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Abstract: To evaluate the crystallization behavior of Ti-bearing blast furnace slag-based glass ceramics, SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-CaO-MgO-TiO\textsubscript{2} systems with various TiO\textsubscript{2} were investigated. The crystallization process and mechanical properties were analyzed. The results show that with TiO\textsubscript{2} increasing, exothermic peak temperature (T\textsubscript{p}) decreases, and the crystallization is promoted by the introduction of TiO\textsubscript{2}. A small amount of TiO\textsubscript{2} (≤4%) addition can significantly promote crystallization, and when TiO\textsubscript{2} continues to increase, the crystallization is decreased slightly. The Avrami parameter (n) of all samples is less than 4, indicating that in prepared glass-ceramics, it is hard to achieve three-dimensional crystal growth. The main crystalline phase is akermanite–gehlenite. The addition of TiO\textsubscript{2} has no obvious effect on the type of main crystalline phase. The prepared glass-ceramic with 4% TiO\textsubscript{2} show good mechanical properties with the hardness values of 542.67 MPa. The recommended content of TiO\textsubscript{2} is 4% for preparing glass-ceramics.

Keywords: glass-ceramics; crystallization kinetics; TiO\textsubscript{2}; blast furnace slag

1. Introduction

China is the largest steel producer in the world, and the steel production capacity constantly increases. Therefore, more and more metallurgical solid waste is discharged during the smelting process. About 50% of the solid waste generated in the metallurgical industry is blast furnace slag, which is one of the important components of metallurgical solid waste [1]. The accumulated amount of Ti-bearing blast furnace slag is up to 3 million tons per year [2,3]. For blast furnace slag accumulated in a slag yard for a long time, improper handling will cause potential and long-term harm to the environment. At present, the main method of comprehensive utilization is to produce building materials with low added value, such as cement, concrete, and bricks. In addition, theblast furnace slag produced by an iron and steel plant contains less than 8% TiO\textsubscript{2}, which is a typical low or medium Ti-bearing blast furnace slag. If this extraction method is used, due to the low grade of TiO\textsubscript{2}, it is difficult to extract titanium, and the economic benefit is low. However, if low and medium Ti-bearing blast furnace slag is used to make cement, concrete, and other building materials, the TiO\textsubscript{2} will affect the stability of building materials [4]. Therefore, efficient and comprehensive utilization of low and medium titanium blast furnace slag is still a difficult problem to be solved.

Glass-ceramic is a homogeneous polycrystalline solid material, which contains a large number of microcrystalline and glass phases [5]. Glass-ceramic has many excellent properties, such as high strength and good thermal shock resistance, which make it more widely used in many fields, such as national defense, automotive, machinery, and construction [6]. Blast furnace slag is a typical silicate material, and the main components are SiO\textsubscript{2}, CaO, MgO, and Al\textsubscript{2}O\textsubscript{3}, which are also important components of
glass-ceramics [7–10]. According to the modern glass structure theory, SiO$_2$ can be used as a network former, MgO and CaO as network modifiers, Al$_2$O$_3$ as a network intermediate, and a small amount of TiO$_2$ is a good crystal nucleating agent so that these components can be used in the glass-ceramics’ production process [11,12]. The use of low and medium Ti-bearing blast furnace slag to prepare glass-ceramics is of great significance, which not only provides a new way for the comprehensive utilization of low and medium Ti-bearing blast furnace slag but also increases the added value of metallurgical solid waste, which improves its utilization and reduces its environmental pollution.

