Investigation on the Iron Oxide Behaviors in the SiO$_2$-based Slag

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Abstract. Various waste blast furnace slag not only occupies a large amount of land, but also seriously pollutes environment. Preparation of glass-ceramics using the waste blast furnace slag receives more and more attention. In this work, effect of iron oxide behaviour on the crystallization and physical and chemical properties in the SiO$_2$-based slag was studied. Results show that the presence of small amount of iron oxide in slag can promote the crystallization of CaO-MgO-Al$_2$O$_3$-SiO$_2$ quaternary basic glass. With the increase of Fe$_2$O$_3$, the crystalline phase content increases, and the glass phase content decreases. Meanwhile, the density of glass-ceramics increases, but the water absorption decreases. Alkali corrosion resistance of glass-ceramics increases with the increase of iron oxide content in range of 0.5 wt.% - 3 wt. %.

1. Introduction

With the rapid development of iron and steel industry, blast furnace slag discharge is increasing significantly. Over the years, slag has accumulated nearly 15 x10$^7$ t [1]. Direct storage not only occupies a large amount of land, but also seriously pollutes environment. The comprehensive utilization of the waste blast furnace slag is an urgent problem. Glass-ceramics is a kind of polycrystalline solid material with homogeneous coexistence of glass phase and microcrystalline phase, which precipitates in a certain basic glass through a specific heat treatment system with addition of nucleating agent. Glass-ceramics [2] concentrates the characteristics of glass and ceramics, which have high mechanical strength, wear resistance, corrosion resistance, excellent electrical insulation, stable dielectric constant, and adjustable expansion coefficient. So, glass-ceramics can be widely used as structural and functional materials in high-tech fields such as optics, electronics, aeronautics and biology. At the same time, glass-ceramics can also be widely used as decorative or protective materials in industrial and civil buildings.

The main components of glass-ceramics are SiO$_2$, CaO and Al$_2$O$_3$, which are similar to those of blast furnace slag. Therefore, researchers [3-6] pay more and more attention to the preparation of glass-ceramics using the waste slag. Agarwell developed wear-resistant microcrystalline ceramics [2] using blast furnace slag. Vecoglu obtained glass-ceramics directly from Turkish blast furnace slag with addition of 3%-5% titanium dioxide. It was found that the grain size changed significantly with the increase of the amount of nucleating agent. The wear resistance, hardness, and bending strength of the product increased with the increase of nucleating agent and crystallization temperature. Khater discovered that the volume crystallization of hedenbergite phase increased, but the volume crystallization degree decreased with the increase of fayalite phase.
Blast furnace slag contains a certain amount of iron, scholars have made a detailed study on the effect of iron on crystallization behaviour of glass-ceramics, magnetic properties and biological activity of products [7, 8]. Zhang [9] prepared glass-ceramics from tailings of a tungsten mine in Hunan Province. The effect of Fe$_2$O$_3$ on crystallization temperature was studied. It was found that when Fe$_2$O$_3$ content reached 6 wt. %, the crystallization temperature of glass-ceramics decreased significantly, and the crystallization ability of glass-ceramics enhanced effectively. In addition, Wu [10] drew a similar conclusion in the the preparation of glass-ceramics with stone powder. Li [11] prepared glass-ceramics with Baiyun Obo tailings and fly ash. The results show that the activation energy of crystallization first increases, then decreases with the increase of iron oxide content. The maximum is 426 kJ•mol$^{-1}$. Rezvani [12] investigated the effect of Fe$_2$O$_3$ on the crystallization behaviour of glass-ceramics using Fe$_2$O$_3$, Cr$_2$O$_3$ and titanium dioxide as mixed nucleating agents. Alizadeh [13] studied the crystallization behaviour and sintering properties of CaO-SiO$_2$-MgO-P$_2$O$_5$ glass-ceramics by sintering method. It was found that the glass-ceramics had high density and mechanical strength with addition of 5.0wt% Fe$_2$O$_3$. The main crystalline phases were white phosphorite and diopside when sintering temperature was low. At high temperatures, the main crystalline phase is calcium silica. Ebisawa [14] found that magnetism and biological activity of the CaO-SiO$_2$-FeO-Fe$_2$O$_3$ glass-ceramics were obvious when the iron oxide content was about 45 wt. % - 50 wt. %.

