

A Glass-Ceramic Derived from High TiO₂-Containing Slag: Microstructural Development and Mechanical Behaviour

Jeremy P. Wu^{1*}, Ivo Dlouhy², Zdenek Chlup², Rees D. Rawlings¹, Aldo R. Boccaccini^{1†} &

¹ Department of Materials, Faculty of Engineering, Imperial College London, London SW7 2AZ, United Kingdom

² Brittle Fracture Group, Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Zizkova 22, CZ-61662 Brno, Czech Republic

* Supported by Tertiary Education Commission of New Zealand, fracture toughness results have been obtained within the project of Czech Science Foundation Nr. 106/05/0495. In addition, financial support from EU-KMM-NoE (Network of Excellence) is acknowledged.

† Corresponding author: Aldo R. Boccaccini, e-mail: a.boccaccini@imperial.ac.uk

& MEMBER, AMERICAN CERAMIC SOCIETY

Abstract

A novel glass-ceramic material was developed from the melt of a TiO₂-containing iron-making slag with additional waste glass. The high percentage (~20wt% TiO₂) of this network-modifying oxide has promoted a crystallisation of the parent glass, resulting in a fine-grained, homogeneous polycrystalline material with high mechanical properties (E = ~120 GPa, flexural strength = ~180 MPa, and Vicker's hardness = 7 GPa) after a heat-treatment at 1100°C for 2 hours. The room temperature (RT) and elevated temperature fracture toughness were also studied. The main crystalline phases of the glass-ceramic material were of the pyroxene series until heat-treatment temperature reached 1000°C, at which titanium-rich perovskite and armalcolite crystals became the dominant phases. The end material is high-strength, aesthetically acceptable (metallic grey or opaque brown coloured), and suitable for structural and architectural applications.

1 Introduction

Finding uses for metallurgical slag is an important issue for the steel industry from both an economic and environmental point of view. Millions of tonnes of slag are produced around the world, so its disposal in special dumpsites is costly and it is not a sustainable solution. These slags consist mainly of CaO, SiO₂, Al₂O₃ and MgO, together with minor constituents such as MnO, Fe₂O₃ and S. Blast-furnace slag was the first silicate waste to be thoroughly investigated as a raw material for glass-ceramics production in the late 1960s and early 1970s.¹⁻³ It has now been established that a wide range of silicate-rich wastes, including coal ash^{4,5}, incinerator filter ash^{6, 7}, and red mud from zinc hydrometallurgy⁸, can be reused in the production of glass-ceramic materials. It is also known that glasses containing from about 2 to 20 wt% TiO₂

crystallise with the formation of uniform fine-grained microstructures⁹⁻¹¹. The optimum amount of TiO₂ is dependent on the composition of the glass, and increases with decreasing SiO₂ content. However, the presence of more than 20wt% TiO₂ can lead to the precipitation of TiO₂ crystals and a decrease in the nucleation and growth of the desired crystalline phases.

Development of “Silceram” glass-ceramics at Imperial College London, United Kingdom, in the 1980s was aimed at reducing the production costs of glass-ceramics from slags by simplifying the heat treatments required for crystallisation.^{12,13} A study by Rogers et al¹² indicated that rather than reheating the parent glass to 950°C, it would be feasible to cool it (after shaping) from a high temperature to the heat treatment temperature, resulting in an energy saving of about 60% when compared to the conventional heat-treatment. It has also been suggested that if the production plant was situated at a steelworks, then significant additional savings could also be made in the energy requirements as hot slag could be used directly as the raw material.¹³

SteelServ Limited (New Zealand), who supplied the slag material for this research work, cooperates with the steel mill in Glenbrook, New Zealand, on slag reduction. One of the by-products of New Zealand steel manufacturing industry, iron-making melter slag, is unique with regards to its composition (>30wt% TiO₂ by chemical analysis). Instead of iron ore, black ironsands from the west coast of New Zealand’s North Island is used as the starting material for the local iron and steel industry. The iron slag is formed by fusion of limestone, ash and other fluxes added to the original ironsand that contains mainly titanomagnetite. Even though slag is not a waste of serious concern in New Zealand, significant amount of effort is being made to establish alternative solutions to utilise such a waste instead of relying on conventional landfill disposals. This study is driven by the need to highlight practical use of slag in glass-ceramic

production and the uniqueness of the chemical composition of the slag chosen from a scientific point of view.

