Technical Note

Preparation of glass–ceramics from molten steel slag using liquid–liquid mixing method

Kai Zhang [a,b], Jianwen Liu [a], Wanchao Liu [a], Jiakuan Yang [a,*]

[a] School of Environmental Science & Engineering, Huazhong University of Science & Technology, Wuhan, China
[b] School of Energy & Environment, Inner Mongolia University of Science & Technology, Baotou, China

ARTICLE INFO

ABSTRACT

A novel approach to prepare glass–ceramics from molten steel slag (MSS) was proposed. In laboratory, the water-quenched steel slag was melted at 1350 °C to simulate the MSS. A mixture of additive powders in wt.% (55 quartz powder, 5 Na_2O, 16 emery powder, 15 CaO, 8 MgO, 1 TiO_2) were melted into liquid at 1350 °C separately. Then the MSS and the molten additives were mixed homogeneously in order to obtain parent glass melt. The proportion of MSS in the melt was 50 wt.%. The melt was subsequently cast, annealed, heat-treated and transformed into glass–ceramics. Their microstructure and crystallization behavior were analyzed. The samples exhibited excellent properties and displayed bulk crystallization. The major crystallized phase was diopside ($(Fe_{0.35}Al_{0.20}Mg_{0.44})Ca_{0.96}(Fe_{0.08}Si_{0.70}Al_{0.20})_2O_{6.12}$), which was uniformly distributed in the microstructure. The novel approach may help iron and steel industry achieve zero disposal of steel slag with utilization of the heat energy of the MSS.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Steel slag output is approximately 20% by mass of the steel output, depending on the type of steel and corresponding production process (Liu et al., 2007; Furlani et al., 2010). The temperature of molten steel slag (MSS) discharged from metallurgical furnace is about 1300–1500 °C. The residual heat in MSS is about 1675 MJ t^{-1} (Yang and Yang, 2006). When MSS is traditionally pretreated and transformed into water-quenched steel slag (WQSS) in water-quenching process, enormous thermal-energy resource is lost, causing heat pollution and generating waste water simultaneously. Therefore, it is necessary to seek an alternative way to manufacture high-value products directly from MSS, which can also reuse energy in MSS and eliminate pollution of waste heat and waste water. Because metallurgical slag is mainly composed of valuable oxides such as silicon dioxide, alumina, and calcium oxide, using this waste to produce slag-based glass–ceramics is a promising route for the commercial utilization of WQSS (Wang and Liang, 2007; Ewais et al., 2010; Sarkar et al., 2010). Several trials of glass–ceramics based on the blast furnace slag, basic oxygen furnace slag, and open-hearth furnace slag were conducted (Ferreira et al., 2002; Gomes et al., 2002; Khater, 2002; Francis, 2004; Boccaccini et al., 2006; Mandal et al., 2006; Badiee et al., 2008; EI-Mahllawy, 2008). However, only the materials of cold WQSS were tested in previous studies, the enormous thermal energy contained in MSS

was not recovered. This leads to higher energy consumption, which is one of the most important restrictions of industrialization. In this study, glass–ceramics directly from MSS was prepared. The liquid–liquid mixing method that combines MSS with molten additives was adopted to adjust the composition of the melt. Some properties of the specimens were investigated.

2. Material and methods

WQSS samples were provided by Baosteel Group Corporation in China. SiO_2-rich quartz sand powder, Al_2O_3-rich emery powder, CaO and MgO were used as the main components of the additives. TiO_2 was added as a nucleation agent while Na_2O was added to improve the ability of glass forming. The proportion of MSS in the melt was 50 wt.%. The chemical compositions of WQSS, additive mixture and parent glass samples are shown in Table 1.

In order to adjust the chemical composition of the parent glass based on the MSS, liquid–liquid mixing method was used to mix MSS with additives homogeneously. WQSS was melted in an alumina crucible and the mixture of additive powders in wt.% (55 quartz powder, 5 Na_2O, 16 emery powder, 15 CaO, 8 MgO, 1 TiO_2) was melted in a quartz crucible respectively at 1350 °C for 1 h in a MoSi electric furnace simultaneously. Then the obtained simulated MSS was poured into the molten additive mixture. The mixture obtained this way was further heated in the furnace to allow them mixing homogeneously. Then the melt was cast into a preheated steel mold. To remove residual thermal stress, the glass

* Corresponding author. Tel.: +86 27 87792207; fax: +86 27 87792101.
E-mail address: jkyang@mail.hust.edu.cn (J. Yang).

Table 1
Chemical compositions of raw materials, additive and parent glass (wt.%).

