Effects of MgO, Na₂O, and B₂O₃ on the Viscosity and Structure of Cr₂O₃-bearing CaO–SiO₂–Al₂O₃ Slags

Qiuhan LI,¹⁾ Shufeng YANG,²⁾ Yanling ZHANG,^{1)*} Zhuoqing AN¹⁾ and Zhancheng GUO¹⁾

1) State Key Laboratory of Advanced Metallurgy, University of Science & Technology Beijing, Beijing, 100083 China.

2) School of Metallurgical and Ecological Engineering, University of Science & Technology Beijing, Beijing, 100083 China.

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The influence of MgO, Na₂O, and B₂O₃ on the viscosity of Cr₂O₃ bearing CaO–SiO₂–Al₂O₃ slags was investigated using the rotating cylinder method. Structural information of slags with different MgO, Na₂O, and B₂O₃ content was obtained via Raman spectroscopy. The viscosity of Cr₂O₃ bearing CaO–SiO₂–Al₂O₃–MgO slags increases with Cr₂O₃ addition. The viscosity and activation energy (E_a) of Cr₂O₃ bearing CaO–SiO₂–Al₂O₃ slags decreases with increased MgO, Na₂O, and B₂O₃ content. The effect of MgO and B₂O₃ on viscosity and activation energy (E_a) of Cr₂O₃ bearing CaO–SiO₂–Al₂O₃ slags was greater than that of Na₂O. This could be due to the different ways in which these additives modify the slag network structure. Raman spectroscopy analysis revealed that MgO and Na₂O work as network modifiers, and the degree of polymerization (DOP) of slags increases with the addition of MgO and Na₂O. MgO is more effective at modifying the structure than Na₂O, because Na₂O may be more likely to produce network former [AlO₄] units. In this study, Cr₂O₃ and B₂O₃ are found to behave as network formers and increase the DOP. This is characterized by the decrease in NBO/Si (the number of non-bridging oxygen per Si atom) value. B₂O₃ addition leads to the formation of low melting point eutectics and weaker polymerization strength, which contribute to the decrease in slag viscosity.

KEY WORDS: Cr₂O₃ bearing slags; raman spectroscopy; structure; viscosity; flux.

1. Introduction

Cr is an important alloying element in many types of metallic materials, such as stainless steel. During smelting and refining of these materials, the poor fluidity of the molten Cr-bearing slag has a major limiting effect on process efficiency. The high viscosity of this Cr-bearing slag, caused by its high melting point, leads to poor separation of the metal melt, which then results in significant metal dross and high impurity content in the final metal products. Much previous work has been carried out on improving the fluidity of Cr-bearing slag. Behera *et al.*¹⁾ reported that the viscosity of aluminothermic ferro-chrome slags decreased with increased MgO content. CaF₂ is another common addition to improve the fluidity of slags with high melting points (such as Cr₂O₃-bearing slag),²⁾ however, increasingly strict environmental protection regulations are limiting the use of this material. B₂O₃ is considered to have analogous behavior to CaF₂, and is becoming increasingly popular in the metallurgical industry. The lower melting point of B₂O₃ was reported to be more effective at lowering the break temperature and decreasing the viscosity of slags,^{3,4)} even though B₂O₃ essentially behaves as an acid oxide (which is usually regarded as a network former and helps polymerize the network structure). Na₂O was also found to be able to

decrease the viscosity of some slags,^{5,6)} however, its application in Cr-bearing slags has not yet been studied.

Recently, a consensus has been reached, that the macroscopic physical properties of a slag, such as viscous flow behavior, are determined by its structure. The decrease of slag viscosity is generally explained by the network modification behavior of basic oxides, which leads to the network structure becoming partly depolymerized.^{7–11)} The viscosities of several types of Cr-bearing slag have been investigated, such as CaO–CaF₂–Cr₂O₃ slags by Ostrovski *et al.*,¹²⁾ CaO–SiO₂–MgO–Cr₂O₃ slags by Minami *et al.*,¹³⁾ and mold fluxes by Xu *et al.*¹⁴⁾ The results of these studies showed that the viscosity of the slags increased as Cr₂O₃ content increased. These studies, however, mainly reported the effects of varying components, such as Cr₂O₃, MgO, and CaF₂, on the viscosity of the slags. Detailed information on the structure of Cr₂O₃-bearing slags, along with the effects of different components, is extremely limited.