Conventionally, a nucleating agent is added to the glass composition for nucleation of crystals within the bulk material to occur efficiently, resulting in a large number of micro or nano-sized crystals. However, through the natural presence of rich TiO_2 in the present slag, it is hoped that a fine-grained microstructure can be obtained, and a high-strength glass-ceramic can be consequently produced without additional nucleating agents. This paper delves into the microstructural analysis of the waste-derived glass-ceramic material (60wt% slag and 40wt% glass cullet) as well as a detailed investigation of its physical and mechanical properties.

2 Experimental

2.1 Raw materials, melting and sample preparation

Crushed waste bottle glass, of soda-lime silica composition, was used as additive to lower the melting temperature of the iron-making slag. The uniqueness of the melter slag and its glass-ceramic material in this study (now referred as MS40G) was the significantly higher percentage of TiO_2 than in a typical blast furnace slag¹⁴ as shown in Table I. Energy dispersive X-ray analysis (EDAX) confirmed the chemical composition of MS40G as similar to the calculated composition from the proportion of the raw components. Some of the minor elements that were undetectable by EDAX are missing in the table. Preliminary experimental results showed that 40wt% of glass cullet is an appropriate amount to be added to the as-received slag for producing a stable amorphous material. The as-received slag was mixed with the glass and milled for 5 minutes to reduce the overall particle size for ease of melting. Electric furnaces were used for both the melting and subsequent heat-treatment of the materials. The parent glass was obtained

by melting the mixture at 1450°C for 2 hours in alumina crucibles and then poured into a preheated graphite mould and annealed at 600°C for 5h before cooling down to room temperature inside the annealing furnace. Part of the as-cast glass was crushed into coarse (> 2 mm) particles and some of these were then milled into fine powder (< 50 µm). Both coarse and fine particles were examined by thermal analysis. The rest of the as-cast glass was heat-treated at temperatures of 900°C and 1100°C for 2h before being cut into test bars, for mechanical testing, of 30x4x3mm³ with a Struers Accutom apparatus equipped with a high-speed diamond wheel.

2.2 Differential thermal analysis

The glass crystallisation behaviour was investigated with differential thermal analysis (DTA; STA-780, Staton Redcroft Thermal Analyser, Labtherm Scientific, UK) of both powder and bulk samples of equal weights (~ 35 mg) at a heating rate of 10 K min⁻¹ in air. Alumina powder was used as the reference material during a controlled temperature programme.

2.3 X-ray diffractometry

The crystalline phases were identified using X-ray diffraction (XRD; Philips X-ray diffractometer PW2273/20 with PW1729 X-ray generator, the Netherlands), using CuK α radiation in the 2 θ range from 15° to 75° on powdered samples before and after heat-treatment. The standard scan consisted of a step size of 0.04° with a 2-second hold per step. High-temperature XRD (HT-XRD; Philips X'Pert equipped with a conduction/radiation furnace capable of temperatures up to 1000°C, the Netherlands) was also used to investigate the crystallisation behaviour of the as-cast glass powder and the evolution of the crystalline phases

with increasing temperature. Measurement was carried out in the 2θ range from 15° to 45° on a thin layer of powdered sample on heated platinum substrate. A step size of 0.04° with 5-second hold per step was used. An initial measurement was taken at room temperature, after which the first high-temperature scan was taken at 600°C (set temperature), and then a scan was taken with every 25°C increase up to 900°C .

2.4 Scanning electron microscopy

Microstructural analysis was performed on pieces of the different glass-ceramics embedded in epoxy resin, ground with silicon carbide paper, then polished with diamond paste ($1\mu\text{m}$), and finally coated with a thin layer of gold or carbon. In addition, a 2vol% HF solution was used as the etching medium to enhance the grain structure by immersing the polished specimens in the solution for 20 seconds and thus removing sufficient amount of residual glass. Scanning electron microscopy (SEM; JSM 5610LV, JEOL), was used in both secondary electron and backscattered electron modes. SEM (JSM 840, JEOL), coupled with EDAX was used to study, in particular, the chemical composition of the glass and the glass-ceramics produced.