Component	WQSS	Additive powder mixture						Parent glass
		Quartz powder 55 wt.%	Emery powder 16 wt.%	Na_2O 5 wt.%	CaO 15 wt.%	MgO 8 wt.%	TiO_2 1 wt.%	
SiO_2	11.4	94.4	0.3	–	0.7	–	–	31.7
CaO	38.3	1.1	0	–	98	–	–	26.8
Al_2O_3	2.7	0	98	–	0.4	–	–	9.2
MgO	10.6	0.2	0	–	0.3	99	–	9.3
MnO	3.5	–	0.6	–	–	–	–	1.8
P_2O_5	1.5	–	0	–	–	–	–	0.8
Cr_2O_3	0.2	–	0	–	–	–	–	0.1
TiO_2	0.8	–	0	–	–	–	99	0.9
Fe_2O_3	30.8	–	0.2	–	–	–	–	15.4
Na_2O	–	–	0	99	–	–	–	2.5
Others	0.4	4.3	0.1	1	0.6	1	1	1.5

Note: "–" means reagent concentration was lower the detection limit.

samples were annealed in a muffle furnace at 550 °C for 2 h followed by slow cooling to the room temperature.

Vickers hardness was measured in a microhardness testing machine (HV-1000Test, Instrument, Laizhou Huayin, China), with a 150 N (gf) load and 30 s loading time. The bulk density of the samples was tested by Archimedes method. Differential thermal analysis (DTA) was carried out for powdered glass specimens with NETZSCH STA 449F3 analyzer at a heating rate of 15 °C min^{-1}. The crystalline phases of the glass–ceramics samples were identified using XRD with copper target operated at 20 kV and 40 mA and in a 2θ range from 10° to 80° at the rate of 4° min^{-1}. The microstructure of the glass–ceramics was observed by SEM (Quanta 200, Holland) after coating with gold.

3. Results and discussion

The typical DTA curve of the parent glass is shown in Fig. 1, in which two endothermic peaks and two exothermal peaks are observed. The first endothermic peak is observed at 714 °C (T_g), which is attributed to the glass transition. The second endothermic peak is observed at 1241 °C (T_m), which is attributed to the glass melting. The main exothermic peak reaches a maximum at 884 °C, which may be due to the formation of crystalline phase. The minor exothermic peak is observed at 1071 °C. The exothermic peaks are associated with the crystallization of glass. Therefore, the crystalline temperature could be chosen in the range of 800–1100 °C.

Fig. 2 shows the XRD patterns of the glass–ceramics samples nucleated at 714 °C for 2 h followed by different crystallization
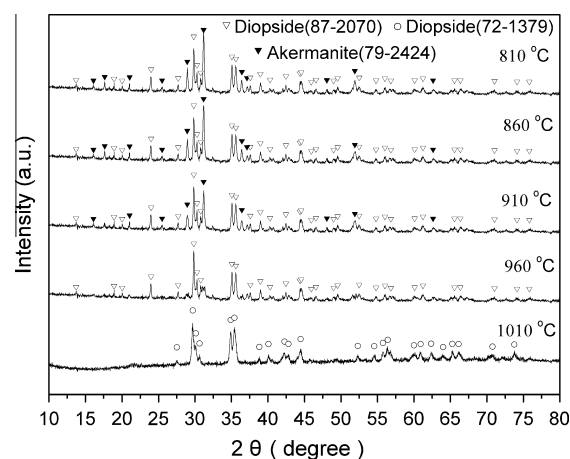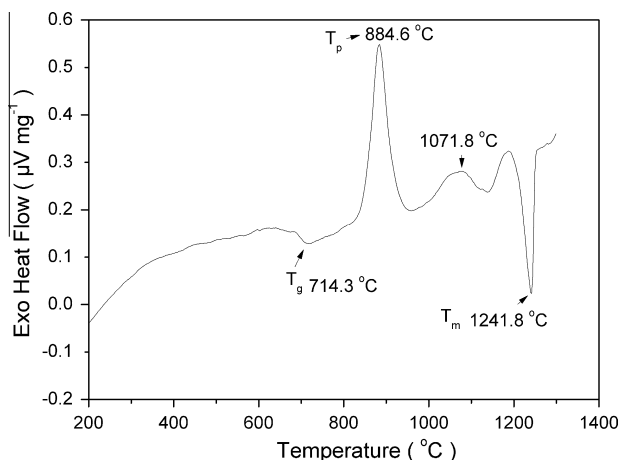

Fig. 2. XRD patterns of the glass–ceramics samples after crystallization at different temperatures.

temperatures of 810–1010 °C. Diopside (($Fe_{0.35}Al_{0.20}Mg_{0.44}$)$Ca_{0.96}$ ($Fe_{0.08}Si_{0.70}Al_{0.20}$)$_2O_{6.12}$) and akermanite ($Ca_2[Mg_{0.75}Al_{0.25}]Si_{1.75}$ $Al_{0.25}O_7$) are the main phases of the glass–ceramics. Other phases are also present in small amounts, but it was not possible to identify them unambiguously. It can be seen from Fig. 2 that the intensity difference of XRD peaks between the five samples indicate that less-crystallized akermanite forms at higher crystallization temperature and is absent above 960 °C.

