Effect of B$_2$O$_3$ on Structure of CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ Glassy Systems

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Titanium-bearing blast furnace slag is an important metallurgical waste, but presently, it is difficult for it to be effectively utilized. B$_2$O$_3$ is an important modifier to greatly promote the mass diffusion of crystallization of Ti-enriched phases in molten slags. To furtherly understand the effect of B$_2$O$_3$ on the structure of Ti-bearing slag, CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses of various B$_2$O$_3$ contents were investigated by combining Raman, FT-IR, and X-ray photoelectron spectroscopy. The results showed that BO$_3$ was the dominant structure, which decreased slightly as the B$_2$O$_3$ content increased, while BO$_4$ increased. Three coordination forms (TiO$_4$, TiO$_5$, and TiO$_6$) of the Ti-structure were discovered in the prepared Ti-bearing glasses. The percentage of TiO$_4$ gradually increased and became the main structural unit as the increased B$_2$O$_3$. The increase of BO$_3$ and TiO$_4$ led to an increased amount of network connection units, such as SiO$_4$, to increase the degree of polymerization of the prepared Ti-bearing glasses.

**KEY WORDS:** B$_2$O$_3$; structure; Raman spectroscopy; X-ray photoelectron spectroscopy; titanium-bearing blast furnace slag.

1. Introduction

Vanadium–titanium magnetite is an important ore resource, of which there are abundant reserves in China, especially in the Panxi area, which account for more than 90% of China’s reserves. During the ironmaking process, vanadium–titanium magnetite is commonly used as a raw material for extracting iron. After smelting in a blast furnace, most of the titanium is transferred to slag, referred to as Ti-bearing blast furnace slag. More than 3 million tons of Ti-bearing blast furnace slag is produced annually, with a total accumulation of more than 7 million tons in China. The accumulation of titanium slag not only wastes valuable titanium resources but also occupies a large amount of land and seriously pollutes the environment. Since the titanium components in blast furnace slag are mainly dispersed in the mineral phase, such as perovskite, carbon (nitrogen) titanium, and a small amount of spinel and diopside, it makes it considerably difficult to extract Ti from blast furnace slag. Presently, the utilization rate of titanium in Ti-bearing blast furnace slag is low. Therefore, new economical and efficient methods of treating Ti-bearing blast furnace slag are of great significance for the comprehensive utilization of titanium-bearing slag.

Modifiers are normally added to blast furnace slag, which can affect the precipitation, growth, and morphology of crystals in molten blast furnace slag. Much research has been done on Ti-bearing blast furnace slag modifiers to improve the Ti-enrichment process. B$_2$O$_3$ is a typical acidic oxide that can change the melting behavior and decrease the viscosity of slags to greatly promote the mass diffusion of crystallization of Ti-enriched phases in molten slags. Previous reports have shown that B$_2$O$_3$ can affect the composition of crystals in solution to some extent. Sun et al. investigated the effect of the addition of SiO$_2$ and B$_2$O$_3$ on the crystallization behavior of Ti-bearing blast furnace slag using a single hot thermocouple technique. They found that the addition of 3 and 7 wt% B$_2$O$_3$ can promote the transformation of the primary crystalline phase from perovskite to rutile, while the precipitation of perovskite is suppressed. It can be concluded that adding a slight amount of B$_2$O$_3$ can have a great effect on the crystallization process of Ti-bearing blast furnace slag.

The physicochemical properties of slag are closely related to its structure. A better understanding of the influence of B$_2$O$_3$ on the structure of Ti-bearing blast furnace slag is of great significance for further improving Ti-bearing slag utilization. Li et al. reported that B$_2$O$_3$ acts as a typical network-forming oxide and exists dominantly as triangular BO$_3$. Liang et al. studied the coordination structure of a CaO–SiO$_2$–TiO$_2$–B$_2$O$_3$ system by molecular dynamics simulation, reporting that boron changes from a frame structure to a layered structure in the slag, which promotes its fluxing performance. Li et al. analyzed the structure of CaO–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses and found that the content of bridging oxygen (BO) and the degree of polymerization increase with the increase of B$_2$O$_3$, and an equilibrium reaction between
non-bridging oxygen (NBO) atoms, tetrahedral BO$_4$, and trigonal BO$_3$ is established. Yang et al.\(^{17}\) also found that the introduction of B$_2$O$_3$ increased the degree of polymerization of a silicate network, forming a 3D borate structure.