In order to find an effective flux to improve the fluidity, a detailed understanding of the effect of some components on the viscosity of Cr₂O₃-bearing slag is necessary, in particular the effect on the structure. In this study, the viscosity-structure relationship of Cr₂O₃-bearing CaO–SiO₂–Al₂O₃–MgO, Na₂O, B₂O₃ slags was investigated by using the rotating cylinder method in conjunction with Raman spectroscopy.

* Corresponding author: E-mail: zhangyanling@metall.ustb.edu.cn
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couple. The crucible and spindle are made of Mo, and their dimensions are shown in Fig. 2(b).

The viscometer was connected to the spindle by a corundum shaft, and calibrated with castor oil with a known viscosity. The crucible with pre-melted sample was placed into the hot zone of the furnace. During the viscosity measurements, a flow of cooling water and a constant stream of pure Ar gas (3 L/min) were maintained throughout the process. The furnace was heated to 1 793 K and held for 1 h, to ensure that the samples were fully melted and homogenized. The spindle was then slowly lowered into the slag along the central axis of the melt, until its tip was about 10 mm above the crucible base. The crucible and spindle were aligned with the axis of the viscometer to minimize experimental errors. Viscosity measurements were performed during the cooling cycles, at intervals of 20 K from 1 793 K to 1 653 K. The temperature was stabilized for 20 min after each temperature drop prior to measurement. The Newtonian behavior of slag can be guaranteed, as there was negligible deviation in the viscosity data obtained with three different rotation speeds. The average value measured across three different rotation speeds was adopted and considered as the final viscosity value at the specific temperature.

After the viscosity measurements, all the slag samples were reheated to 1 793 K for 1 h and then quenched in water. The samples were then dried and crushed. Samples were confirmed to be amorphous by X-ray diffraction analysis. Composition of samples were analyzed using X-ray fluorescence spectroscopy, and the composition changes after viscosity measurements were very small, initial composition of samples is seen as the final composition for the sake of convenience. The glassy samples were tested using a Raman spectrometer (JY-HR800, JobinYvon SAS, France), with an excitation wavelength of 532 nm and using a 1 mW semiconductor laser as light source. Raman spectra were recorded in the range 200–1 600 cm^{-1} and the wavenumber precision was 1 cm^{-1} .

3. Results and Discussion

3.1. Effect of Cr_2O_3 , Na_2O , MgO and B_2O_3 on Slag Viscosity

Figure 3(a) shows the effect of Cr_2O_3 addition on the viscosity of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-3%MgO-Cr}_2\text{O}_3$ slags with a C/S ratio of 0.9 at 1 793 K. It was found that the slag viscosity increases with increasing Cr_2O_3 content. When the Cr_2O_3 content was increased from 0% to 5%, the viscosity increased from 0.51 Pa·s to 0.95 Pa·s. A similar trend was observed in previous research.^{12–14)}

The effect of Na_2O , MgO and B_2O_3 on the viscosity of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-1%Cr}_2\text{O}_3$ slag with a fixed C/S ratio of 0.6 are illustrated in Figs. 3(b), 3(c) and 3(d), respectively. It can be seen that viscosity decreases with increasing MO content (denoting Na_2O , MgO , and B_2O_3). Similar trends have been observed in Cr_2O_3 free slags.^{5,6,15)} On increasing Na_2O content from 0% to 16%, MgO content from 0% to 12%, and B_2O_3 content from 0% to 16%, the viscosity of this slag decreased from 2.82 Pa·s to 1.40 Pa·s, from 2.83 Pa·s to 0.86 Pa·s, and from 2.82 Pa·s to 0.89 Pa·s, respectively. All of these decrement were much larger than those observed in Cr_2O_3 free slags.^{5,6,15)} This suggests that Na_2O ,

Fig. 3. Effect of (a) Cr_2O_3 , (b) Na_2O , (c) MgO , and (d) B_2O_3 on slag viscosity.