2.5 Physical and mechanical properties measurements

The density of bulk specimens was measured using the Archimedes principle in water. A Netzsch dilatometer (402E, Netzsch) was employed to measure the coefficient of thermal expansion of the glass-ceramic material using solid bar specimens of dimension 25 mm in length and typically 25 mm^2 symmetrical cross-section. The modulus of elasticity was determined using the impulse excitation technique (Mk5 Grindosonic, J.W. Lemmens Ltd, Belgium). Microhardness tester (Zwick/Roell Indentec ZHV, at 500g load, 10s) integrated with computer

software was used for determination of microhardness as well as indentation fracture toughness. Based on the work by Ponton and Rawlings¹⁵ on a range of equations for calculating the fracture toughness directly from indentation crack length, an equation derived by Anstis et al (1976) was used to calculate indentation fracture toughness (K_C):

$$K_C = 0.016 \times \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (1)$$

Where E is Young's modulus, H is Vickers hardness value, P is the indenter load and c is the mean surface radial crack length measured optically. Each reported value is the average of ten indentations made on each specimen.

For fracture toughness (K_{IC}) determination, the Chevron notch technique was used in conjunction with 3-point bending test. Measurements at room and elevated temperature were carried out. The reliability of this technique on glass specimens has been demonstrated by Boccaccini et al.¹⁶ The cross-sectional dimensions of the bars were 3mm by 4mm. Chevron notches were cut on each sample by a thin diamond wheel saw (thickness = 0.2mm). A Zwick Z50 testing machine equipped with high temperature furnace (up to 1200°C) was used. The heating rate was 8-10 K min⁻¹, the holding time at the test temperature before starting the test was 15 minutes. The temperature was measured by two independent systems: the furnace control system, which measures and controls the temperature in the three zones, and by another thermocouple located directly on the specimen surface.

Special high-temperature fixtures allowing deflection measurements on the test piece were used. The crosshead speed was 0.01 mm per minute and the load cell capacity was 1kN. After testing, the sample fragments were removed by means of tweezers and put on a ceramic pad for normal

cooling. Graphs of load versus deflection were recorded and the fracture toughness was calculated from the maximum load (F_{max}) and the corresponding minimum value of geometrical compliance function (Y_{min}^*) using the following equation¹⁶:

$$K_{Ic} = \frac{F_{max}}{BW^{1/2}} Y_{min}^* \quad (2)$$

where B and W are the width and height of the specimens, respectively. The calculation of the function Y_{min}^* for chevron notched bars was based on the Bluhm's slice model, as reported in earlier publications.¹⁷ The initial notch depths necessary for fracture toughness determination were measured from optical macrographs by "Vtip" image analysis software. The software (supplied by TESCAN company) enabled optimisation of optical macrographs capturing and direct quantitative measurements on digital pictures of fracture surfaces.

The flexural strength (σ) was measured using 3-point bend test (H5KS, Hounsfield tensile/compression testing machine), loading at 0.5 mm per minute, and using a span of 20 mm.

The following expression was used for calculating the flexural strength:

$$\sigma = \frac{3F_{max}L}{2BW^2} \quad (3)$$

where F_{max} is the load at fracture, L is the span (20 mm), W is the height and B is the width of the sample. The nominal dimensions of the specimens were: 35 mm in length and a cross-section of 3 mm by 4 mm. The surfaces of the specimens were polished to a 1 μ m diamond paste finish. At least 10 samples were tested for each condition.

The compression strength (plate to plate) was recorded using a Zwick Benchtop tensile/compression tester with a 10 kN load cell at a crosshead speed of 0.5 mm per minute. Five samples were used for the measurements, sample dimensions were approximately 6×3×3 mm³.

3 Results and Discussion

3.1 Thermal analysis

Powder samples of different specific area (different particle size) were studied by DTA to determine the nature of crystallisation mechanism. Fig. 1 shows the DTA curves for finely (< 50 µm) powdered and coarse (> 2 mm) particles (termed 'bulk' in Fig. 1). The first transition was an endothermic trough approaching 700°C associated with the glass transition temperature. The next visible transition is two minor peaks (at around 770°C and 810°C) followed by a major peak at about 840°C corresponding to the main crystallisation process. No further exothermic transitions were visible at higher temperatures, suggesting that the glass can be converted into a glass-ceramic at a relatively low temperature. Finally, an endothermic reaction at ~1070°C, which was originally presumed to be the melting of the glass, may have been in fact the dissolution of a particular crystalline phase since the resulting sample did not melt. The curves for both samples were similar (indeed the measured differences in peak temperatures were probably within experimental error considering the different morphology of the samples and hence different sample-thermocouple contact) indicating that the specific area of the sample was not significantly affecting any of the reactions. Consistent with the DTA results were the scanning electron microscopy observations which showed that surface crystallisation was not extensive and that the crystallisation process was dominated by internal (bulk) nucleation.

