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SINTERING MECHANISMS OF GLASS-CERAMIC DERIVED FROM RESIDUAL MOLTEN SLAG

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Abstract

In this paper, glass-ceramics prepared from the residual molten slag after extracting iron were investigated by XRF, DTA, XRD and SEM and a linear shrinkage test. The results showed that the obtained glass ceramic had good performance with a bending strength of 54.4MPa. The main crystalline phases are akermanite and gehlenite with size of about 0.5μm. The whole sintering process could be divided into 4 stages. The maximum nucleation temperature of the parent glass is about 775°C, which overlapped with the optimum temperature of the densification process. This overlapping contributed to the sintering process.

Introduction

In China, the amount of crude steel production in 2012 reached about 700 million tonnes. Consequently, approximately 100 million tonnes of steel-making slag (SS) are discharged. At present, utilisation of both the heat from the molten slag and the slag itself after solidification are great challenges. The molten steel slag has about 2000 kJ/kg thermal energy at above 1600°C. If this heat could be used, energy saving of each ton of slag would be around 68 kg of coal equivalent. However, this heat cannot be recovered with the existing technology. Moreover, utilisation rate of the slag is still low. The accumulated steel-making slag is more than 300 million tonnes in China[1]. The slag is currently used only in low value applications such as sintering ingredients and cement additives[1]. Slag glass-ceramics have undergone rapid development and have been widely used in the construction industry[2]. Lately, a lot of work has been published[2-5] on expanding the sources of raw materials by using industrial wastes and on exploring formation and control mechanisms of the glass-ceramics. Glass ceramic by mixing steel slag at the content of 60 wt% have been successfully prepared before[2]. A new method has been developed, that combines the utilisation of the slag and its heat[4-6]. The method involves conversion of molten slag into materials by reducing and extracting iron from the hot molten steel slag and then directly preparing glass-ceramic by using the residual molten slag. In this paper, sintering mechanisms of glass-ceramic derived from the residual molten slag were studied. Batches of glass ceramics were prepared and the sintering processes for the glass ceramics were analysed by XRF, DTA, XRD and SEM and a linear shrinkage test.

Experimental

Steel slag, fly ash, quartz and coal were purchased from LaiWu Iron and Steel Group Co. Ltd and Na_2CO_3 from Tianjin JHTY Chemical Reagent Company. Steel slag mixed with fly ash, quartz and coal was melted at 1550°C and then cooled in air for iron separation. Then the residual slag was re-melted at 1550°C for 20min and Na_2CO_3 (Na_2CO_3:slag was 1:20) was added into it. Finally, the molten slag was quenched into water to produce parent glasses. These glasses were collected, dried, grinded and sieved through a 100 mesh sieve. The glass powder was analysed by XRF (XRF-1700, Shimadzu, Japan). The results are presented in Table 1. DTA (WTC-2C, Beijing Optical Instrument Company, China) was conducted with a reference sample for α-Al_2O_3 and at a heating rate of 10°C/min. Glass powder was placed into a corundum crucible ($50 \times 35 \times 20mm^3$), and then placed in a muffle furnaces (KSL1400X, Hefei Kejing Co., Ltd., China) and kept for 1h at 778°C for the sintering temperature and 867°C for the crystallisation temperature which were deduced from DTA curve of the glass. A linear shrinkage test was conducted. XRD (Model DMax-RB, Rigaku, Japan) analysis was conduct with a scanning rate of 4°/min and and X-ray diffractions were recorded with a CuKα diffractometer. SEM (EVO18 Special Edition, Carl Zeiss, Germany) analysis of the prepared glass ceramics were performed.

Table 1: Chemical composition of raw materials (wt%)

	SiO_2	CaO	MgO	Al_2O_3	MnO	P_2O_5	Na_2O	K_2O	FeO	Fe_2O_3
Steel slag	13.04	32.88	5.42	0.88	2.33	1.54	0.13	0.04	21.96	4.37
Parent glass	41.34	28.94	5.01	15.94	1.94	1.42	3.44	1.08	0.26	--

Results and Discussion

XRD patterns of the samples are shown in Figure 1. The glass phase of the sample remains unchanged until the temperature reaches 778°C. At 798°C, the crystals of akermanite and gehlenite appear and increase in intensity. For heating higher than 798°C, the intensity of diffraction peaks of the crystals decreased gradually. Shrinkage of the samples at different sintering temperatures is shown in Figure 2. At low temperatures (738 - 778°C), there is no crystal in the matrix and the pores among particles are large. Thereby, shrinkage increases rapidly with the raising temperature. This is a rapid densification stage. The shrinkage rate remains almost unchanged during