Glass–ceramics samples nucleated at 714 °C for 2 h followed by different crystallization at 810–1010 °C for 2 h were analyzed by SEM. As shown in Fig. 3, the samples revealed a remarkable difference in SEM micrographs of the glass–ceramics texture. In the sample recrystallized at 810 °C (Fig. 3a), the glass–ceramics body was still glassy matrix with a few crystallites sparsely scattered in. As shown in Fig. 3b, increasing crystalline temperature to 860 °C resulted in formation of a denser crystallite structure in which major crystals and secondary crystals were distributed uniformly in glassy matrix and the proportion of crystal phase increased greatly. In Fig. 3c, the granular crystalline phases were distributed in the glass matrix after crystallization at 910 °C. In Fig. 3d, more spherical crystal was observed after crystallization at 960 °C. In Fig. 3e, columnar crystals appeared when crystallization temperature increased from 960 to 1010 °C.

Fig. 4 shows the changes in density and microhardness of the glass–ceramics with crystallization temperature. With the increase in crystallization temperature, the microhardness of the samples increased, which may be attributed to the refining of crystal size. The density of glass–ceramics first increased and then decreased

Fig. 1. DTA curve of the parent glass sample.
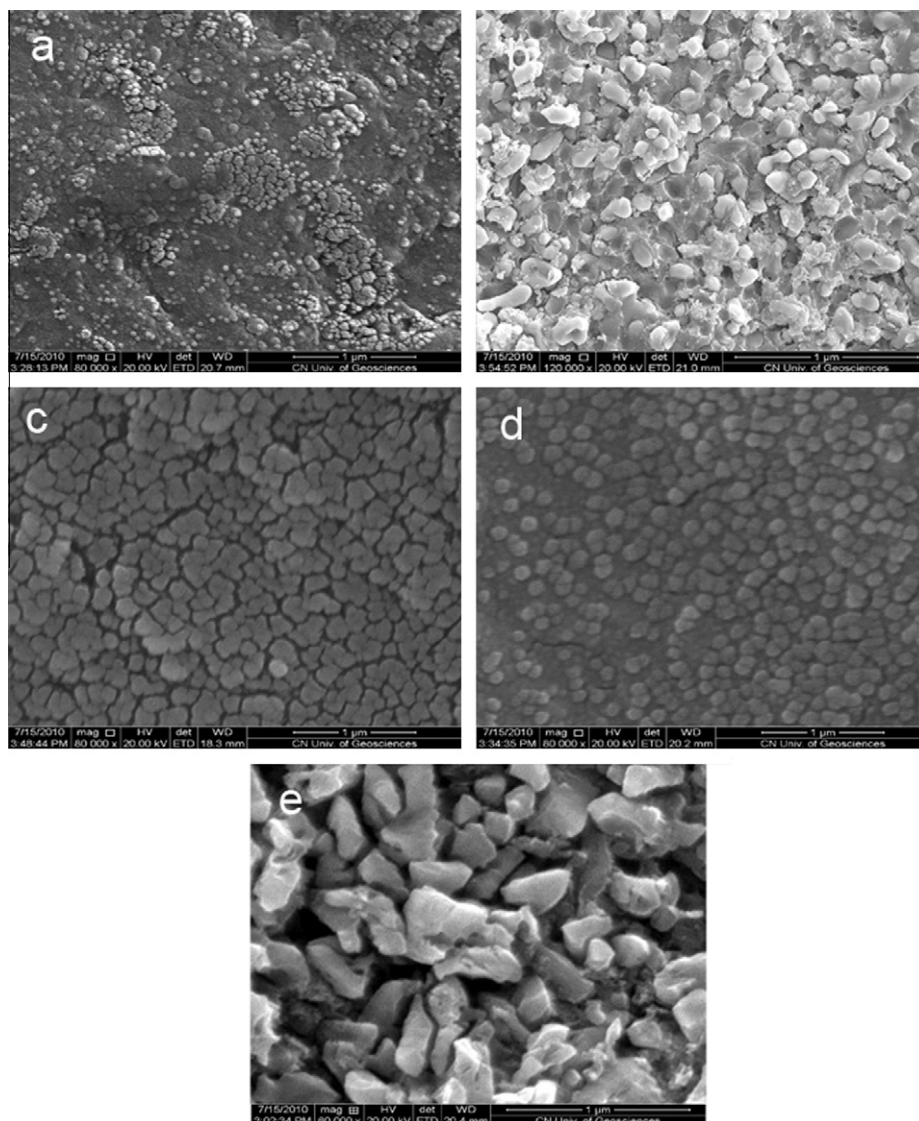
Fig. 3. SEM micrographs of the glass–ceramics samples nucleated at 714 °C for 2 h followed by crystallization for 2 h at (a) 810 °C; (b) 860 °C; (c) 910 °C; (d) 960 °C; (e) 1010 °C.
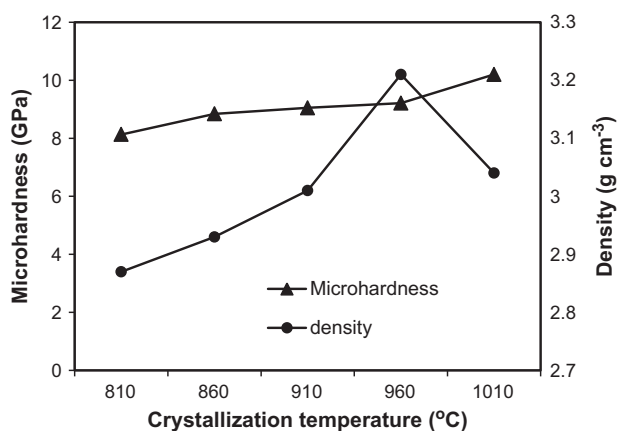
Fig. 4. Correlation between crystallization temperature, microhardness and density.

