

Effects of basicity and MgO content on the viscosity of the SiO₂–CaO–MgO–9wt%Al₂O₃ slag system

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Abstract: The effects of basicity and MgO content on the viscosity of SiO₂–CaO–MgO–9wt%Al₂O₃ slags with basicity from 0.4 to 1.0 and MgO content from 13wt% to 19wt% were investigated using the rotating cylinder method. A correlation between the viscosity and the slag structure was determined by Fourier transform infrared (FTIR) spectroscopy. It is indicated that the complex network structure of the slag melt is depolymerized into simpler network units with increasing basicity or MgO content, resulting in a continuous decrease in viscosity of the slag. The viscosity is strongly dependent on the combined action of basic oxide components in the slag. Under the present experimental conditions, increasing the basicity is found to be more effective than increasing the MgO content in decreasing the viscosity of the slag. At higher temperatures, the increase of basicity or MgO content does not appreciably decrease the viscosity of the slag, as it does at lower temperatures. The calculated activation energy of viscous flow is between 154 and 200 kJ·mol⁻¹, which decreases with an increase in basicity from 0.4 to 1.0 at a fixed MgO content in the range of 13wt% to 19wt%.

Keywords: slags; viscosity; basicity; magnesia; activation energy; Fourier transform infrared spectroscopy

1. Introduction

Slag viscosity is one of the most important physico-chemical properties that clarify the reaction kinetics and optimize the metallurgical processes at high temperatures. Viscosity is often sensitive to the structural changes in molten slag, which implies that the analysis of viscosity is an effective means to understand the structure of molten slag. It is well known that the SiO₂–CaO–MgO–Al₂O₃ slag system is widely applied in various metallurgical processes. Thus far, several studies have reported both the experimental and modeling methods for determining the viscosity of this slag system [1–6]. However, most studies pertain to slag systems with relatively high basicity beyond 1.0, relatively high Al₂O₃ beyond 20wt%, and relatively low MgO content within 13wt%. Moreover, these viscosity data represent slags processed with a limited temperature range. However, from the application viewpoint, it is highly imperative to study the viscosity of slag systems with a wide range of slag constituents as well as a wide temperature range.

Slag systems with low basicity offer the advantage of improving the cleanliness of molten steel [7], and are also considered as a potential candidate for electrolytic medium in the extraction of iron by the electrolysis method [8–9]. As we know, both basicity and MgO content are two important factors that can affect slag viscosity, and have been widely studied for various slag systems [2–3, 10–19]. However, the extent to which these factors affect the viscosity is generally different for various slag systems and slag compositions [2, 10, 13–17]. Therefore, in the present study, we have experimentally determined the viscosity of the SiO₂–CaO–MgO–Al₂O₃ slag system by using the rotating cylinder method, under conditions of relatively low basicity in the range of 0.4 to 1.0, relatively high MgO content in the range of 13wt% to 19wt%, and Al₂O₃ content of 9wt%. The effects of basicity, MgO content, and temperature on the slag viscosity were investigated in the temperature range of 1573 to 1813 K. A correlation between the viscosity and the slag structure was verified by Fourier transform infrared (FTIR) spectroscopy. The phase characteristics of the slag were examined by X-ray diffraction (XRD).

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2. Experimental

2.1. Sample preparation

The chemical composition of the slag samples is summarized in Table 1. The liquidus temperature for each slag, as calculated by using the FactSage thermodynamic software [20], is also presented in Table 1.

Table 1. Chemical composition of the SiO₂–CaO–MgO–9wt%Al₂O₃ slag as well as measured viscosity values and calculated activation energy in the present work

No.	<i>B</i>	MgO / wt%	<i>T</i> _{LQ} / K	Viscosity, η / (Pa·s)			Activation energy, E_{η} / (kJ·mol ⁻¹)
				1773 K (1st)	1763 K (1st)	1763 K (2nd)	
1	0.4	13	1572	2.21	2.38	2.38	199.7 ± 1.4
2*	0.4	16	1576	1.73	1.86	1.90	200.5 ± 1.0
3	0.4	19	1625	1.09	1.16	1.12	190.5 ± 1.4
4*	0.6	13	1564	0.98	1.05	1.05	182.5 ± 1.0
5*	0.6	16	1566	0.84	0.90	0.90	188.5 ± 1.3
6*	0.6	19	1629	0.63	0.67	0.71	180.8 ± 0.5
7	0.8	13	1639	0.57	0.61	0.60	179.4 ± 1.4
8*•	0.8	16	1641	0.55	0.59	0.59	173.5 ± 1.7
9	0.8	19	1629	0.41	0.43	0.43	169.5 ± 1.1
10	1.0	13	1673	0.44	0.47	0.45	170.0 ± 1.2
11*	1.0	16	1693	0.41	0.43	0.41	159.2 ± 1.7
12	1.0	19	1733	0.33	0.35	0.35	154.3 ± 1.5

Note: *B* (basicity) = $w(\text{CaO})/w(\text{SiO}_2)$; *T*_{LQ} is the liquidus temperature; * represents slag samples for FTIR spectra, and • represents for XRD.