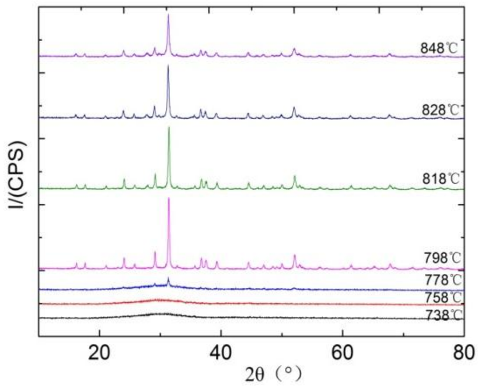

Figure 1: XRD patterns of the sintering samples at different temperature for 1h

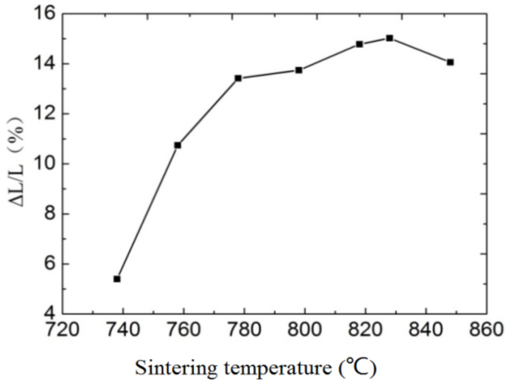

Figure 2: Sintering shrinkage rate with increasing temperature

778°C - 798°C. Figure 1 show that crystals precipitate at 798°C and the formation of crystals leads to the rapid increase of glass viscosity, which would hold back the densification process.

This is a stagnant densification stage. When heated at high temperatures (798~828°C), the glass falls into its softening temperature and its liquid viscosity decreases, and the densification is dominated by liquid phase sintering. Figure 1 shows that the diffraction peaks of the crystalline phase in the glass ceramic decreased, which also indicates that the crystals begin to re-melt. Therefore, limited densification stage would happen in the stage. Under re-melting temperature (higher than 848°C), crystalline phase and glass were re-melted significantly and their diffraction peaks were apparently reduced at 848°C (Figure 1). Meantime, a large number of bubbles could occur, which lead to an increase in the size of the glass ceramic, and its properties would deteriorate rapidly. So, this is a deteriorative densification stage.

The crystallisation peak temperature Tp and the nucleation temperature Tn were calculated[7], and the relation between the two is shown in Figure 3. The optimal nucleation temperature of the glass samples is the maximum of the curves at about 775°C. The temperature overlapped with the best sintering range of 738-778°C, under which a maximum nucleation process was reached and would not impede its densification process. So the optimum sintering temperature of the system is at about 775°C. Figure 4 shows that crystalline phases in glass-ceramic have a size of about 0.5µm and a granular morphology. Tests showed that the glass-ceramic bending strength is 54.4MPa, exceeding the national standard requirements of 30MPa, while the compressive strength reached 292.5MPa and micro-hardness was 4.3GPa.

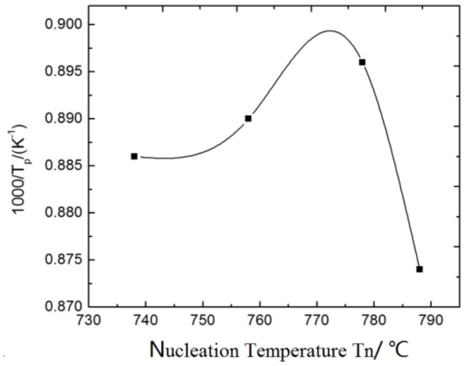

Figure 3: Relationship between Tp and Tn

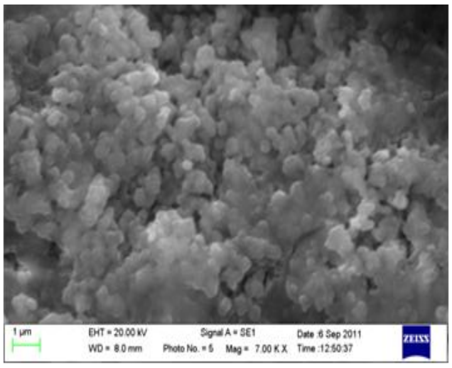

Figure 4: SEM photographs of glass ceramic

Summary

Glass-ceramic could be successfully prepared by using the residual molten slag with bending strength of 54.4MPa achieved and akermanite and gehlenite as main crystalline phases. The whole sintering process could be divided into 4 stages: rapid densification stage, stagnant densification stage, limited densification stage and deteriorative densification stage. The maximum nucleation temperature range is near 775°C which overlapped with the favourable temperature of densification process; this overlapping contributed to the sintering process.

Acknowledgements

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