Fig. 4. Comparison of the effect of Na_2O , MgO , and B_2O_3 on the viscosity.

MgO , and B_2O_3 are more useful for reducing the viscosity of Cr_2O_3 -bearing slags than Cr_2O_3 -free slags, probably because the viscosity of Cr_2O_3 -free slag is too low compared to that of Cr_2O_3 -bearing slag. A comparison of the effects of Na_2O , MgO , and B_2O_3 on the slag viscosity values above is shown in Fig. 4. This indicates that, in this study, MgO and B_2O_3 are more effective than Na_2O in decreasing the viscosity of the slag. Increasing the MgO content to 12% and the B_2O_3 content to 16% reduced the viscosity of the slag to below 1.0 Pa·s. In the case of $\text{Na}_2\text{O} = 16\%$, the viscosity of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-1%Cr}_2\text{O}_3\text{-16%Na}_2\text{O}$ slag was nearly 1.40 Pa·s. This could be due to the MgO , B_2O_3 , and Na_2O performing different functions in modifying the structure of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-1%Cr}_2\text{O}_3$.

The temperature-viscosity relationship can be described by the Arrhenius equation, Eq. (1).

$$\ln \mu = \ln A + (E_\mu / RT) \quad \text{..... (1)}$$

where μ , A , R , T , and E_μ denote the slag viscosity, pre-exponential factor, gas constant, absolute temperature, and the apparent activation energy for viscous flow, respectively. It is generally considered that E_μ represents the energy barrier that fluid units have to overcome for movement to occur.¹⁶⁾ In addition, the variation of E_μ suggests a structure change in the melts. The value of E_μ evaluated from the slope of linear fitting of $\ln \mu$ with $1/T$ in Fig. 5, and the results obtained, are displayed in Table 2. The E_μ values of sample M_1 , N_1 , and B_1 are expected to be the same due

Fig. 5. Plots of $\ln(\mu)$ as a function of $(10\,000/T)$.

Table 2. Calculated activation energy for studied samples.

Sample	N ₁	N ₂	N ₃	N ₄	N ₅
E_{μ} (kJ/mol)	232	216	208	196	183
Sample	B ₁	B ₂	B ₃	B ₄	B ₅
E_{μ} (kJ/mol)	232	213	206	191	181
Sample	M ₁	M ₂	M ₃	M ₄	
E_{μ} (kJ/mol)	232	212	204	192	

to the same slag compositions (with no addition of Na_2O , MgO , and B_2O_3).

It can be seen that the addition of MgO , Na_2O , and B_2O_3 results in a decrease of E_{μ} . Similar E_{μ} values were observed in the case of B_2O_3 and MgO with the same addition levels, while that of Na_2O is noticeably higher. This also suggests that B_2O_3 and MgO are more effective than Na_2O at decreasing the energy barrier for viscous flow, which decreases the slag viscosity. This could be due to their different structural modification behaviors on the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-1\%Cr}_2\text{O}_3$ slag.