As discussed in the existing literature above for the preparation of glass-ceramics from industrial waste blast furnace slag, it can be seen that most of them are designed as SiO$_2$-CaO-Al$_2$O$_3$ ternary system, and their main crystalline phases are usually diopside, wollastonite or corresponding solid solutions, such as calcium-iron limestone and magnesium. The structure and properties of glass-ceramics depend on the mineral composition of crystal phase and the chemical composition of glass phase. However, the effect of iron on the basic glass structure, crystallization behaviour and physical and chemical properties of SiO$_2$-CaO-MgO-Al$_2$O$_3$ quaternary system has rarely been reported. In this work, effect of iron oxide on the crystallization and physical and chemical performance was investigated.

2. Experimental

2.1. Sample Preparation

In order to study the effect of Fe$_2$O$_3$ on the crystallization of glass-ceramics, five basic glass samples, with chemical compositions presented in Tab. 1, were prepared by mixing SiO$_2$, Al$_2$O$_3$, MgO, CaO and Fe$_2$O$_3$ to simulate the waste blast furnace slag. The melting of these glass samples was carried out in corundum crucible using a high temperature furnace with MoSi$_2$ heating element. The melts were kept at 1450 °C for 2 h, and were immediately poured on a pre-heated metallic mould with annealing at 500 °C for 2 h to obtain the basic glass samples.

| Samples | CaO (wt.%) | MgO (wt.%) | Al$_2$O$_3$ (wt.%) | SiO$_2$ (wt.%) | Fe$_2$O$_3$ (wt.%) |
|---------|------------|------------|-------------------|---------------|-------------------|
| 1#      | 21.000     | 15.000     | 10.000            | 54.000        | -                 |
| 2#      | 20.895     | 14.925     | 9.95              | 53.730        | 0.500             |
| 3#      | 20.790     | 14.850     | 9.90              | 53.460        | 1.000             |
| 4#      | 20.580     | 14.700     | 9.80              | 52.920        | 2.000             |
| 5#      | 20.370     | 14.550     | 9.70              | 52.380        | 3.000             |

2.2. Analysis Methods

Differential scanning calorimetry (DSC) analysis was made using a Netzsch STA 449F3 thermal balance from 200 to 1200°C. The particle size of the basic glass samples ranged from 74 to 104 mesh. Crystallization temperature was determined under condition of heating rates of 5, 10, 15, and 20 °C/min, respectively. Density of glass-ceramics product is calculated by (1), in which $\rho$ is the density of glass-ceramics product, g/cm$^3$, and $\rho_w$ is the density of water, g/cm$^3$. $m$ and $m_1$ are the mass...
of glass-ceramics product in air and in water, respectively. Water absorption of glass-ceramics was tested by GB/3299-1996 [15]. Acid and alkali resistance of glass-ceramics product was tested in laboratory by the following procedures: Firstly, glass-ceramics were washed with 1% NaOH or 1% HCl solution to remove the surface impurities, then dried after rinsing with distilled water 3-5 times. Mass of glass-ceramics product \( m_1 \) was obtained. Secondly, the glass-ceramics product was immersed in 1% NaOH or 1% HCl solution at 60 °C for 3 hours. The pretreated glass-ceramics product was rinsed distilled water 3-5 times washing with, and dried in a vacuum drying chamber. The final mass \( m_2 \) was obtained. The acid-alkali corrosion resistance of glass-ceramics can be expressed as follows:

\[
\rho = \frac{m}{m_1 - m_1} \times \rho_w \tag{1}
\]

\[
C=\frac{m_1 - m_2}{m_1} \times 100\% \tag{2}
\]