The content and distribution of the crystal and glass phases of glass-ceramic determine its performance [5,9,13]. An appropriate amount of nucleating agent can reduce the activation energy (E) of glass crystallization and increase the bulk growth index, thereby promoting glass bulk crystallization. A significant amount of research has been performed on the effects of nucleating agents in glass-ceramics. Tan et al. [14] studied the crystallization of glasses with different contents of TiO$_2$ and phase evolution with temperature and found that the viscosity of the base glasses at high temperature decreased with the addition of TiO$_2$ in glass-ceramics, which favored nucleation and crystal growth. Erkmen et al. [15] used blast furnace slag with Cr$_2$O$_3$ and TiO$_2$ as nucleating agents to prepare glass-ceramics. The crystal phase components of glass-ceramics were mainly akermanite and gehlenite. Moreover, Back et al. [16] analyzed the effects of TiO$_2$ and Cr$_2$O$_3$ on nucleation in the SiO$_2$-Al$_2$O$_3$-CaO-MgO system by differential scanning calorimetry (DSC), and showed that TiO$_2$ was effective in decreasing the crystallization temperature, while Cr$_2$O$_3$ effectively decreased the activation energy. Mukherjee et al. [17] found that the addition of TiO$_2$ can act as a nucleating agent, which improved the nucleation and crystallization processes of glass and changed the crystalline distribution in glass-ceramics. When the content of crystals and the microstructure changed, the density of glass-ceramics increased, while microhardness strengthened with increasing TiO$_2$. He et al. [18] evaluated the effects of TiO$_2$ on the phase composition and structural properties of the prepared glass-ceramics with diopside as the main crystalline phase by DSC, X-ray diffraction (XRD), and scanning electron microscopy (SEM), and found that the optimal dosage of TiO$_2$ was 7.69%. In addition, Javed et al. [19] studied the mechanical properties of glass-ceramics and the stability of the metal-glass-ceramic interface found that the volume fraction of the crystalline phase in glass-ceramics was a key factor in controlling mechanical properties and fracture. It was shown that TiO$_2$ is an important crystal nucleating agent for preparing glass-ceramics, and the amount of crystal nucleating agent has an important effect on the crystallization process. What is more, the mechanical properties of glass-ceramics are closely related to crystallization. Exploring the crystallization kinetics is of great significance for glass-ceramics prepared from Ti-bearing blast furnace slag.

In the present work, the DSC method was used to analyze the crystallization kinetics of the base glass, and the influence of TiO$_2$ as the nucleating agent on the crystallization mode of the base glass was studied. According to the results of the crystallization kinetics of the base glass, the phase composition and microstructure of SiO$_2$-Al$_2$O$_3$-CaO-MgO-TiO$_2$ based glass-ceramic were investigated with XRD and SEM. This study can provide a theoretical basis on the controlled crystallization of slag and the preparation of glass-ceramics with excellent performance. In addition, this study can provide more techniques and experimental technical support for the efficient resource utilization of low and medium Ti-bearing blast furnace slag.

2. Experimental Procedures

2.1. Sample Preparation

Based on the composition of blast furnace slag from an iron and steel plant, which mainly contains SiO$_2$, Al$_2$O$_3$, CaO, and MgO, chemical reagents were used to prepare SiO$_2$-Al$_2$O$_3$-CaO-MgO-TiO$_2$ samples with various contents of TiO$_2$ in this study. To explore the effect of TiO$_2$ content on the preparation of glass-ceramics from blast furnace slag composition. The chemical composition of the samples is listed in Table 1. After accurately weighing the components of each sample, the prepared
samples were ground in an agate mortar for half an hour, so that the various components could be uniformly mixed. Then the powder samples were placed into a clean platinum crucible, and the temperature was raised to 1500 °C in a high-temperature tube furnace in air for 2 h. The melting temperature of blast furnace slag is usually about 1400 °C. Furthermore, according to the phase diagram of the SiO$_2$-Al$_2$O$_3$-CaO ternary slag system, the melting temperature of this slag system is 1400 °C, approximately under the condition of the designed composition content in this experiment. So 1500 °C was chosen to make the ingredients uniformly melted and mixed. Then the samples were removed and quenched with water to obtain the basic glass samples. The basic glasses were ground into powder about 200 mesh in an agate mortar; some powder were identified by XRD; for example, see the 8% TiO$_2$ shown in Figure 1. In addition, 1% polyvinyl alcohol and 5% zinc stearate were added to the remaining powder as binders. This study used a FYD-30 electric powder compactor to press the basic glass powder into a cylinder with a diameter of 8 mm, and the cuboid with 50 × 6 × 6 mm was pressed to be used for hardness strength detection. The pressed sample was placed on a platinum sheet and heated to 600 °C for 1 h in a high-temperature tube furnace, which was to reduce the glass stress and remove the binders. According to the results of DSC, the transition temperature ($T_g$) of the investigated glasses was determined at about 750 °C, and the crystallization temperature was about 920 °C. The heating stage microscopy was used to observe the sintering process of the 4% TiO$_2$ glass samples, shown in Figure 2. The figures show that the sample began to shrink when the temperature was 775 °C and remained basically unchanged after 904 °C, which is similar to the glass transition and crystallization temperature of the DSC test result. Therefore, the nucleation temperature was estimated by 800 °C, because the optimum nucleation temperature usually lies at 50–100 °C above $T_g$ of glasses. Then, the samples were held at their crystallization temperature for 1.5 h to obtain the glass-ceramics.