Analytical reagent (A.R.) chemicals of CaCO₃, SiO₂, MgO, and Al₂O₃ were employed as raw materials. In the typical process, all the chemicals were calcined at 1223 K for 6 h in a muffle furnace, in order to decompose the carbonates and hydroxides in the sample. Slag samples with desired proportions, as listed in Table 1, were prepared by mixing pre-determined quantities of the heated powders.

2.2. Experimental apparatus

In this study, the viscosity of the SiO₂–CaO–MgO–9wt%Al₂O₃ slag system was determined by the rotating cylinder method. A RTW-10 melt physical property comprehensive testing instrument with a digital viscometer developed by Northeast University was used to measure the viscosity. Fig. 1 shows a schematic of the experimental setup used in this study. The viscosity was measured by using a molybdenum spindle and a graphite crucible, the dimensions of which are shown in Fig. 1. The molybdenum

spindle consisted of a bob and a Mo shaft. A thin corundum tube of 500 mm in length and 4 mm in diameter was used as a corundum shaft. The mass of the spindle (bob + Mo shaft) was about 57 g, while the total mass of the spindle and the corundum shaft was about 77 g. The viscometer head was connected to the molybdenum spindle via the corundum shaft. The viscometer was installed in a lift, which allowed the immersion and subsequent removal of the spindle from the molten slag. The top cover of the viscometer had a marked level, which facilitates the adjustment of the apparatus, so as to maintain the spindle in the vertical position. The viscometer head could drive the spindle at a constant angular velocity and digitally record the torque exerted on the spindle by the molten slag. According to the instruction manual, the rotating speed of the spindle could be configured in the range of 150–450 r/min. A higher rotating speed is favorable for measuring a lower viscosity, with a resolution of 0.002 Pa·s. The rotating speed of the spindle should be decreased for a higher viscosity. The maximum viscosity measured in this study was 10 Pa·s, with the measurement error of within ±2.5% over the full-scale range. The slag samples were heated and melted by using a resistance furnace consisting of six U-shaped MoSi₂ heating elements. The alignment of the corundum furnace tube was verified to be vertical. Furthermore, the uniform temperature zone of the furnace was determined, so as to ensure that the crucible could be placed precisely in central position. The furnace temperature was controlled by using a B-Type (Pt–10wt%Rh/Pt–13wt%Rh) thermocouple in a corundum sheath, which is placed in contact with the outside of the bottom surface of the graphite crucible, integrated with a proportional integral differential controller. Before measurements, the system was calibrated by using castor oil (A.R.) of known viscosity (0.986 to 2.418 Pa·s) at different room temperatures.

2.3. Procedure adopted for viscosity measurements

In the typical process, 140 g of the mixed slag powder was placed in a high-pure graphite crucible, and positioned on a graphite base in the uniform temperature zone of the resistance furnace. As the entire 140 g of the slag powder could not be placed in the graphite crucible, a disassembled graphite sleeve (49 mm outer diameter, 40 mm inner diameter, and 250 mm height) was installed on the graphite crucible to hold the extra slag powder. The furnace was programmed to heat at the rate of 5 K·min⁻¹. Upon melting of the slag powder in the graphite crucible, the slag powder in the graphite sleeve drops freely into the graphite crucible. In case of high temperature treatment in air atmosphere,

there is a possibility for the graphite sleeve near the furnace top to be oxidized to CO. Therefore, the viscosity measurement process was performed under reducing atmosphere.

Inspection of the molybdenum spindle and the graphite crucible before and after viscosity measurements indicated no oxidation or noticeable geometric variations.

