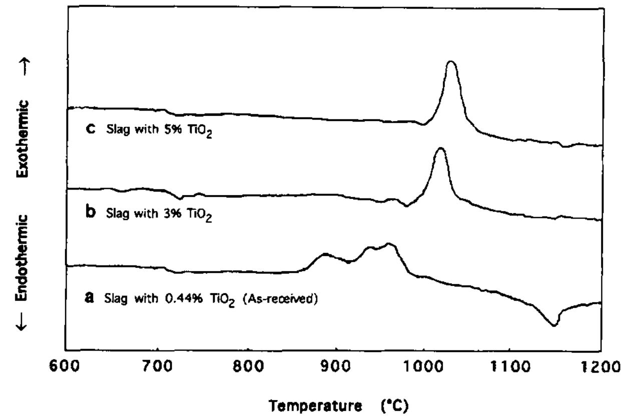


Fig. 1. DTA plots of (a) as-cast slag-based glass and slag-based glass-ceramics comprising : (b) 3 wt% TiO_2 and (c) 5 wt% TiO_2.

initial glass, and the crystallization of a second phase at a higher temperature with the same composition as the initial glass.

The effect of adding different amounts of TiO_2 as the nucleating agent can be seen in Figs 1(b) and (c). As seen in Figs 1(b) and (c) for the cases of slag glass-ceramic doped with 3% and 5% TiO_2, respectively, the nucleant addition causes the smoothing out of the shallow exotherms and the disappearance of the endotherm at 1150°C. It is suggested that the vanishing of these exotherms and the partial melting endotherm at 1150°C is caused by bulk heterogeneous crystallization coupled with complete transformation to melilite solid solution in the microstructure. Thus, the exothermic peak at 1019°C for the glass-ceramic doped with 3% TiO_2 (Fig. 1(b)) and the other one at 1030°C for the glass-ceramic containing 5% TiO_2 (Fig. 1(c)) can be attributed to the formation of the melilite solid solution. As reported by Orsini *et al.*,[24] at temperatures near 1000°C, merwinite disappears completely after transforming into a solid solution of akermanite and gehlenite. To test the applicability of their observation to the devitrification of the slag-based glass-ceramic materials of this study, X-ray diffractometry scans were carried out on titania containing glass-ceramic samples crystallized at 1100°C. In all samples devitrified at 1100°C, the X-ray scans revealed small deviations of the measured d-values from the card values of the two endmembers of the melilite group, namely the gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$) phases and increasing amount of crystallinity with increase in the nucleant content. As seen in the X-ray diffraction pattern of the slag glass-ceramic doped with 5% TiO_2 nucleated at 725°C/18 h and crystallized at 1100°C/12 min shown in Fig. 2, all the diffraction peaks can be indexed as arising both from the reflection planes of the akermanite phase of the chemical formula $Ca_2MgSi_2O_7$ which has a tetragonal structure with lattice parameters $a = 0{\cdot}783$ nm and $c = 0{\cdot}501$ nm[25] and the gehlenite phase with the same lattice parameters mentioned earlier.[22] It should be mentioned here that since both gehlenite and akermanite phases have the same crystal structure with lattice parameters very close to each other, the respective X-ray peaks for both phases, for all practical purposes, are coincident with each other. However, slight deviations of the measured d-values from the card values of each phase verifies that there exists a