3. Results and Discussion

3.1. Effect of Iron Oxide on Crystallization

Table 2 shows the DSC profiles of glass samples about crystallization peak temperature \( T_p \) with different \( \text{Fe}_2\text{O}_3 \) content heating rates of 5, 10, 15, and 20 °C/min, respectively. It is found that the glass crystallization peak temperatures \( T_p \) decrease with increasing the \( \text{Fe}_2\text{O}_3 \) content at the same heating rate.

| samples | Crystallization peak temperature (°C) |
|---------|--------------------------------------|
|         | 5°C/min | 10°C/min | 15°C/min | 20°C/min |
| 1#      | 994.4   | 1015.3   | 1026.5   | 1038.9   |
| 2#      | 972.4   | 991.2    | 1004.5   | 1018.6   |
| 3#      | 990.4   | 1008.1   | 1020.0   | 1030.6   |
| 4#      | 975.6   | 997.8    | 1010.5   | 1017.0   |
| 5#      | 969.9   | 986.6    | 992.2    | 999.5    |

Crystallization peak temperature of sample 2# is lower than that of 1#, 3# and 4#. This abnormal phenomenon may be caused by the decomposition of \( \text{Fe}_2\text{O}_3 \) in the basic glass system. The decomposition reaction of \( \text{Fe}_2\text{O}_3 \) occurs during the melting and clarifying process of basic glass as follows:

\[
\text{Fe}_2\text{O}_3 = \text{FeO} + \frac{1}{2}\text{O}_2 \tag{3}
\]

\[
3\text{Fe}_2\text{O}_3 = 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \tag{4}
\]

The decomposition equilibrium is calculated by HSC software as shown in Figure 1. It can be found that mole ratio of \( \text{Fe}_2\text{O}_3 \) decreases with the increase of temperature, which coincides with the increase of mole ratio of \( \text{Fe}_3\text{O}_4 \) and \( \text{FeO} \).
In glass systems, iron generally exists in the valence states of Fe$^{2+}$ and Fe$^{3+}$, but they play opposite roles in the glass grid [16]. Fe$^{2+}$ can decrease the viscosity of molten basic glass and crystallization temperature. On the contrary, Fe$^{3+}$ can increase the crystallization temperature by forming a grid structure when there are more monovalent (Na$^+$, K$^+$) or bivalent (Mg$^{2+}$, Ca$^{2+}$) ions in the molten basic glass. According to figure 1, 70 mol % Fe$_2$O$_3$ will decompose into FeO or Fe$_3$O$_4$ when the temperature rises to 1450°C. However, reactions (3) and (4) are affected by the viscosity of glass system and the oxidizing atmosphere in the melting environment. It can be inferred that when a small amount of Fe$_2$O$_3$ is introduced into the CaO-MgO-Al$_2$O$_3$-SiO$_2$ quaternary system, the decomposition reaction of Fe$_2$O$_3$ will occur. Fe$^{3+}$ will be changed into Fe$^{2+}$. Ratio of Fe$^{3+}$/Fe$^{2+}$ in the system decreases, thus reducing its crystallization temperature. When the Fe$_2$O$_3$ content is high, Fe$^{3+}$ greatly increases the system viscosity, and produces more oxygen in melting environment. The decomposition reaction is inhibited by the atmosphere, leading the increase of crystallization temperature.