with increasing crystallization temperature. The reason for the decrease in density of glass–ceramics may be that the fast phase transition at higher temperature resulted in increased porosity of

glass–ceramics (Fig. 2). Increase in hardness may be due to the formation of more crystals (Fig. 3e).

4. Conclusions

The method of mixing MSS with molten additives can shorten the melting and mixing time, simplify the facilities, and reduce equipment corrosion because of lower stirring intensity. With appropriate additives and mixing method to adjust the chemical compositions, the melt was easily transformed into glass–ceramics. The dominant crystalline phase in the samples was diopside. The glass–ceramics samples exhibited excellent properties. The liquid–liquid mixing method is feasible for iron and steel industry to produce glass–ceramics directly from MSS and to realize zero disposal. The optimal composition of additives and parent glass will be investigated.

Acknowledgments

References

Badiee, H., Maghsoudipour, A., Dehkordi, B.R., 2008. Use of Iranian steel slag for production of ceramic floor tiles. Adv. Appl. Ceram. 107, 111–115.

Boccaccini, A.R., Han, W.X., Dimech, C., Rawlings, R.D., 2006. Glass ceramics of high hardness and fracture toughness developed from steel fly ash. Mater. Sci. Tech. – Lond. 22, 1148–1154.

El-Mahllawy, M.S., 2008. Characteristics of acid resisting bricks made from quarry residues and waste steel slag. Constr. Build. Mater. 22, 1887–1896.

Ewais, E.M.M., Grathwohl, G., Ahmedz, Y.M.Z., 2010. Crystallization of mixer slag-derived glass–ceramic composites. J. Am. Ceram. Soc. 93, 671–678.

Ferreira, E.B., Zanotto, E.D., Scudeller, L.A.M., 2002. Glass and glass–ceramic from basic oxygen furnace (BOF) slag. Glass Sci. Technol. 75, 75–86.

Francis, A.A., 2004. Conversion of blast furnace slag into new glass–ceramic material. J. Eur. Ceram. Soc. 24, 2819–2824.

Furlani, E., Tonello, G., Maschio, S., 2010. Recycling of steel slag and glass cullet from energy saving lamps by fast firing production of ceramics. Waste Manage. 30, 1714–1719.

Gomes, V., De Borba, C.D.G., Riella, H.G., 2002. Production and characterization of glass ceramics from steelwork slag. J. Mater. Sci. 37, 2581–2585.

Khater, G.A., 2002. The use of Saudi slag for the production of glass–ceramic materials. Ceram. Int. 28, 59–67.

Liu, C.J., Shi, P.Y., Zhang, D.Y., Jiang, M.F., 2007. Development of glass ceramics made from ferrous tailings and slag in China. J. Iron Steel Res. Int. 14, 73–78.

Mandal, S., Chakrabarti, S., Ghatak, S., Das, S.K., 2006. Low expansive glass–ceramic material produced from blast furnace slag and china clay. Ind. Ceram. 26, 53–59.

Sarkar, R., Singh, N., Das Kumar, S., 2010. Utilization of steel melting electric arc furnace slag for development of vitreous ceramic tiles. Bull. Mater. Sci. 33, 293–298.

Wang, S., Liang, K., 2007. High infrared radiance glass–ceramics obtained from fly ash and titanium slag. Chemosphere 69, 1798–1801.

Yang, H., Yang, W.S., 2006. The possibility of production building materials using sensible heat of industrial slag and materials. China Build. Mater. 3, 78–80.