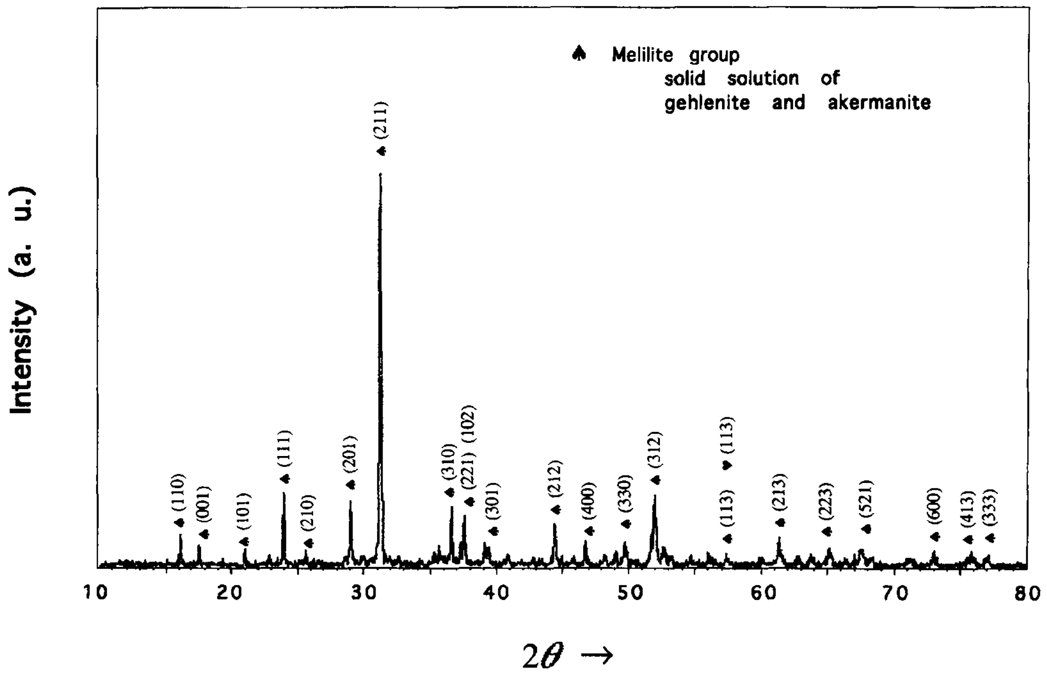
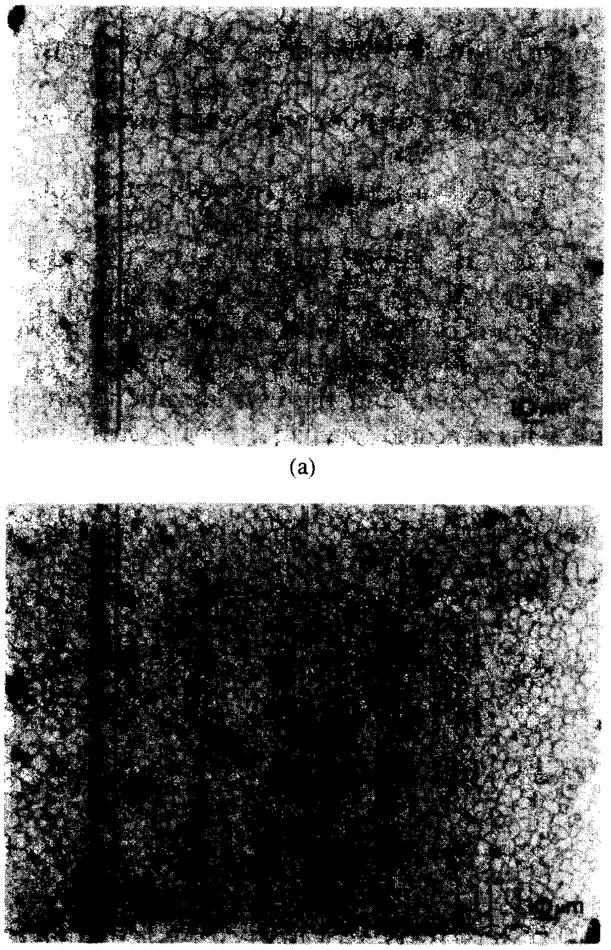


Fig. 2. A representative X-ray diffraction pattern of the slag-based glass-ceramic sample nucleated at 725°C for 18 h and crystallized at 1100°C 12 min^{-1} scanned in the 2θ range from 20°–60°.