3.2. Effect of Iron Oxide on Density and Water Absorption

![Figure 2. Relationship between Fe$_2$O$_3$ content and glass-ceramics density and water absorption](image)
Figure 2 shows the patterns of density and water absorption versus iron oxide content on condition of the basic glass samples nucleated at 750 °C for 2 h and crystallized at 1050 °C for 2 h. The results are shown in table 3. From the data in table 3 and the patterns in figure 2, it can be seen that the density of glass-ceramics increases with the increase of iron oxide content. This is mainly due to the close relationship between the density of glass-ceramics and the composition and heat treatment process. The density of glass-ceramics increases with the addition of iron oxide. By precisely controlling the density of glass-ceramics, it can be sensitively detected the fluctuation of basic composition of glass-ceramics and the change of crystallization effect caused by heat treatment. To some extent, water absorption reflects the degree of crystallization and compactness of glass-ceramics. From Fig. 2, it can be seen that the change of water absorption is not significant when iron oxide is less than 1 wt. %. As the Fe<sub>2</sub>O<sub>3</sub> content is more than 1 wt. %, the water absorption decreases, but all of the experimental data shown in figure 2 meet the requirements of national standards. This irregular change is caused by bubbles on the surface of glass-ceramics.

3.3. Effect of Iron Oxide on Acid and Alkali Resistance

![Figure 3. Relationship between Fe<sub>2</sub>O<sub>3</sub> content and the acid and alkali resistance of glass-ceramics](image)

**Table 3. Results of glass-ceramics properties**

| Samples | Density g/cm<sup>3</sup> | Water absorption % | Acid resistance % | Alkali resistance % |
|---------|--------------------------|---------------------|-------------------|---------------------|
| 1#      | 2.73                     | 1.395               | 0.53              | 0.51                |
| 2#      | 2.76                     | 1.392               | 0.31              | 0.17                |
| 3#      | 2.77                     | 1.384               | 0.28              | 0.2                 |
| 4#      | 2.81                     | 0.868               | 0.49              | 0.22                |
| 5#      | 2.82                     | 0.611               | 1.36              | 0.32                |

Figure 3 shows the relationship between acid and alkali resistance of the glass-ceramics versus iron oxide content under conditions that the basic glass samples nucleated at 750 °C for 2 h and crystallized at 1050 °C for 2 h. The results are shown in table 3. It can be seen from the figure 3 that after soaking in 1% sodium hydroxide solution for 3 hours, the mass loss rate of glass-ceramics with iron oxide is lower than that of glass-ceramics without iron oxide. Alkali corrosion resistance of glass-ceramics varies gradually with the increase of Fe<sub>2</sub>O<sub>3</sub> content. It can be inferred that the glass phase in glass-ceramics corrodes in alkaline solution. With the increase of Fe<sub>2</sub>O<sub>3</sub>, the crystalline phase content
increases, and the glass phase content decreases. The alkali corrosion resistance of glass-ceramics increases. After soaking in 1% hydrochloric acid solution at constant temperature for 3 hours, the mass loss of glass-ceramics sample decreases slightly with the addition of iron oxide, which indicates that adding a small amount of iron oxide will enhance its acid corrosion resistance, but it will increase slightly with the increase of iron oxide content, indicating that the addition of excessive iron oxide will reduce the acid corrosion resistance.

4. Conclusions
   (1) With the increase of iron oxide content, the crystallization peak temperature ($T_p$) of glass-ceramics decreases obviously. When Fe$_2$O$_3$ content is 0.5 wt. %, the crystallization peak temperature is lower than that without Fe$_2$O$_3$, and also lower than that with Fe$_2$O$_3$ content 1 wt. % and 2 wt. %, respectively.
   (2) With the increase of iron oxide content, the density of glass-ceramics increases, but the water absorption decreases. Alkali corrosion resistance of glass-ceramics increases with the increase of iron oxide content in range of 0.5 wt. % - 3 wt. %. When iron oxide content is higher than 1 wt. %, the acid corrosion resistance decreases slightly.
   (3) The presence of small amount of iron oxide less than 1 wt. % in slag can promote the crystallization of basic glass of CaO-MgO-Al$_2$O$_3$-$SiO_2$ quaternary system and improve the physical and chemical properties of glass-ceramics.