Fig. 2 shows three DTA curves terminated at the end of each crystallisation peak and illustrates the reproducibility of the thermal analysis data, and Fig. 3 shows the corresponding XRD plots of samples heat-treated at the temperature of each peak, indicating the crystalline phase(s) present at each stage.

Examining Fig. 3, it is clear that the degree of crystallisation is small after the first two exothermic peaks and it is difficult to conclude which phases were present. At the end of the last exothermic reaction, the XRD plot clearly indicates the presence of nepheline ($\text{NaAlSi}_3\text{O}_8$) and diopside ($\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$) from the pyroxene group. Extensive XRD analysis, in particular, high-temperature XRD was carried out to determine how each crystalline phase evolves with time and during prolonged heat-treatments, as shown next.

3.2 X-ray diffraction and microstructural analysis

XRD analysis of powdered samples from heat-treatment at various temperatures (Fig. 4) suggests that the first crystalline phases to precipitate after heat-treatment at 850-900°C (for an hour) are of the pyroxene series. This is in agreement with XRD results (Fig. 3) on samples from interrupted DTA runs in which both nepheline and diopside phases were detected. At 900°C, calcium titanate (perovskite, CaTiO_3) began to precipitate in increasing amount with increasing heat-treatment temperature. The most dramatic change occurred at 1100°C, where the relative amount of pyroxene crystals has dropped dramatically. This may account for the endothermic reaction at 1070°C shown in the DTA plot (Fig. 1), i.e. the final endothermic transition was caused by the dissolution of pyroxene crystals rather than melting of the material. Meanwhile, another titanium-rich phase, armalcolite ($\text{FeMgTi}_4\text{O}_{10}$), formed and became the main crystalline phase in the material at temperatures over 1000°C although there was no evidence of this

reaction in the DTA data. The sequence of crystalline phase evolution with increasing temperature originally derived from the standard XRD analysis is well supported by HT-XRD analysis, as shown in Fig. 5. It should be noted that the set temperature of the HT-XRD furnace, which are the temperatures quoted in Fig. 5, can be 100-150°C lower than the actual temperature of the specimen. Taking this into account, it was seen that the precipitation of Ti-rich phases, such as armalcolite and perovskite, do not occur until temperatures of around 900-950°C (actual temperature), which agrees with the results from standard XRD analysis (Fig. 4).

SEM micrographs of relevant glass-ceramic microstructures are shown in Fig. 6. Fig. 6(a) shows an etched surface of the heat-treated MS40G at 900°C. The dark voids are the residual glass phase that was removed during etching. However, the two crystalline phases (nepheline and diopside), which were detected by XRD, cannot be differentiated under SEM. A significant amount of titanium-rich phases (perovskite and armalcolite) were visible as brighter phases when the glass-ceramic material was heat-treated at temperatures above 1000°C. The image in Fig. 6(b) corresponds to the material that was heat-treated at 1100°C; the microstructure consists of clusters of irregular shaped calcium titanate perovskite crystals distributed throughout the multiphase matrix (pyroxene, titanium-rich armalcolite and residual glass). The multiphase matrix is shown in detail in Figs. 6(c) and (d), where the most noticeable feature is the light-coloured acicular armalcolite crystals embedded in the original pyroxene-and-glass matrix. Fig. 7(a) shows the room temperature fracture surface of sample MS40G heat-treated at 1100°C. Unlike typical fracture surfaces of brittle material, the fracture surface of this glass-ceramic material is rugged. Further microscopic examination on a polished surface with a crack initiated from Vickers' hardness indentation (Fig. 7(b)) confirms crack deflections and was consistent with the rugged fracture surface.

3.3 Physical and mechanical properties

A range of experiments, including 3-point bending test, Vickers' hardness indentation, dilatometry, and compression strength test were conducted to determine physical and mechanical properties of the resulting glass-ceramic. The results for the glass and glass-ceramics heat-treated at 900°C and 1100°C for 2h are given in Table II. Crystallisation yielded a material with better mechanical properties than the parent glass. The increase in heat-treatment temperature, which resulted in the precipitation of titanium-rich phases, also had a positive effect on the room-temperature mechanical properties of the glass-ceramic material, except for the hardness. As mentioned before, XRD showed the reduction in the relative ratio between pyroxene and titanium-rich phases (Fig. 4), which may explain the reduction in the apparent density, thermal expansion coefficient, and hardness.