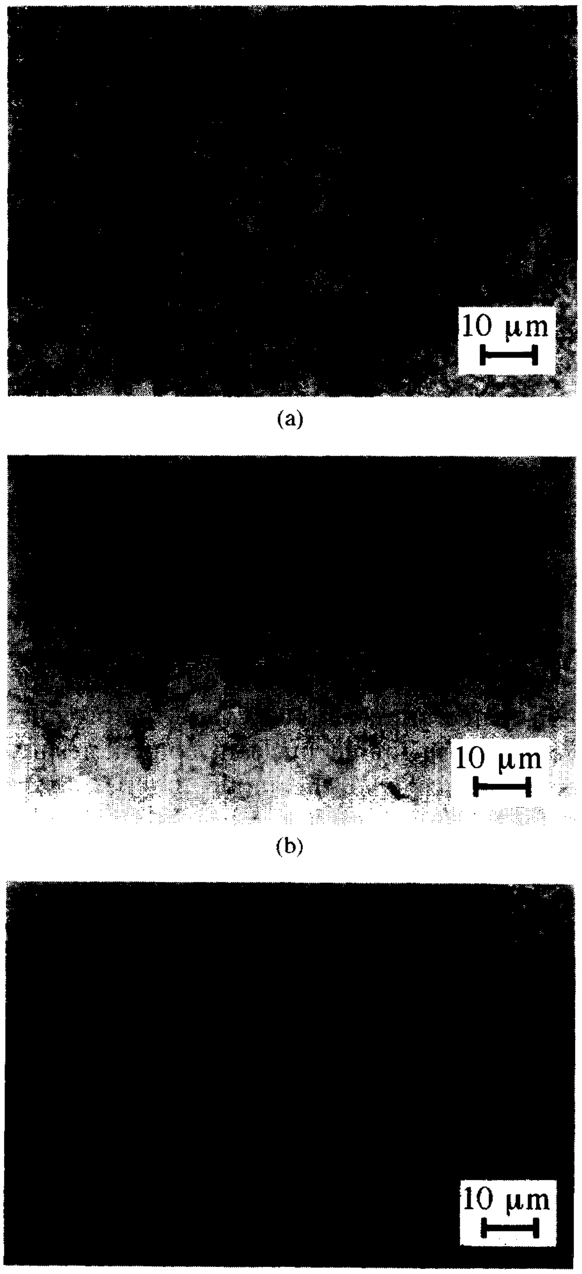
solid solution of the gehlenite and akermanite phases belonging to the melilite group.

Optical microscopy investigations were conducted in order to obtain better understanding of the morphology and size of the resultant microstructure. Figures 3(a) and (b) are typical optical micrographs of the slag glass-ceramic nucleated at 725°C for 18 h and crystallized at 950°C containing 3 and 5% TiO_2, respectively. As seen in Fig. 3(a), 3% TiO_2 coupled with a low crystallization temperature of 950°C is not sufficient to induce bulk crystallization. Large crystals of average sizes of 10–15 μm have been formed indicating the fact that surface crystallization is predominant. As seen in Fig. 3(b), although an increase in the nucleant content (5% TiO_2) results in an average grain size of 4–6 μm, this sample is still far from optimization. In other words, since the transformation to melilite solid solution of akermanite and gehlenite does not take place, inherent surface crystallization becomes predominant over bulk heterogeneous crystallization at low crystallization temperatures (950°C) resulting in large crystalline sizes. Further, it can be inferred that due to slower transformation kinetics at 950°C, some glassy regions might still be retained in the nucleant containing glass-ceramic materials. In order to test this hypothesis, using the method of Ohlberg and Strickler,[26] the amount of glassy regions in the glass-ceramics (containing both 3 and 5% TiO_2 nucleant) crystallized at 950°C was predicted as 8–10%. It is likely that the glassy regions will vanish as the transformation of merwinite to the melilite solid solution is completed at the crystallization temperature of 1100°C.


(a)

(b)

Fig. 3. Representative optical micrographs of the slag glass-ceramics nucleated at 725°C for 18 h followed by crystallization at 950°C for 12 min comprising : (a) 3 wt% TiO_2 and (b) 5 wt% TiO_2.



(a)

(b)

(c)

Fig. 4. Representative optical micrographs of : (a) slag (containing 0·44 wt% TiO_2) nucleated at 725°C for 18 h and crystallized at 1100°C, slag-based glass-ceramics containing (b) 3 wt% TiO_2 and (c) 5 wt% TiO_2 nucleated at 725°C for 18 h and crystallized at 1100°C for 12 min.