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6. References
[1] Yanfei Zou, Huiqing Jiang. Present situation of blast furnace slag treatment method and comprehensive utilization technology [J]. 2011 Gold Mountain 6 42 (In Chinese).
[2] Jinshu Cheng, Hong Li, Liying Tang, Feng He. Glass-ceramics [M]. 2006 Beijing: Chemical Industry Press p 352 (In Chinese).
[3] Karamanov A, Pisciella P, Pelino M. The effect of Cr$_2$O$_3$ as a nucleating agent in iron-rich glass-ceramics [J]. 1999 Journal of the European Ceramic Society 19 2641.
[4] Alexander Karamanov, Paola Pisciella, Carlo Cantalini, Mario Pelino. Influence of Fe$^{3+}$/Fe$^{2+}$ Ratio on the Crystallization of Iron-Rich Glasses Made with Industrial Wastes [J]. 2000 Journal of the American Ceramic Society 83 3153.
[5] Karamanov A, Pisciella P, Pelino M. The crystallisation kinetics of iron rich glass in different atmospheres [J]. 2000 Journal of the European Ceramic Society 20 2233.
[6] Karamanov A, Pisciella P, Pelino M. The effect of Cr$_2$O$_3$ as a nucleating agent in iron-rich glass-ceramics [J]. 1999 Journal of the European Ceramic Society 19 2641.
[7] Kai Zhang. Study on crystallization behavior of glass-ceramics derived from simulated molten steel slag [D]. 2012 Wuhan, Huazhong University of Science and Technology p 32 (In Chinese).
[8] Hirose K, Homma T, Doi Y, et al. Mssbauer analysis of Fe ion state in lithiumiron phosphate glasses and their glass-ceramics with olivine-type LiFePO$_4$ crystals [J]. 2008 Solid State Communications 146 273.
[9] Shugen Zhang, Qi Wei, Dawei Wang. The study on the crystallization of glass-ceramics with Fe$_2$O$_3$ as nucleation agent [J]. 1999 Bulletin of the Chinese Ceramics Society 4 77 (In Chinese).
[10] Dandan Wu. Crystallization of Fe$_2$O$_3$ on glass from crystallization and microstructures in R$_2$O-CaO-MgO-Al$_2$O$_3$-Fe$_2$O$_3$-$SiO_2$ system and application of stone powder in glass-ceramics. [D]. 2007 Overseas Chinese University p 45 (In Chinese).
[11] Li Baowei, Du Yongsheng, Zhang Xuefeng, Jia Xiaolin, Zhao Ming, Chen Hua. Effects of Iron Oxide on the Crystallization Kinetics of Baiyunbo Tailing Glass-Ceramics [J]. 2013 Transactions of the Indian Ceramic Society 2 119.
[12] Rezvani M, Eftekhar-Yekta B, Solati-Hashjin M, et al. Effect of Cr$_2$O$_3$, Fe$_2$O$_3$ and TiO$_2$ nucleants on the crystallization behaviour of SiO$_2$-Al$_2$O$_3$-CaO-MgO (R$_2$O) glass-ceramics [J]. 2005 Ceramics international 3175.
[13] P. Alizadeh, B. Eftekary Yekta, A. Gervei. Effect of Fe₂O₃ addition on the sinterability and machinability of glass-ceramics in the system MgO-CaO-SiO₂-P₂O₅ [J]. 2004 *Journal of the European Ceramic Society* 24 3529.

[14] Ebisawa Y, Miyaji F, Kokubo T, et al. Bioactivity of ferromagnetic glass-ceramics in the system FeO-Fe₂O₃-CaO-SiO₂ [J]. 1997 *Biomaterials* 18 1277.

[15] Standard test method for water absorption of domestic ceramic ware. 1996 *State Bureau of Technical Supervision* p 3.

[16] Z. J. Yang, Y. Li, A. Q. Cang, M. L. Diao, W. B. Guo, The influence of Fe²⁺ and Fe³⁺ on crystallization of CaO-Al₂O₃-SiO₂-MgO system glass-ceramic [J]. 2012 *Materials Science and Technology* 20 45.