Many researchers have investigated the effect of B$_2$O$_3$ on the structure of silicate slags. However, there have been few studies on glass or melts bearing both TiO$_2$ and B$_2$O$_3$. The influence of the addition of B$_2$O$_3$ on the Ti structure in silicate is also unclear. Therefore, the effect of B$_2$O$_3$ on the structure of CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glassy systems was investigated in this study. Raman spectroscopy, FT-IR, and X-ray photoelectron spectroscopy (XPS) detection techniques were employed, and the effect of B$_2$O$_3$ on the Ti structure of silicate was analyzed.

2. Experimental Methods

2.1. Sample Preparation

Glasses were synthesized using analytical-grade powders of CaO, Al$_2$O$_3$, SiO$_2$, TiO$_2$, and H$_3$BO$_3$, with H$_3$BO$_3$ being the source of B$_2$O$_3$. The chemical composition of the investigated CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses is listed in Table 1. In order to obtain CaO, CaCO$_3$ was calcined in a muffle furnace at 1 273 K for 6 h. After carefully weighing the ingredients, the prepared samples were grinded in an agate mortar for 40 min. Then, the mixed powder sample was placed into a platinum crucible and heated to 1 773 K, which was held for 2 h in a high-temperature tube furnace. The heating and melting process were kept in air atmosphere. Afterwards, the molten slags were quenched with water to obtain glassy samples. To identify the glassy state, the prepared samples were analyzed by X-ray diffraction (XRD), as shown in Fig. 1.

Table 1. The chemical compositions of slag samples with different B$_2$O$_3$.

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<tr>
<th>Sample number</th>
<th>Composition (mol%)</th>
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<tr>
<td>1</td>
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2.2. Spectroscopy Analysis

This study combined XPS, FT-IR, and Raman spectroscopy techniques to detect and analyze the structures. XPS was performed to detect glass powder samples in 100–200 mesh, including the spectra of B1s and O1s, which using ESCALAB250Xi XPS designed by Thermo Fisher under the pressure of $5 \times 10^{-9}$ Pa. The FT-IR spectra, with a spectral resolution of 4 cm$^{-1}$, were recorded in the wavenumber range of 4 000–400 cm$^{-1}$ using an iS50 spectrometer (Thermo Fisher, USA). The LabRAM HR Evolution type micro-confocal Raman spectrometer (HORIBA Jobin Yvon S.A.S, France) with an excitation wavelength of 532 nm was used. The power of the light source was 1 mW. Raman spectra were recorded in the wavenumber range of 120–3 000 cm$^{-1}$.

3. Results and Discussion

3.1. X-ray Photoelectron Spectroscopy Analysis

3.1.1. B1s XPS Spectra

The B1s spectra were smoothened by averaging the raw data of the CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses, as shown in Fig. 2(a). There was a main peak in the binding energy range of 190–194 eV. With the increased amount of B$_2$O$_3$,
the intensity of the main peak was enhanced, and the whole peak moved slightly toward the higher binding energy direction. In order to explore the coordination information of boron in CaO–Al2O3–SiO2–TiO2–B2O3 glasses, the B1s XPS smoothed spectra were further analyzed. As reported in a previous work, B2+ ions can form two coordination bonds (BO3 and BO4) in a silicate network, which correspond to the bending energy at about ~191 and ~192 eV in the B1s XPS spectra, respectively. For the present B1s spectra, the whole peak slightly moved toward the higher binding energy direction, indicating that the tetrahedral BO4 had slightly increased. These results were supported by the further fitting of B1s spectra results using Gaussian functions, taking the example of 3 mol% B2O3, as shown in Fig. 2(b).

The changes of BO3 and BO4 with the increased B2O3 calculated from the deconvolved results of the B1s XPS spectra are shown in Fig. 3. With the increasing content of B2O3, the proportion of BO3 decreased, while BO4 increased. The triangular BO3 usually formed a 2D structure, which was the dominant structure compared with the 3D structure, tetrahedral BO4. This kind of 2D structure was simpler and less structurally complex compared with the 3D structures, such as tetrahedral SiO4 and BO4. Additionally, for the investigated system of CaO–Al2O3–SiO2–TiO2–B2O3, Ca2+ is the charge-compensator to make BO4 structure, which consumed the total cation in the system leading to the increase of polymerization degree. Therefore, it was concluded that the increasing percentage of tetrahedral BO4 may make the structure of the glass more polymerized.