Figures 4(a), (b) and (c) are respective representative optical micrographs of the slag material and slag-based glass-ceramics containing 3% and 5%

TiO_2 subjected to nucleation heat-treatment at 725°C for 18 h followed by crystallization at 1100°C for 12 min. The centrosymmetric and large spherulitic crystals seen in Fig. 4(a) are developed by undesired surface crystallization effects and are the consequence of having a deficient amount of TiO_2 in the slag-based material. An increase in the nucleant content automatically increases the amount of sites required for heterogeneous nucleation and consequently the average distance between the nucleating sites decreases. The average crystalline grain size is about 4–5 μm for the 3% TiO_2 containing slag (Fig. 4(b)). A further increase in the nucleant amount causes an extremely fine microstructure, as can be seen in Fig. 4(c) for the case of 5% TiO_2. Here, the average grain size is stabilized around 1–2 μm and thus this sample depicts the optimized heat in terms of titania composition. In the light of microstructural observations, it can be stated that the combination of crystallization at a high temperature of 1100°C and the progressive increase in the titania nucleant content results in finer grain size and the mode of crystallization undergoes a transition from surface to bulk volume crystallization, a further consequence of more uniform nucleant dispersing in the microstructure. In other words, crystallization mode of spherulites changes to refined and equiaxed shapes due to increased concentration of the added nucleant.

It is expected that differences in thermal results and in microstructural characterizations will reflect upon differences in the resultant mechanical properties of the slag-based glass-ceramic materials crystallized at two different crystallization temperatures. For this reason, it was decided to carry out a combination of mechanical tests to determine the microhardness, 3-point bending, wear and fracture toughness properties. In the following section, the mechanical properties of slag-based glass-ceramics crystallized at 950 and 1100°C are presented and evaluated.

3.3 Mechanical properties

Figure 5 is the error-bar representation of the Knoop microhardness values taken from the slag glass-ceramic sample having varying amounts of titania and crystallized at 950 and 1100°C. It is clear that hardness values increase with the nucleant content for a given crystallization temperature. This is expected since in parallel with the increase in titania content, the average crystal size decreases causing an increased amount of grain boundary area and thus increased resistance to indentation. However, due to inadequate crystallization, a maximum value of only 870 kg mm^{-2} is achieved for the glass-ceramic containing 5% TiO_2 devitrified at 950°C. However, as expected, the hardness values are higher for slag glass-ceramics crystallized at T = 1100°C than for those crystallized at 950°C clearly showing the effect of temperature. Here a maximum Knoop hardness value of 1040 kg mm^{-2} is achieved for the slag-based glass-ceramic containing 5 wt%. This value is an equivalent of about 7·9 in the Mohs' scale, agrees very well with scratch hardness values of 8–8·5 Mohs' measured by Davies *et al.*[4] and is much higher than typical hardness values of floor tiles which usually range between 5 to 7 Mohs.[27]

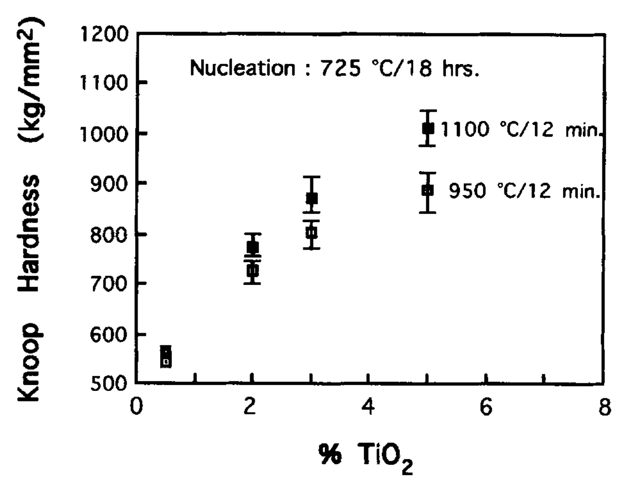


Fig. 5. Knoop microhardness values of the slag-based glass-ceramics nucleated at 725°C for 18 h followed by crystallization for 12 min. at 950°C and at 1100°C plotted as a function of the nucleant content.