Table 1. The chemical composition of SiO$_2$-Al$_2$O$_3$-CaO-MgO-based samples (wt%).

| Samples | CaO | SiO$_2$ | MgO | Al$_2$O$_3$ | TiO$_2$ | CaO/SiO$_2$ |
|---------|-----|--------|-----|------------|--------|------------|
| S1      | 38.5| 38.5   | 8   | 15         | 0      | 1          |
| S2      | 38  | 38     | 8   | 15         | 1      | 1          |
| S3      | 37.5| 37.5   | 8   | 15         | 2      | 1          |
| S4      | 36.5| 36.5   | 8   | 15         | 4      | 1          |
| S5      | 35.5| 35.5   | 8   | 15         | 6      | 1          |
| S6      | 34.5| 34.5   | 8   | 15         | 8      | 1          |

Figure 1. X-ray diffraction (XRD) pattern of the quenched sample with 8% TiO$_2$.
The glass-ceramic samples surfaces were polished and then observed by scanning electron microscopy (SEM) (JSM-7800F, JEOL, Tokyo, Japan). The microhardness was measured by a microhardness-tester (MH-5L, Everone Precision Instruments Ltd., Shanghai, China) with a measuring force of 200 N and a load time of 15 s. The microhardness values were obtained by calculating the average of five detection values.

3. Results and Discussion

3.1. Crystallization Kinetics Analysis

Shown in Figure 3a–f are the DSC curves of the glass samples with different TiO$_2$ contents at heating rates of 5, 10, 15, and 20 °C/min, respectively. The crystallization temperature can be determined as the exothermic peak temperature ($T_p$). The variations in the crystallization temperature of the investigated samples for the first crystal are shown in Figure 4, which indicates that the crystallization temperature increased with the increase in the heating rate, while it decreased with the increase in TiO$_2$ content when the content of TiO$_2$ was less than 4%. When TiO$_2$ content was at a relatively high level, the increasing effect became weaker. Only negligible changes in $T_p$ were observed with 4%, 6%, and 8% TiO$_2$.  

![Figure 2](image_url)  
**Figure 2.** Typical sequence of images of the 4% TiO$_2$ glass sample obtained with the heating microscope digital camera.

2.2. Analysis Methods

The basic glass powders were examined by DSC (449F3, NETZSCH, Frankfurt, Germany) in air from room temperature to 1300 °C at heating rates of 5, 10, 15, and 20 °C/min, respectively, to evaluate the activation energy of crystallization ($E$) and Avrami parameter ($n$). The phase of the basic glasses and obtained glass-ceramics were examined by X-ray diffraction (XRD) (PANalytical X’Pert Powder, Spectris Pte, Amsterdam, The Netherlands). The glass-ceramic samples surfaces were polished and then observed by scanning electron microscopy (SEM) (JSM-7800F, JEOL, Tokyo, Japan). The microhardness was measured by a microhardness-tester (MH-5L, Everone Precision Instruments Co., Ltd., Shanghai, China) with a measuring force of 200 N and a load time of 15 s. The microhardness values were obtained by calculating the average of five detection values.
According to some research [22–24], Ti network to reach a 6-fold coordination structure. The amount of Ti ions changing from TiO$^4$, TiO$_5$, and TiO$_6$ structural units, and the TiO$_6$ unit is used as network modifier, which will decrease the degree of polymerization of glasses. Ti$^{4+}$ ions remain 4-fold coordination in low temperature process [25,26]. And Cheng et al. [27] concluded that heat treatment may lead silicate to depolymerize, and Ti$^{4+}$ will break away from the network to reach a 6-fold coordination structure. The amount of Ti$^{4+}$ ions changing from TiO$_4$ to TiO$_6$