3.1.2 O1s XPS Spectra

As shown in Fig. 4(a), there was one main peak located at the 527–535 eV binding energy of the O1s spectra in all glassy samples. According to previous works, the main peak of the O1s spectrum can be distinguished by two main oxygen contributions in the silicate glass network due to the bridging oxygen (BO) and NBO atoms. The NBO atoms were located in the low binding energy peak at 530–531 eV, and the peak of BO atoms corresponded to 531–533 eV binding energy. From Fig. 4(a), the O1s XPS spectra slightly moved toward the high binding energy direction with the increased B2O3 content, showing that the bridging oxygen increased. All O1s XPS spectra were fitted using two Gaussian functions (BO and NBO), taking the example of 0 mol% B2O3 shown in Fig. 4(b). The fitting results are presented in Fig. 5. It was observed that the fraction of bridging oxygen increased and that of non-bridging oxy-
gen decreased with the increasing content of B$_2$O$_3$, which demonstrated that the addition of B$_2$O$_3$ enhanced the degree of polymerization of the Ti-bearing silicate structure. This maybe because the tetrahedral BO$_4$ had a 3D structure, which participated in the SiO$_2$ network to increase the network connectivity.

### 3.2. FT-IR Analysis

The FT-IR transmission spectra between 500 and 1 600 cm$^{-1}$ are shown in Fig. 6. According to previous studies, the structural assignments of B-bearing silicate glasses are summarized in Table 2. The FT-IR spectra curves were divided into three domains: the 600–800, 800–1 200, and 1 200–1 600 cm$^{-1}$ bands. The highest intensity bands in 800–1 200 cm$^{-1}$ range corresponded to the combined stretching vibrations of the SiO$_4$ and BO$_4$ tetrahedral network. It was observed that the intensity of the band centered at about 845 cm$^{-1}$ gradually weakened with the increase of B$_2$O$_3$, which was assigned to Q$^0$ (Si). This may have increased the degree of polymerization of the silicate structure. The weaker band at 600–800 cm$^{-1}$ was attributed to the bending vibrations of [AlO$_4$]$^{5-}$ and B–O–B. Especially, the band at about 710 cm$^{-1}$ was assigned to the bending vibrations of bridging oxygen formed by two trigonal BO$_3$ units, and the signal of the absorption region of polymerization of the Ti-bearing silicate structure. This had been proved in the results of the B1s spectra. According to Li et al., Kamitosos et al., and Hidi et al., two bands centered at about 1 210 and 1 350 cm$^{-1}$ were assigned to the stretching vibrations of tetrahedral BO$_4$ and BO$_3$ antisymmetric stretching vibration in the domain of 1 200–1 600 cm$^{-1}$. Similarly, the signal of trigonal BO$_3$ gradually became stronger with the increase of B$_2$O$_3$, while the signal of tetrahedral BO$_4$ was not obvious. Combined with the previous analysis, it can be concluded that trigonal BO$_3$ was the main type of boron-related structural group in the investigated Ti-bearing glassy slags.

### 3.3. Raman Spectroscopy Analysis

The original Raman spectra for CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses at room temperature are shown in Fig. 7. The spectra can be subdivided into two main regions, referring to the [SiO$_4$] tetrahedron (850–1 000 cm$^{-1}$) and the Ti structure (600–850 cm$^{-1}$) respectively. Ti can form three coordination forms of fourfold (~850 cm$^{-1}$), fivefold (~780 cm$^{-1}$), and sixfold (~700 cm$^{-1}$). According to previous studies, the [SiO$_4$] tetrahedron structural units have been separated into five types—Q$^i$ (i = 0, 1, 2, 3, 4) which is based on the number of bridging oxygen atoms in each SiO$_4$ structural unit. In the present work, all original Raman spectra were fitted by the Gaussian deconvolution method (the minimum correlation coefficient $r^2 \geq 0.99$) as exhibited in Figs. 8(a)–8(d). It can be seen in Fig. 8(a) that there were two stronger bands at about 926 and 997 cm$^{-1}$, and two relatively weaker bands near 892 and 1 042 cm$^{-1}$. Based on related research, the Raman band centered at about 926 cm$^{-1}$ was defined as Q$^1$, due to Si$_2$O$_7^{4-}$ having one bridging oxygen in the dimer structure unit. Another band at about 997 cm$^{-1}$ was referred to as Q$^2$, due to SiO$_4^{6-}$ having two bridging oxygen atoms in the chain structure unit. Similarly, the Raman bands centered at about 892 and 1 042 cm$^{-1}$ were assigned to Q$^3$ in the monomer structure and Q$^4$ in the sheet structure. There were three bands at about 698, 791, and 856 cm$^{-1}$ that corresponded...
to TiO₆, TiO₅, and TiO₄ structural units, respectively. The Raman band with the highest peak intensity was due to the TiO₅ structural unit in the B₂O₃-free glass. However, with the introduction of B₂O₃, the TiO₄ structural unit gradually increased and became the main structural unit.