3.2. Structural Characteristics of Cr_2O_3 -bearing $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ Slag

The Raman spectra for Cr_2O_3 content in the range of 0 to 5%, are shown in Fig. 6(a). The relative intensity of bands at around 450 cm^{-1} and 550 cm^{-1} increases as the Cr_2O_3 content increases. This indicates that the number of bridging oxygen atoms (BO) increases with the addition of Cr_2O_3 , and that the network structure polymerizes. The peak at around 950 cm^{-1} shifts to lower frequency with the addition of Cr_2O_3 . This peak shift indicates that the added Cr_2O_3 is introduced into the silicate network as a network former, which increases the degree of polymerization (DOP), but decreases the polymerization strength. The typical silicate Raman band is in the region of $800\text{--}1\,200\text{ cm}^{-1}$, which corresponds to tetrahedral $[\text{SiO}_4]$ structural units. The relative intensity of the stretching vibration Q^n_{Si} (n is the number of bridging oxygen per tetrahedral unit, $n = 0$ to 4),^{17–19} increases with the addition of Cr_2O_3 . According to Jiang *et al.*,²⁰ the variation of Q^n_{Si} structural units is considered as the main reason affecting the DOP of the network structure, and viscosity.

In order to carry out a detailed investigation into the

Fig. 6. Effect of varying Cr_2O_3 content on the (a) Raman spectra and (b) structural units of the $\text{CaO-SiO}_2\text{-13 Al}_2\text{O}_3\text{-3\%MgO-Cr}_2\text{O}_3$ slag with $\text{C/S} = 0.9$.

Table 3. Structure assignments of Raman bands.

Units	Frequency (cm^{-1})	Structure assignment	Ref.
Q^0_{Si}	850–880	Zero bridging oxygen in $[\text{SiO}_4]$	[23–29]
Q^1_{Si}	900–920	One bridging oxygen in $[\text{SiO}_4]$	[23–29]
Q^2_{Si}	950–980	Two bridging oxygen in $[\text{SiO}_4]$	[23–29]
Q^3_{Si}	1 040–1 060	Three bridging oxygen in $[\text{SiO}_4]$	[23–29]
Q^4_{Si}	1 060, 1 190	Four bridging oxygen in $[\text{SiO}_4]$	[23–29]
Si–O–Si	500–650	Symmetric Si–O ⁰ bending	[30]
Al–O–Al	550	Vibration of Al–O ⁰	[31]
Cr–O–Cr	420–440	Asymmetric Cr–O ⁰ stretching	[32]

Fig. 7. Deconvoluted Raman spectra of the slag samples with $\text{C/S} = 0.9$ and different Cr_2O_3 contents. Cr_2O_3 content = (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, and (d) 5 wt.%.

structure of slags, quantitative peak deconvolution of the Raman band from $800\text{ to }1\,200\text{ cm}^{-1}$ was conducted using the Gaussian-deconvolution method (Mysen *et al.*^{21,22}). The recommended frequencies of Raman bands are summarized in Table 3. The deconvolution results for $\text{CaO-SiO}_2\text{-13\%Al}_2\text{O}_3\text{-3\%MgO-Cr}_2\text{O}_3$ slags are shown in Fig. 7. The relative fractions of Q^n_{Si} units as a function of bulk composition are shown in Fig. 6(b).

It can be seen in Fig. 6(b) that the relative fraction of simpler Q^0_{Si} units decreases with increasing Cr_2O_3 content, and the relative fractions of Q^1_{Si} , Q^2_{Si} and Q^3_{Si} units then

increase. Increasing Cr_2O_3 content makes the network structure more complex, which results in increased slag viscosity. The viscosity decrease of Cr_2O_3 containing slags in section 3.1, could be attributed to the variation of multiple structural units, and was caused by the addition of MgO , Na_2O , and B_2O_3 to the silicate network structure.

3.3. Effect of Na_2O Addition on Slag Structure

The Raman spectra for glass samples with different Na_2O content are shown as a function of wavenumbers in Fig. 8(a).