The slight improvement in the indentation fracture toughness of the glass-ceramic material may be caused by presence of one of the titanium-rich crystals, armalcolite, because of its high aspect ratio. A crack will therefore have to travel around these crystals in order to propagate further. Hence, the fracture toughness improves as it takes higher energy for a crack to propagate.

The behaviour of the glass-ceramic material (heat-treated at 1100°C) at elevated temperatures was examined during the determination of fracture toughness by Chevron-notched specimen technique. Tests were firstly carried out at room temperature and at 500°C. The fracture toughness slightly decreased with increasing temperature up to 500°C (Fig. 8). There was an acceptable scatter of data from all measurement and the mean values give a trend of variation of K_{IC} ($1.35 \pm 0.12 \text{ MPa m}^{1/2}$ at room temperature comparing to $1.13 \pm 0.20 \text{ MPa m}^{1/2}$ at 500°C). A standard Student's t-test was carried out on the two datasets with the hypothesis that the data

ranges overlap by chance. The result, however, showed that the difference in the fracture toughness values between room temperature and 500°C was significant and thus the hypothesis was rejected. The decrease in fracture toughness was surprising as it is unlikely that the elastic modulus decreases significantly over that temperature range. An earlier study on a monolithic lithium aluminosilicate (LAS) glass-ceramic by Brennan and Prewo¹⁸ has shown that the elastic modulus has minimal reduction and the fracture toughness of the material remained constant from room temperature to 800°C.

Fig. 9 shows a typical load-displacement trace of a Chevron notched specimen tested by 3-point bending. In the case of high temperature tests, a very sharp trace can be seen. This is associated with poorer function of the Chevron notch tip (higher accommodation of elastic energy in the system of specimen and machine). However, there is still some small departure from the linearity showing that crack initiation occurred before reaching the maximum load and data obtained from these records have been taken as valid.

Samples were also tested at temperatures close to the glass transition temperature (650°C and 730°C). There was an increase of fracture toughness when the test temperature was higher than 500°C. This phenomenon was observed for the fracture strength measurements of Brennan and Prewo, however, the fracture toughness of their LAS monolithic glass-ceramic material did not follow the same trend but remained constant up to 1000°C.¹⁸

In general, the possible toughening mechanisms based on crack blunting, induced by the softening of the residual glass phase at $T > 500^\circ\text{C}$, in addition to some extent of crack deflection, can be supported by the series of SEM images shown in Fig. 10, where the fracture surfaces appeared much more rounded in samples tested in at elevated temperatures in comparison to those of samples tested at room temperature. In theory, at temperatures well beyond the glass

transition temperature, the residual glassy phase within the matrix should become too low in viscosity. Hence, the effective flexural strength will drop off significantly.

Additional tests were carried out at a temperature of 800°C. The results (also shown in Fig. 8) exhibit a very large scatter and thus they are only indicative of a complex material behaviour at that temperature. The possibility of microstructural changes at elevated temperature, which led to the marked fluctuation of measured fracture toughness values, has been ruled out by additional thermal analysis on the heat-treated glass-ceramic. Results showed that there was no apparent phase transformation up to a temperature of ~870°C. Because of the inhomogeneous nature of the starting waste material, perhaps small variations in the overall composition of the parent glass and/or slight changes in the degree of crystallisation results in sufficient variation in the proportion and/or composition of the residual glass to account for the scatter at this temperature. Further work needs to be carried out in order to understand the true behaviour of the material at temperatures above the glass transition temperature.

Overall, the present samples exhibited similar or comparable mechanical properties in comparison with other glass-ceramics produced from silicate waste from which a reasonable amount of data was available, as summarised in Table II. For technical applications, however, other technological properties need to be assessed, which include wear and thermal shock resistance as well as machinability.

4 Conclusion

A glass-ceramic material was successfully obtained from a parent glass made from an unusual TiO₂-containing slag material with additional waste glass cullet. The resulting polycrystalline material possesses high hardness, Young's modulus, flexural and compressive strengths and

good fracture toughness. The overall performance of the material is optimized when heat-treated at higher temperatures at which the precipitation of titanium-rich phases occurs, prompting the possibility of tailoring material properties by heat-treatment. K_{IC} measurement at elevated temperature has been carried out on these waste-derived silicate glass-ceramics, which will be relevant if these materials will find applications in specialised high-temperature applications. The end product has the potential to be used as load-bearing structural components, e.g. high-temperature resistant machine elements, as well as wear resistant components in the architectural and building industry.