Figure 6 is a graphical representation of the wear-rate values of slag-based glass-ceramics nucleated at 725°C for 18 h and crystallized respectively at 950°C and 1100°C containing varying amounts of TiO_2 added as nucleants. The wear rate decreases consistently with the increase in the nucleant content and the crystallization temperature. This expected behaviour can be attributed to

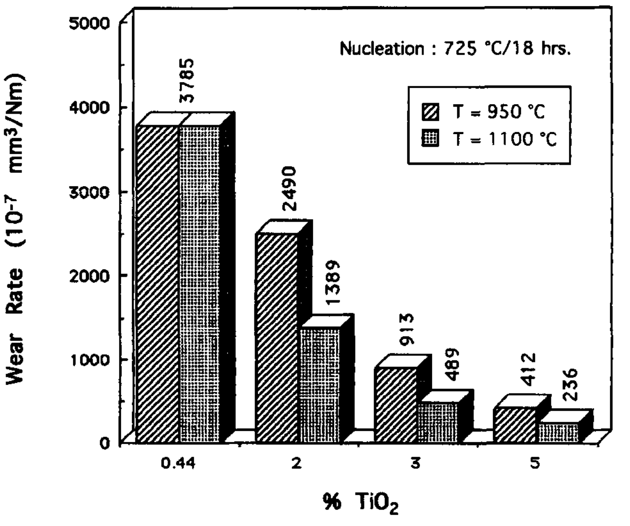


Fig. 6. Wear rate of the slag-based glass-ceramics nucleated at 725°C for 18 h followed by crystallization for 12 min. at 950°C and at 1100°C plotted as a function of the nucleant content.

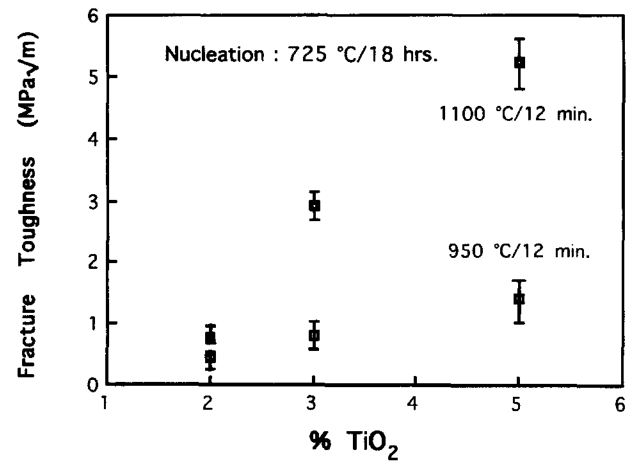


Fig. 7. Fracture toughness of the slag-based glass-ceramics nucleated at 725°C for 18 h followed by crystallization for 12 min at 950°C and at 1100°C plotted as a function of the nucleant content.

the fact that effects of both the nucleant content and temperature increase the amount of sites required for heterogeneous nucleation and volume/bulk crystallization prevails throughout the matrix glass-ceramic phase. In parallel with the increase in titania content, the average crystal size decreases causing an increased amount of grain boundary area and thus increased resistance to wear, in compliance with Hall-Petch relation. On the other hand, the measured friction values which varied between 0·25 to 0·29 were found to be insensitive to nucleant addition and crystallization temperature. Figure 7 is a plot of fracture toughness values of the slag-based glass-ceramic material as a function of the crystallization temperature and the nucleant content. As seen in Fig. 7, fracture toughness values increase slowly with the titania content for the slag glass-ceramic samples crystallized at T = 950°C whereas at T = 1100°C their increase with titania content is quite remarkable. Higher crystallization temperatures enable increased competition for crystallization thus, as shown previously, resultant volume crystallization causes the formation of fine crystallites in the microstructure.[18] The maximum value of 5·2 MPa$\sqrt{m}$ achieved for 5 wt% TiO_2 content at T = 1100°C is better than most traditional ceramics intended for floor tile applications.