It can be seen in Fig. 8(a) that the Raman peak near 1050 cm^{-1} shifts towards lower frequency with increasing Na_2O . This implies that the degree of polymerization (DOP) of the silicate network structure decreases at higher Na_2O content. The Raman band near 440 cm^{-1} , which relates to the stretching vibration of Cr-O-Cr , is not discernible. The peak at 510 cm^{-1} vanishes, and the peak at 630 cm^{-1} turns into a shoulder with the addition of 4% Na_2O , both bands are assigned to the symmetric bending of Si-O-Si . The addition of 4% Na_2O leads to a decrease in relative intensity, which indicates that the number of bridging oxygen bonding with Si radically decreases, and the silicate network structure is partly broken. The peak at around 550 cm^{-1} , which is related to the transverse motion of bridging oxygen in Al-O-Al , becomes more pronounced with the

addition of Na_2O , and an increase in intensity means that the number of bridging oxygen increases, this phenomenon could be ascribed to the incorporation of $[\text{AlO}_4]$ into the silicate network structure as a result of charge balancing mechanisms arising from the addition of Na_2O . The band near 694 cm^{-1} ,³³⁾ corresponding to $[\text{CrO}_6]$, is also not discernible. The bands corresponding to $[\text{CrO}_4]$ and Q_{Al}^4 stretch vibrations at 873 cm^{-1} ³³⁾ and 850 cm^{-1} ³¹⁾ respectively, are overlapped with the Si-O stretching vibration in Q_{Si}^0 units. Because the combined capacity of Al^{3+} , Cr^{3+} and O^{2-} is less than that of Si^{4+} .^{32,33)} In consequence, the effect of $[\text{AlO}_4]$ and $[\text{CrO}_4]$ units on the network is much less than the predominant $[\text{SiO}_4]$ units.

All the spectra in high-frequency region from 800 to 1200 cm^{-1} were fitted properly in Fig. 9. The deconvolution results as a function of Na_2O content are shown in Fig. 8(b). The fraction of fully polymerized Q_{Si}^4 units decreases as Na_2O content increases from 0 to 16%. The predominant Q_{Si}^3 units are also found to significantly decrease with increasing Na_2O content. The relative fraction of Q_{Si}^2 units varies slightly with the increasing Na_2O content. The relative fractions of Q_{Si}^1 and Q_{Si}^0 units both increase. When the Na_2O content reaches 16%, Q_{Si}^1 becomes the predominant unit present in the slag systems, and the relative fractions of Q_{Si}^0 and Q_{Si}^3 are equal.

The basic oxide Na_2O (a so-called network modifying oxide) dissociates into ‘free oxygen’ O^{2-} anions in silicate melts. With the addition of Na_2O , the O^{2-} can react with ‘bridging oxygen’ O^0 (connected with two Si atoms) and break the existing bonds. The silicate network structure polymerized by O^0 can be modified into discrete structural polymeric units by the formation of ‘non-bridging oxygen’ O^- (connected with one Si atom), as shown in the reaction below:

This reaction describes the breaking event of complex

Fig. 8. Effect of varying Na_2O content on the (a) Raman spectra and (b) structural units of the $\text{CaO-SiO}_2\text{-15 wt.\% Al}_2\text{O}_3\text{-1 wt.\% Cr}_2\text{O}_3\text{-Na}_2\text{O}$ slags with $\text{C/S} = 0.6$.

Fig. 9. Deconvoluted Raman spectra of the slag samples with $\text{C/S} = 0.6$ and different Na_2O contents. Na_2O content = (a) 0 wt.%, (b) 4 wt.%, (c) 8 wt.%, (d) 12 wt.% and (e) 16 wt.%.

structural units Q^4_{Si} and Q^3_{Si} into simple Q^1_{Si} and Q^0_{Si} units, which can be attributed to the supply of Q^{2-} anions to the silicate network from the addition of Na_2O .

The DOP was used to characterize the structural change of the network. The parameter $NBO/Si^{9-11)}$ (average number of non-bridging oxygen per Si atom) is adopted to explain DOP in the silicate slags. The effect of multiple Q^n_{Si} species on the modification of silicate network structure, and consequently on the variation of DOP, can be calculated from the following equation:

$$NBO/Si = \sum_{n=0}^4 (4-n) \cdot A_n \quad \text{..... (4)}$$

where A_n is the relative fraction of Q^n_{Si} units, and n is the number of bridging oxygen of each Q^n_{Si} unit. The NBO/Si calculation results are summarized in Fig. 10.