Acknowledgements

The authors would like to thank SteelServ Ltd in Glenbrook, New Zealand for supplying slag and relevant information regarding the material. The authors also like to thank Richard Sweeney for his contribution in discussions and technical assistance in particular in HT-XRD analysis.

References

- ¹ M.W. Davies, G.S.F. Hazeldean, and W.J. Robson, "Science of Ceramics"; Edited by C. Brosset and E. Knopp. Swedish Institute of Silicate Research, Gothenburg, 1970
- ² M.W. Davies, B. Kerrison, W.E. Gross, W.J. Robson, and D.F. Wichell, "Slagceram: a glass-ceramic from blast-furnace slag", *J. Iron Steel Institute*, 208 [4] 348-370 (1970).
- ³ N.M. Pavlushkin, Principles of Sital Technology. Mashinostroenie, Moscow. (In Russian), 1970.
- ⁴ E.J. DeGuire and S.H. Risbud, "Crystallization and properties of glasses prepared from Illinois coal fly ash", *J. Mater. Sci.*, 19 1760-1766 (1984).
- ⁵ A.R. Boccaccini, M. Bucker, and J. Bossert, "Glass and Glass-Ceramics from Coal Fly-Ash and Waste Glass", *Tile & Brick International*, 12 [6] 515-518 (1996).
- ⁶ A.R. Boccaccini, M. Kopf, and W. Stumpfe, "Glass-Ceramics From Filter Dusts From Waste Incinerators", *Ceramics International*, 21 [4] 231-235 (1995).
- ⁷ M. Romero, R.D. Rawlings, and J.M. Rincon, "Development of a New Glass-Ceramic by Means of Controlled Vitrification and Crystallisation of Inorganic Wastes from Urban Incineration", *J. Eur. Ceram. Soc.*, 19 [12] 2049-2058 (1999).
- ⁸ M. Pelino, C. Cantalini, F. Veglio, and P.P. Plescia, "Crystallization of Glasses Obtained by Recycling Goethite Industrial-Wastes to Produce Glass-Ceramic Materials", *J. Mater. Sci.*, 29 [8] 2087-2094 (1994).
- ⁹ G.H. Beall and D.A. Duke, "Glass-Forming Systems"; pp. 403-445 in *Glass Science and Technology*. Edited by D.R. Uhlmann and N.J. Kreidl. Academic Press, Inc., New York, 1983.
- ¹⁰ P.W. McMillan, "Glass-Ceramics", 2nd ed. Non-Metallic Solids, Vol. 1., edited by J.P. Roberts. Academic Press Inc., London, 1979.

- ¹¹ Strnad, Z., “Glass-ceramic materials: liquid phase separation, nucleation and crystallization in glasses”, *Glass Science and Technology*. Vol. 8. Elsevier, Amsterdam, 1986.
- ¹² P.S. Rogers, J. Williamson, J.F. Bell, and M. Campbell, “Ceramic Materials from Molten Blast-furnace Slag by Direct Controlled Cooling”, Commission of the European Communities, Energy R&D Programme - Energy Conservation, Final Report, EUR 10389 EN, 1986.
- ¹³ P.S. Rogers, J. Williamson, J.F. Bell, and M. Campbell, Proceedings of International Seminar on Energy Conservation Industry, p.280. Edited by A. Strub and H. Ehringer. Commission of the European Communities/VDI, Dusseldorf, 1984.
- ¹⁴ C. Fredericci, E.D. Zanotto, and E.C. Ziemath, “Crystallization mechanism and properties of a blast furnace slag glass”, *Journal of Non-Crystalline Solids*, 273 [1-3] 64-75 (2000).
- ¹⁵ C.B. Ponton and R.D. Rawlings, “Vickers Indentation Fracture-Toughness Test .1. Review of Literature and Formulation of Standardized Indentation Toughness Equations”, *Materials Science and Technology*, 5 [9] 865-872 (1989).
- ¹⁶ A.R. Boccaccini, R.D. Rawlings, and I. Dlouhy, “Reliability of the Chevron-notch technique for fracture toughness determination in glass”, *Materials Science and Engineering A*, 347 [1-2] 102-108 (2003).
- ¹⁷ I. Dlouhy, M. Holzmann, J. Man, L. Valka, “The Use of Chevron Notched Specimen for Fracture Toughness Determination”, *Metallic Materials*, 32 3-13 (1994).
- ¹⁸ J.J. Brennan, K.M. Prewo, “Silicon Carbide Fibre Reinforced Glass-Ceramic Matrix Composites Exhibiting High Strength and Toughness”, *J. Mater. Sci.*, 17 [8] 2371-2383 (1982).