**Figure 3.** The differential scanning calorimetry (DSC) curves of the samples with different contents of TiO$_2$. (a) S1; (b) S2; (c) S3; (d) S4; (e) S5 and (f) S6.

**Figure 4.** The Crystallization temperature of the samples with different heating rates.

The crystallization was affected by both the nucleation rate and the crystal growth velocity. More time is needed to initiate nucleation and subsequent crystal growth for the higher heating rates. Therefore, the crystallization temperature correspondingly increased at a higher heating rate [20,21].
The nonisothermal crystallization kinetics of the investigated glass-ceramics was analyzed. Many models on nonisothermal crystallization kinetics have been provided by previous reports [28–32]. As the glass transforms into a crystalline structure, a certain activation energy is required to overcome the potential barrier to rearrangement of the structural units. The potential barrier affects the $E$ required, which affects the crystallization ability of the glass. $E$ reflects the ability of crystallization to some extent [20,33,34]. To obtain the activation energy of the investigated samples, the modified Kissinger equation was used [30–32], as shown in Equation (1):

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \frac{E}{RT_p} + C$$  \hspace{1cm} (1)$$

where $\alpha$ is the heating rate and $R$ is the universal gas constant. This equation is also used by Back et al. [16], which analyzes the nucleation and crystallization of the SiO$_2$-Al$_2$O$_3$-CaO-MgO system from DSC curves. The linear plots of $\ln\left(\frac{T_p^2}{\alpha}\right)$ vs. $1/T_p$ for glass samples are exhibited in Figure 5.

Based on the slopes of these lines, the $E$ was calculated for each glass sample, as showed in Figure 6. It was observed that $E$ first greatly decreased as the TiO$_2$ content increased from 301.96 kJ/mol to 222.56 kJ/mol, and then slightly increased with further increasing TiO$_2$ from 224.30 kJ/mol to 239.94 kJ/mol. It can be concluded that the addition of a small amount of TiO$_2$ ($\leq$4%) can significantly promote crystallization, and when TiO$_2$ continues to increase, the crystallization ability decreases slightly. This may be because TiO$_2$ is an amphoteric compound. At low content of TiO$_2$, TiO$_6$ is mainly formed to reduce the degree of network polymerization, thus promoting crystallization. On the contrary, TiO$_4$ is formed to make network polymerization and reduce crystallization.

There are two crystallization mechanisms of glasses: surface crystallization and bulk crystallization. As the glass has a strong crystallization ability, the crystallization process performs bulk crystallization. Conversely, glass only crystallizes on the surface. The Avrami parameter, $n$, is also known as the crystallization index, which reflects the difficulty of crystallization and the crystal growth mechanism. According to Johnson–Mehl-Avrami (JMA) theory, $n \approx 2$ indicates the surface crystallization, $n \approx 3$ indicates two-dimensional crystal growth, and $n \approx 4$ indicates three-dimensional crystal growth.
growth [21,35–37]. In current experiments, \( n \) was evaluated by DSC experiments using the Augis–Bennett equation [38], as shown as Equation (2):

\[
n = \frac{2.5 \times RT^2}{\Delta T} \approx \frac{2.5 \times R}{E} \tag{2}
\]

where \( \Delta T \) is the full width of the exothermic peak at the half-maximum intensity. The meanings of other parameters are consistent with those of Equation (1). Table 2 shows the values of \( n \). It can be seen that the \( n \) of all samples were less than 4, indicating that for the investigated Ti-bearing blast furnace slag-based glass-ceramics, it was hard to achieve three-dimensional crystal growth and the further improvement in crystallization behavior will be our future works. The biggest value of \( n \) was found to be 3.03 for the specimen S3, revealing that a two-dimensional crystallization proceeded in the sample with 2% TiO\(_2\). However, the crystallization of other samples was only performed by surface crystallization at any other heating rate.