It can be seen that the value of NBO/Si increases as Na_2O content increases from 0 to 16%. This can be explained by the Na_2O playing the role of network modifier and causing depolymerization of the network structure, which decreases the DOP of silicate network and results in a decrease in slag viscosity.

3.4. Effect of MgO Addition on Slag Structure

The Raman spectra of the $CaO-SiO_2-15\%Al_2O_3-1\%Cr_2O_3-MgO$ slags ($C/S = 0.6$) with MgO content in the range of 0 to 12% are shown in Fig. 11(a).

As seen in Fig. 11(a), the intensity of the Raman band at around 550 cm^{-1} (which is related to the Al–O–Al bonds as discussed in section 3.3) slightly increases with the increased MgO content, this increase of bridging oxygen contributes to the formation of $[AlO_4]$ units charge balanc-

ing by MgO. The peak at around 640 cm^{-1} is related to Si–O–Si bending, and the increase of its relative intensity indicates an increase of bridging oxygen. The typical silicate Raman peak between 800 and 1200 cm^{-1} shifts significantly to lower frequency, which implies that higher MgO content leads to severe depolymerization of the silicate network structure.

The results of Gaussian deconvolution were shown in Fig. 12, the variation of Q^n_{Si} species (derived by Gaussian deconvolution) is shown in Fig. 11(b). It can be seen that the relative fraction of fully polymerized Q^4_{Si} units varies slightly as MgO content increase. The fraction of Q^3_{Si} units greatly decreases. The fraction of Q^2_{Si} units slightly decreases with the addition of 8% MgO, but then increases. The relative fraction of Q^1_{Si} increases with increasing MgO. Finally, for Q^0_{Si} units, the relative fraction increases to a maximum at MgO content of 8% and then remains almost constant. The NBO/Si values are found to increase with the addition of MgO, as shown in Fig. 10.

Amphoteric aluminum oxide (Al_2O_3) usually exists as a four-coordinated tetrahedral configuration $[AlO_4]$ in a silicate network structure, when the mole ratio of $Al_2O_3/\text{Basic oxides}$ is less than unity.³⁴⁻³⁶⁾ Na_2O is more capable of catalyzing the formation of network former $[AlO_4]$ units than MgO, due to the higher priority of Na^+ over Mg^{2+} for charge balancing Al^{3+} .³⁷⁾ More $[AlO_4]$ units produced by the consumption of Na_2O would polymerize with the silicate network, and a small proportion of the Na_2O would modify the silicate network structure. In consequence, the NBO/Si values of MgO are higher than that of Na_2O , as shown in Fig. 10. The slag viscosity therefore increases when Na_2O is substituted by equal amounts of MgO.

3.5. Effect of B_2O_3 Addition on Slag Structure

Figure 13(a) shows the Raman spectra for $CaO-SiO_2-15\%Al_2O_3-1\%Cr_2O_3-B_2O_3$ slags with different B_2O_3 content. The intensity of the Raman band at around 500 cm^{-1} greatly increases with the addition of B_2O_3 . This Raman band corresponds to Si–O–Si bending. Fan and Li *et al.*^{38,39)} suggested that the Raman band between 430 and 600 cm^{-1}

Fig. 10. Calculation results of NBO/Si for studied samples.

Fig. 11. Effect of varying MgO content on the (a) Raman spectra and (b) structural units of the $CaO-SiO_2-15\text{ wt.}\% Al_2O_3-1\text{ wt.}\% Cr_2O_3-MgO$ slags with $C/S = 0.6$.