List of Figures

Fig. 1. Combined DTA plot of MS40G glass in bulk and powder form, each sample weighed about 35mg.

Fig. 2. DTA plots showing consistency over 3 individual runs of powder samples each weighed about 15mg.

Fig. 3. Corresponding XRD patterns (bottom to top) to the DTA peaks (left to right) of results from previous figure

Fig. 4. XRD pattern of powdered samples from bulk specimens heat-treated at 850, 900, 1000, 1100°C for 2h. ▲ perovskite ■ armalcolite ○ nepheline × diopside ◇ loveringite

Fig. 5. HT-XRD of MS40G showing the precipitation and dissolution of ▲ perovskite ■ armalcolite ○ pyroxene (nepheline and diopside) and ◇ loveringite

Fig. 6. (a) MS40G heat-treated at 900°C for 2h; (b) MS40G heat-treated at 1100°C for 2h; (c) and (d) magnified area of the matrix under secondary electron and back-scattered electron, respectively

Fig. 7. Micrographs showing (a) fracture surface of MS40G heat-treated at 1100°C for 2h; (b) microscopic crack deflection across the material.

Fig. 8. Summary plot of fracture toughness values of MS40G heat-treated at 1100°C for 2 hours with testing temperature, showing the range from the minimum to the maximum of each dataset as vertical lines, and the mean K_{IC} values as the solid horizontal lines

Fig. 9. A typical force-displacement plot of high temperature (500°C) 3-point bending test with Chevron notched MS40G beams

Fig. 10. SEM images of fracture surfaces of MS40G specimens at point of failure at (a) ambient temperature, (b) 500°C, (c) 650°C, and (d) 730°C.

Table I. Compositions (wt%) of the Raw Materials and Material Investigated

Raw Materials	Blast furnace slag ¹⁴	Iron-making melter slag (MS)	Waste bottle glass cullet (G)	Typical Silceram ¹²	Slag with 40wt% glass cullet (MS40G)	
					Calculated	EDAX
SiO ₂	35.8	12.1	72.7	48.3	36.3	32.3
Al ₂ O ₃	11.8	17.6	1.6	13.3	11.2	11.2
Fe ₂ O ₃	0.3	4.1	0.3	4.0	2.6	3.4
CaO	43.5	14.5	11	24.7	13.1	15.8
MgO	6.2	13.6	0.5	5.7	8.4	9.2
MnO	0.7	1.1	0.01	0.4	0.7	-
TiO ₂	0.8	34.3	0.04	0.6	20.6	21.0
Cr ₂ O ₃	-	-	-	0.8	-	-
K ₂ O	-	-	0.36	1.1	0.1	-
V ₂ O ₃	-	0.2	-	-	0.1	-
Na ₂ O	0.1	-	13.0	1.2	6.0	7.2

Table II. Physical and Room Temperature Mechanical Properties of MS40G glass and glass-ceramics

Material Property	Unit	Heat-treatment			Silceram ¹²	Slagsital ³
		As-cast	900°C	1100°C		
Density	g cm ⁻³	2.9	3.2	3.1	2.9	2.6-2.9
Thermal Expansion Coefficient [30-400°C]	10 ⁻⁶ K ⁻¹	9.1	10.6	9.5	7.5	6.5-8.5
Vickers' Hardness	GPa	6.5±0.1	9.1±0.2	7.8±0.2	7	-
Indentation Toughness	MPa.m ^{1/2}	0.9±0.1	1.0±0.1	1.6±0.2	-	-
Fracture Toughness	MPa.m ^{1/2}	-	-	1.4±0.1	2.1	-
Young's Modulus	GPa	103±7	125±5	121±4	122	93
Bending Strength	MPa	101±10	134±43	184±26	180	90-130
Compressive Strength	MPa	-	500±100	700±100	850	700-900