![Figure 6](image-url)

**Figure 6.** The change in the activation energy of crystallization with different contents of TiO\(_2\).

| Heating Rate (°C/min) | Content of TiO\(_2\) (wt%) |
|-----------------------|-----------------------------|
|                       | 0  | 1  | 2   | 4  | 6  | 8   |
| 5                     | 1.44 | 2.42 | 3.03 | 2.27 | 2.47 | 1.94 |
| 10                    | 1.74 | 2.16 | 2.08 | 1.94 | 2.03 | 1.94 |
| 15                    | 1.98 | 1.89 | 2.24 | 2.13 | 2.60 | 2.22 |
| 20                    | 1.71 | 1.73 | 2.13 | 2.08 | 2.42 | 2.07 |

3.2. Crystal Phase and Morphology Analysis

The XRD patterns of the SiO\(_2\)-Al\(_2\)O\(_3\)-CaO-MgO-TiO\(_2\) glass-ceramic specimens are represented in Figure 7. It is seen that the glass-ceramic samples precipitated akermanite–gehlenite \((\text{Ca}_2\text{Mg}_{0.5}\text{Al}_{0.5}(\text{Si}_{1.5}\text{Al}_{0.5}\text{O}_7))\) (PDF card: 79-2423) and augite \((\text{Ca(Mg}_{0.70}\text{Al}_{0.30})(\text{Si}_{1.70}\text{Al}_{0.30})\text{O}_6)\) (PDF card: 78-1392) in the crystalline phases, which is mostly consistent with the precipitation of related reports [15,39]. Additionally, Figure 7 illustrates that the intensity of the diffraction peak corresponding to the main crystal \((\text{Ca}_2\text{Mg}_{0.5}\text{Al}_{0.5}(\text{Si}_{1.5}\text{Al}_{0.5}\text{O}_7))\) gradually increased in the process of increasing the
content of TiO₂ from 0% to 2%, and the negligible change in the intensity of that was observed when the content of TiO₂ increased from 4% to 8%. The addition of TiO₂ had no effect on the precipitation type of the main crystalline phase. However, according to XRD detection results, the fitting calculation exhibited that the crystallinity of S1 to S6 was approximately 95.37%, 95.83%, 96.62%, 97.55%, 97.51%, and 97.46%, respectively. It demonstrates that the increase in TiO₂ content promotes crystallization when TiO₂ content is less than 4 wt%, and the crystallinity remains basically unchanged as TiO₂ continues to increase.

![Relative Intensity and 2θ](image)

**Figure 7.** X-ray diffraction patterns of glass-ceramics.

Figure 8 shows SEM images of the original glass-ceramics with different contents of TiO₂. The plots show the surface morphology of a glass-ceramic with different contents of TiO₂ in Figure 8a–f. The surface of the sample contained many holes, resulting in the surface looking loose and porous in the TiO₂-free sample shown in Figure 8a. As the concentration of TiO₂ increased to 4%, the surface gradually became more compact. With further increases in TiO₂ content, the densification decreased. According to the theoretical calculations of crystallization kinetics, when TiO₂ content is 4%, the glass sample has the lowest crystallization activation energy with 222.56 kJ/mol, resulting in a stronger crystallization ability, so the growth of grain is denser.