Fig. 12. Deconvoluted Raman spectra of the slag samples with $C/S = 0.6$ and different MgO contents. MgO content = (a) 0 wt.%, (b) 4 wt.%, (c) 8 wt.%, and (d) 12 wt.%.

also represented the Al–O–Al vibrations within $[\text{AlO}_4]$ tetrahedral units. An increase in the relative intensity of the Raman band between 430 and 600 cm^{-1} indicates that the number of bridging oxygen is increased by increasing the B_2O_3 content.

The typical silicate Raman band between 800 and 1 200 cm^{-1} shifts towards higher frequency, which implies the DOP of the silicate network increases with increased B_2O_3 content. Taking into consideration the effect of B_2O_3 on the network structure, some assignments of B_2O_3 related Raman bands that are of interest to the present work are summarized in **Table 4**. According to Cochain *et al.*,⁴⁰⁾ the stretch band reflecting B–O⁰ vibrations in $[\text{BO}_4]$ tetrahedral units also exists in this region, at the frequency region of 900 to 920 cm^{-1} . As shown in Fig. 13(a), the continuous addition of B_2O_3 reduces the peak intensity at around 920 cm^{-1} , which indicates a decrease of bridging oxygen in the three dimensional $[\text{BO}_4]$ tetrahedral units. The relative intensity of the Raman band between 1 360 and 1 520 cm^{-1} significantly increases with increased B_2O_3 . This band is related to the stretch vibrations of B–O[−] non-bridging oxygen bonds in two dimensional $[\text{BO}_3]$ triangular structural units.^{40–44)} An increase in the relative intensity of this band indicates the $[\text{BO}_3]$ units and non-bridging oxygen content increase with increasing B_2O_3 content. The $[\text{BO}_3]$ triangular structure is simpler compared to the $[\text{BO}_4]$ tetrahedral structure, and consequently, the network structure becomes inherently less

complex at higher B_2O_3 content.

The Gaussian deconvolution of the Raman band between 800 and 1 200 cm^{-1} has been carried out in **Fig. 14**, the variation of structural units Q^n_{Si} is shown as a function of B_2O_3 content in Fig. 13(b). It can be seen that Q^0_{Si} units only exist in the B_2O_3 free slag, and are not observed in any other samples containing B_2O_3 . The relative fraction of Q^1_{Si} units significantly decreases with the addition of 4% B_2O_3 and slightly decreases with a further increase of B_2O_3 . The Q^2_{Si} fraction increases with the addition of 4% B_2O_3 and then slightly decreases with increased B_2O_3 content. The fraction of Q^3_{Si} units significantly increases with the addition of 4% B_2O_3 and then increases slightly at higher B_2O_3 content. The fraction of Q^4_{Si} units is also found to increase slightly with increased B_2O_3 content. Consequently, an increase in B_2O_3 content must cause the polymerization of simple Q^0_{Si} and Q^1_{Si} units into complex Q^3_{Si} and Q^4_{Si} ones. B_2O_3 behaves as a network former and may capture non-bridging oxygen in $[\text{SiO}_4]$ to form B–O bonds, which causes the decrease of NBO/Si in Fig. 10 due to the formation of Si–O–B bonds. Consequently, the DOP of borosilicate network structure increases with increased B_2O_3 content.

B_2O_3 is seen as a network former, however, it was observed that viscosity decreased as B_2O_3 content increased. This means that the decrease of viscosity (but not the lower DOP) might be caused by three phenomena described below.

Firstly, B–O bonds are weaker than Si–O bonds, and the flow units containing B–O bonds are easily broken. The polymerization of B_2O_3 into the silicate network will give rise to a higher DOP but a weaker polymerization strength.

Fig. 13. Effect of varying B_2O_3 content on (a) Raman spectra and (b) structural units of $\text{CaO-SiO}_2\text{-15 wt.\% Al}_2\text{O}_3\text{-1 wt.\% Cr}_2\text{O}_3\text{-B}_2\text{O}_3$ slags with C/S = 0.6.

Table 4. Assignments of borate-related Raman bands.