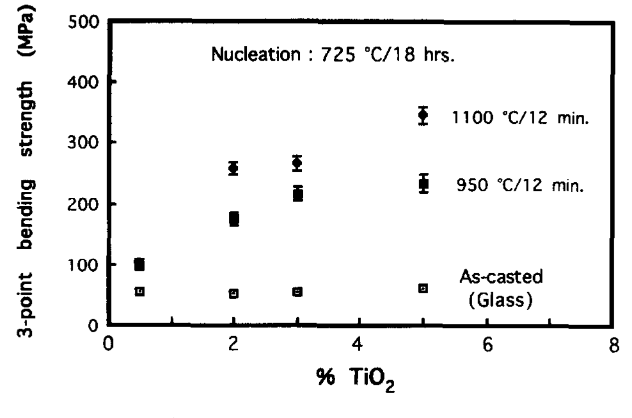


Fig. 8. Three-point bending strength of the slag-based glass-ceramics nucleated at 725°C for 18 h and crystallized for 12 min at 950°C and at 1100°C as a function of the nucleant content plotted with the respective values of as-cast glass for comparison.

Figure 8 displays the 3-point bending strength values of the slag-based glass-ceramic material as a function of the titania content and the crystallization temperature. The bending values of the as-cast glass which were also given for comparison purposes are invariant with titania addition and range between 50 to 55 MPa. On the other hand, similar to microhardness and toughness results, a maximum bending strength value of 340 MPa is achieved for the slag-based glass-ceramic comprising 5% TiO_2 and crystallized at 1100°C. This value is about 7·5× the overall bending strength of an ordinary floor tile.

4 Conclusions

On the basis of characterization investigations and mechanical properties, slag-based glass-ceramics have been found to be quite sensitive to nucleant addition and increases in crystallization temperatures. Based on the results reported in the present investigation, the following conclusions can be drawn:

(1) The devitrification of slag-based glass-ceramics involves the formation of the gehlenite and merwinite phases and retained glassy regions at temperatures less than 1000°C, followed by complete transformation to a melilite solid solution of akermanite and gehlenite phases at temperatures larger than 1000°C.
(2) Whereas large crystalline grains with some retained glassy regions inherent of surface crystallization exist in glass-ceramics crystallized at 950°C, crystalline size decreases progressively with increasing titania content for glass-ceramics crystallized at 1100°C.
(3) The progressive decrease in the grain size with increases in the titania nucleant content and crystallization temperature results in overall increases in mechanical properties such as microhardness,resistance to wear, fracture toughness and bending strength.
(4) The slag-based glass-ceramic material with optimum properties for the present study is the one containing 5% titania as nucleant crystallized at 1100°C. This sample has a bending strength of 340 MPa, a fracture

toughness of 5·2 MPa$\sqrt{m}$, a microhardness value of 1020 kg mm^{-2} and/or 7·9 Mohs and a wear resistance of $2{\cdot}36 \times 10^5$ mm^{3}Nm^{-1}.

Overall, slag-based glass-ceramic materials are excellent candidates for interior and exterior wall cladding and/or as ordinary floor tile applications.

Acknowledgements

The author would like to acknowledge the contribution of several people at the Materials Science department of Marmara Research Center, namely Mr Remzi Ersoy, Mr Ergin Kaymak and Mr Yılmaz Emre in carrying out the melting, casting and heat-treatment procedures. The author wishes to thank his colleagues Dr Seher Kımıkoğlu and Mr Mehmet Taşar for useful discussions regarding this work and Mr Metin Tanoğlu for his help in microhardness testing. In addition, Dr Sakin Zeytin for his help in metallography and optical reflection microscope investigations and Ms Zülal Mısırlı for her contribution in conducting electron microscope experiments are gratefully acknowledged.