Furthermore, the distribution of crystal phases of the polished glass-ceramics with different contents of TiO₂ are shown in Figure 9. It can be found that crystal phases are formed in glass-ceramics with different TiO₂ contents, and the crystals formed are relatively uniformly distributed in the glass-ceramics. The results of EDS analysis show that the crystal phase composition in the glass-ceramic is mainly akermanite-gehlenite (Ca₂Mg₀.₅Al₀.₅(Si₁.₅Al₀.₅O₇)), taking the example of 2 wt% TiO₂, shown in Figure 10, which is consistent with the XRD results. Additionally, it can be seen from Figure 9a that some large size (between 10–30 µm) crystals existed in the TiO₂-free sample. The crystal size gradually decreases with the increase in TiO₂. When the content of TiO₂ increased from 2% to 4%, the crystal size decreased to less than 10 µm, while large bulk crystals were observed with further increases in TiO₂ content. TiO₂ as a nucleating agent, can promote nucleation and crystallization. The number of nuclei formed is small with the TiO₂-free sample, and the crystals can grow to a larger size. With the increase in TiO₂ content, the number of nuclei formed increases, and the growth space of the nuclei restrict each other during crystallization so that the crystal grain size is gradually reduced, and the crystals are denser. However, when there are a large number of nuclei formed, the grains bond to each other to form the bulk crystals during the growth process. In summary, this research demonstrated that a certain amount of TiO₂ can promote the precipitation of crystals and generate crystallites produced in glass-ceramics so as to improve the related performance of glass-ceramics.
Figure 8. SEM images of the original glass-ceramics. (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, and (f) S6.

Figure 9. Scanning electron microscopy (SEM) images of the polished glass-ceramics. (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, and (f) S6.
was the lowest, which would promote more crystals and smaller size of crystals were precipitated, reaching the highest value. Therefore, the recommended content of TiO$_2$ is about 4% when preparing glass-ceramics using Ti-bearing blast furnace slag.

3.3. Hardness Performance Analysis

The Vickers hardness values for the glass-ceramic samples are presented in Figure 11. As the content of TiO$_2$ increased, the hardness values initially increased gradually and then decreased, reaching the maxima at 4% TiO$_2$. The prepared glass-ceramic with 4% TiO$_2$ content showed good mechanical properties with a hardness of 542.67 MPa. According to the results of crystallization kinetics analysis and SEM, when the content of TiO$_2$ was 4%, the crystallization activation energy was the lowest, which would promote more crystals and smaller size of crystals were precipitated, resulting in a denser surface of the glass-ceramic so that the Vickers hardness under this condition reached the highest value. Therefore, the recommended content of TiO$_2$ is about 4% when preparing glass-ceramics using Ti-bearing blast furnace slag.

Figure 10. SEM image of a sample with 2% TiO$_2$, with EDS analysis overlaid on the photographs.

Figure 11. The Vickers hardness of the samples with different contents of TiO$_2$ (MPa).
4. Conclusions

The crystallization behaviors of the SiO$_2$-Al$_2$O$_3$-CaO-MgO-TiO$_2$ based glass-ceramics were investigated. The crystallization process and the mechanical properties of glass-ceramics were analyzed. The following conclusions are obtained:

With TiO$_2$ content increasing, $T_p$ decreases. The crystallization is promoted by the introduction of TiO$_2$. According to the calculation results of the crystallization activation energy, a small amount of TiO$_2$ (≤4 wt%) addition can significantly promote crystallization, and when TiO$_2$ continues to increase, the crystallization ability decreases slightly.

The Avrami parameter (n) of all samples was less than 4, indicating that it was hard to achieve three-dimensional crystal growth in the investigated Ti-bearing blast furnace slag-based glass-ceramics. A two-dimensional crystallization proceeded in the sample with 2 wt% TiO$_2$. However, the crystallization of other samples was only performed by surface crystallization. The main crystalline phase of the prepared glass-ceramic was akermanite–gehlenite. The addition of TiO$_2$ had no effect on the precipitation type of the main crystalline phase.

The prepared glass-ceramics with 4 wt% TiO$_2$ content showed good mechanical properties with a hardness value of 542.67 MPa. The recommended content of TiO$_2$ is 4 wt% when preparing glass-ceramics using the Ti-bearing blast furnace slag.

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