Units	Frequency (cm^{-1})	Structure assignment	Ref.
$[\text{AlO}_4]$	430–600	Al–O ⁰ stretching in $[\text{AlO}_4]$	[38,39]
$[\text{BO}_4]$	900–920	Symmetric B–O ⁰ stretching in $[\text{BO}_4]$	[40]
$[\text{BO}_3]$	1 350–1 530	B–O [−] stretching in $[\text{BO}_3]^-$	[40–44]

Fig. 14. Deconvoluted Raman spectra of the slag samples with C/S = 0.6 and different B_2O_3 contents. B_2O_3 content = (a) 0 wt.%, (b) 4 wt.%, (c) 8 wt.%, (d) 12 wt.%, and (e) 16 wt.%.

With the continuous addition of B_2O_3 above 4%, the relative fraction of simpler two dimensional $[BO_3]$ triangular structural units increases in borosilicate melts, which is advantageous for decreasing the connectivity of the network. Secondly, by increasing B_2O_3 content, and decreasing SiO_2 content, the silicate network structure is less dominant. Even if the $[SiO_4]$ structural units become more complex, the DOP of the silicate network structure is enhanced. Thirdly, due to the lower melting point of B_2O_3 , B_2O_3 could combine with basic oxides and form some eutectics, which will help lower the melting point of the slags and enhance the fluidity of molten slags.

3.6. Error Sources of Viscosity Values

The error sources are inaccuracies of the temperature measurement, compositional analysis and viscosity measurement apparatus. Firstly, there is a difference between the slag temperature and thermocouple reading (variation less than $\pm 2^\circ C$), though the thermocouple and the crucible were both in the uniform temperature zone of the furnace. Secondly, slag samples were prepared using pure oxides with about 1% impurities. Though, the weighing was done carefully, there is still an error in the composition of the slags. Thirdly and most importantly, the spindle may be not completely in the central region of the crucible, the nonuniform gap between the walls of crucible and spindle will magnify the boundary effects. The heavy spindle in the tip of corundum shaft will sway, especially easily at a higher rotational speed and measurement of low viscosity. Therefore, taking the average of measured values in three rotational speeds could minimize the error.

4. Conclusions

The effects of MgO , Na_2O and B_2O_3 addition on the viscosity and structure of $CaO-SiO_2-Al_2O_3-Cr_2O_3$ slags were investigated in this study. The following conclusions were made:

(1) The viscosity of the slags investigated in this study increased with the addition of Cr_2O_3 and decreased as the MgO , Na_2O , and B_2O_3 content increased. The activation energy decreased with increased MgO , Na_2O , and B_2O_3 . MgO and B_2O_3 are confirmed as more effective fluxing agents than Na_2O for decreasing the viscosity of $CaO-SiO_2-Al_2O_3-Cr_2O_3$ slag under experimental conditions.

(2) The introduction of basic oxides Na_2O and MgO into Cr_2O_3 bearing $CaO-SiO_2-Al_2O_3$ slags as network modifiers, helps to destroy the silicate network structure. Thus, the DOP of silicate network decreases, proved by the decrease in the relative fractions of Q^4_{Si} and Q^3_{Si} as well as the increase of Q^1_{Si} and Q^0_{Si} species.

(3) As Na^+ has a higher priority than Mg^{2+} for charge compensation of Al^{3+} and its surrounding O^{2-} , the formation of network former $[AlO_4]$ units catalyzed by Na_2O results in a higher DOP. This leads to the increase of viscosity and E_μ in Cr_2O_3 bearing $CaO-SiO_2-Al_2O_3$ slags, when comparable amounts of Na_2O and MgO are added.

(4) The addition of B_2O_3 into the silicate network, as a network former, gives a higher DOP for silicate network. But, the silicate network is weakened by the introduction

of B_2O_3 , and the existence of two dimensional $[BO_3]$ units reduces the complexity of the network. Additionally, low melting point eutectics are formed. These factors contribute to the decrease of slag viscosity and E_μ with increasing B_2O_3 content.

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