References

1. Klemantaski, S., Archibald, W. A., Scholes, S., Sikorski, A. P. and Rogers, P. S., British Patent 986289, 1965.
2. Löcsei, B. P., Acid resistance of vitroceramic materials on a Feldspar-Diopside base. In *Symposium on Nucleation and Crystallization in Glasses and Melts*, ed. M. K. Reser, M. K. G. Smith, G. and Insley, H. American Ceramic Society, 1964, pp. 71–74.
3. Kitaigorodskii, I. I., Glass crystalline substances frommetallurgical slag, German Patent 1496570, 1970.
4. Davies, M. W., Kerrison, B., Gross, W. E., Robson, W. J. and Wichell, D. F., Slagceram: a glass-ceramic from blastfurnace slag. *Journal of Iron Steel Inst.*, 1970, **208**(4), 348–370.
5. Davies, M. W., Hazeldean, G. S. F. and Robson, M. J., Nucleation and crystallization in Fe-S and Fe-Cr containing glass-ceramics based on slag. In *Science of Ceramics*, ed. C., Brosset and E., Knopp Swedish Institute for Silicate Research, Gothenburg, 1970.
6. Bondarev, K. T., Slag-Sitall—a material of the future. In *9th International Congress on Glass. Versailles*, 1971, p. 1237.
7. Berezhnoi, A. I., *Glass-Ceramics and Photo-Sitalls*. Plenum Press, New York - London, 1972, p. 257–262.
8. Scholes, S., Glass Ceramics in U.S.S.R. *The Glass Industry*, 1974, III(1), 14–15.
9. Scholes, S., Glass Ceramics in U.S.S.R. *The Glass Industry*, 1974, III(2), 20–21.
10. Scholes, S., Glass Ceramics in U.S.S.R. *The Glass Industry*, 1974, III(3), 10–11.
11. Mulevanov, S. V. and Bliskovskii, V. Z., Sitalls from beneficiation wastes of phosphorite ores. *Steklo i Keramika*, 1987, **11**, 11–13.
12. Topping, J. A., The fabrication of glass-ceramic materials based on blast furnace slag—a review. *Journal of the Canadian Ceramic Society*, 1976, **45**, 63–67.
13. O'Keefe, J., How blast furnace slag is being turned into profit. *Canadian Machinery and Metalworking*, 1975, **8**, 48–49.
14. McMillan, P. W., *Glass-Ceramics*, Academic Press, London, 1964.
15. Stookey, S. D. Method of making ceramics and product thereof. US Patent 2920971, 1960.
16. Takehara, T., Method of manufacturing porcelain articles by crystallizing glass materials. US Patent 3170780, 1965.
17. Beall, G. H. and Duke, D. A. In *Glass: Science and Technology, Vol. 1*, ed. D. R. Uhlmann and N. J. Kreidl. Academic Press, New York, 1983, pp. 403–445.
18. Öveçoğlu, M. L., Kımıkoğlu, S. and Taşar, M. S., Development and Characterization investigations of titania nucleated slag-based glass-ceramics. In *International Ceramics Congress Proceedings-Istanbul*, ed. M. L. Öveçoğlu. Turkish Ceramic Society, Istanbul, 1992, pp. 108–118.
19. Ponton, C. P. and Rawlings, R. D., Vickers Indentation Fracture toughness test—Part 1. Review of literature and formulation of standardized indentation toughness equations. *Materials Science and Technology*, 1989, **5**, 865–871.
20. ASTM G 99-90, Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus.
21. Powder Diffraction File, Card no. 35-755, 1992 Database Edition, Joint Committee on Powder Diffraction Standards, Swathmore, PA, USA.
22. Powder diffraction file, card no. 25-161, 1992 database edition, Joint Committee on Powder Diffraction Standards, Swathmore, PA, USA.
23. Orsini, P. G., Ceramic materials from blast furnace slags: microstructure and microfractography. *Chim. Ind. (Milan)*, 1968, **50**(3), 297–302.
24. Orsini, P. G., Buri, A. and Marotta, A., Devitrification of Glasses in the Akermanite-Gehlenite System. *Journal Am. Ceram. Soc.*, 1975, **58**(7–8), 306–311.
25. Powder diffraction file, card no. 35-592, 1992 database edition, Joint Committee on Powder Diffraction Standards, Swathmore, PA, USA.
26. Ohlberg, S. M. and Strickler, D. W., Determination of percent crystallinity of partly devitrified glass by X-ray diffraction. *Jr. Amer. Ceram. Soc.*, 1962, **45**(4), 170–171.
27. McClintock, F. A. and Argon, A. S., *Mechanical Behaviour of Materials*. Addison-Wesley, Menlo Park, 1966, pp. 446, 450.