The area percentages of each structural unit of the CaO–Al₂O₃–SiO₂–TiO₂–B₂O₃ glasses are shown in Table 3. The ratio of the dimer (Q¹) and sheet (Q³) gradually increased, while the ratio of the monomer (Q⁰) and chain (Q²) decreased as the B₂O₃ content increased, which revealed that the addition of B₂O₃ is beneficial to enhancing the connectivity of the [SiO₄] tetrahedral network structure. These results are consistent with the work done by Li et al. (16)

According to some studies, (30,34,37) the average number of bridging oxygen atoms of each sample (BO/Si) can be estimated by the area ratio of each structural unit in the Raman spectra multiplied by the number of its bridging oxygen atoms, as shown in Fig. 9. It was observed that the number of BO/Si slightly increased with the increasing B₂O₃ content, which was consistent with the results of the O1s XPS spectra results. Additionally, it can be seen that the intensity of the TiO₄ and TiO₅ structural units slightly increased, while the relative intensity of the TiO₆ unit decreased with the increasing content of TiO₂. This demonstrated that the Ti structure can be changed by the addition of B₂O₃ in silicates. According to Mysen et al., (38) Ti⁴⁺ can be substituted for Si⁴⁺ in the structural units of Ti-bearing silicate glasses when Ti⁴⁺ exists in tetrahedral coordination to enhance the network structure as a network former, while TiO₅ and TiO₆ work as network modifiers, which decreased the degree of polymerization of CaO–Al₂O₃–SiO₂–TiO₂ glasses. It can

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<th>Sample number</th>
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Fig. 8. Deconvolved results of Raman spectra for CaO–Al₂O₃–SiO₂–TiO₂–B₂O₃ glasses with different B₂O₃ contents. (Online version in color.)

Fig. 9. Effects of B₂O₃ content on the number of the average bridging oxygen.

Table 3. Deconvolved results of Raman spectra for CaO–Al₂O₃–SiO₂–TiO₂–B₂O₃ glasses.
be concluded BO$_3$ and TiO$_4$ increased with the increasing content of B$_2$O$_3$, which could lead to the increase of network connection units, such as SiO$_4$, to increase the degree of polymerization of CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses.

The structural information of slags could be used to explain the change of properties. Ren et al. investigated the effect of B$_2$O$_3$ on precipitation behavior of perovskite and anosovite crystals, showed that the increasing B$_2$O$_3$ content in the present slags suppress the precipitation of perovskite and promote the formation of anosovite crystal. Zhang et al., also found that the perovskite was suppressed by B$_2$O$_3$ addition in Ti-bearing blast furnace slag. From the present structure investigation, as the increase of B$_2$O$_3$, both the TiO$_4$ and BO$_4$ increased. The formation of BO$_3$ would consume Ca$^{2+}$ as a charge compensator. These results probably suppressed the perovskite precipitation.

4. Conclusions

The structures of CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glassy systems with various B$_2$O$_3$ contents were investigated by XPS, FT-IR, and Raman spectroscopy techniques. The following conclusions were obtained:

(1) B$^{3+}$ ions could form trigonal BO$_3$ and tetrahedral BO$_4$ structural units in Ti-bearing silicate networks. BO$_4$, as the dominant structure of the boron-related structural group, decreased slightly with the increasing content of B$_2$O$_3$ while BO$_3$ slightly increased.

(2) Three coordination forms of TiO$_4$, TiO$_3$, and TiO$_2$ were discovered in Ti-bearing glasses. The percentage of the TiO$_4$ unit gradually increased and became the main structural unit in the Ti structure as the B$_2$O$_3$ increased.

(3) There was an increase of BO$_3$ and TiO$_4$ units as the B$_2$O$_3$ content increased, which could lead to the increase of network connection units, such as SiO$_4$, to increase the degree of polymerization of CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–B$_2$O$_3$ glasses.

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