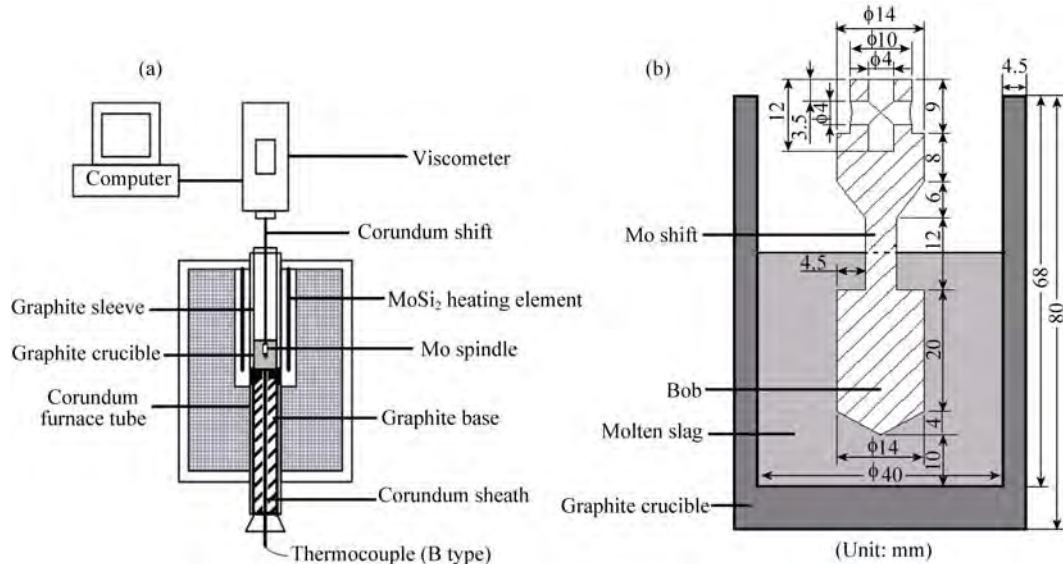


Fig. 1. Schematic diagram of the experimental setup: (a) the experimental setup; (b) the dimensions of the crucible and the spindle.

Upon complete melting, the amount of molten slag was about 40 mm in depth. In order to accelerate the homogenization and allow release of any remaining gas bubbles, the molten slag was stirred evenly for about 3 min by using a corundum tube of 6 mm in diameter, at temperatures of about 1723 and 1773 K. The slag was heated up to the maximum temperature (about 1813 K) and held for more than 8 min, so as to stabilize the temperature and homogenize the molten slag. Upon stabilization of the temperature, the rotating spindle was slowly immersed in and placed at the middle of the molten slag. The tip of the bob was carefully placed at a distance of about 10 mm above the bottom of the graphite crucible, and about 6 mm length of the Mo shaft was immersed in the slag. The rotating spindle further mixed and homogenized the molten slag.

In order to acquire the relationship between viscosity and temperature in a wide temperature range for all the slags, viscosity measurements were also performed during continuous cooling [6, 15, 17–18, 21–22]. The furnace was programmed to cool at a rate of 2 K·min⁻¹ from the maximum temperature, with viscosity measurements being performed at regular intervals. Before the furnace was set to cooling, the viscosity of the slag was initially measured at the maximum temperature, at various rotation speeds of the spindle. The changes in the viscosity values as a function of rotation speed were found to be less than 2%. This confirms that the slag melt is a Newtonian fluid. Therefore, a fixed rotation speed of 180 r/min was selected for each measure-

ment. After measuring the viscosity at the maximum temperature, subsequent measurements were automatically performed, continuously during the cooling process, while viscosity data was manually recorded at every 10 K interval. Table 1 shows the viscosity values recorded at 1773 and 1763 K. The spindle was lifted out of the slag melt when the measurement could not be continued under the conditions of very high viscosity or rapidly increasing viscosity conditions. Under such situations, the slag was reheated to 1763 K and held for 10 min, followed by re-measuring the viscosity at 1763 K. These values are simultaneously presented in Table 1. As is seen, both the viscosity values measured at 1763 K are in good agreement with each other. This indicates that the initial slag melt used to measure viscosity in the first round is homogenous, and that the viscosity measurement system used in this study is highly stable and reliable.

After completing the viscosity measurements for all the slags, some graphite crucibles containing slag melt were removed rapidly from the furnace at 1763 K and then quenched in water. The structural and phase characteristics of the amorphous slag samples thus obtained were measured by using FTIR (Bruker Vertex 70 FTIR spectrometer) and XRD (Panalytical Xpert Pro MPD diffractometer), respectively. As expected, the typical XRD pattern of an as-quenched slag (No. 8) shown in Fig. 2 showed no characteristic peaks, suggesting that the sample is amorphous. It also seems reasonable to regard the molten slags as uniform Newtonian fluid, as the liquidus temperatures for all the

slags were below 1763 K (Table 1). Furthermore, the FTIR transmission spectra of the samples were recorded in the spectral range of 4000–400 cm^{-1} using a spectrometer equipped with a KBr detector. A spectral resolution of 2 cm^{-1} was chosen for this FTIR measurement.

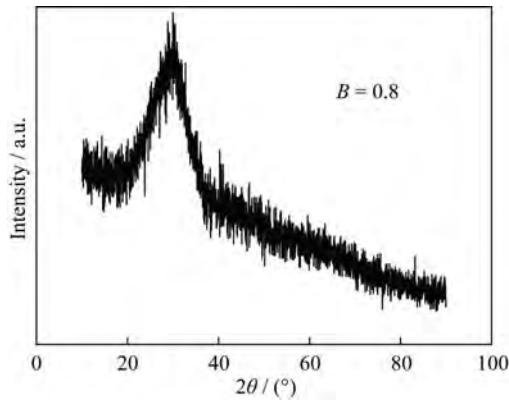


Fig. 2. Typical XRD pattern of the as-quenched $\text{SiO}_2\text{-CaO-16wt\%MgO-9wt\%Al}_2\text{O}_3$ slag from 1763 K.

3. Results and discussion

3.1. Effect of basicity on the viscosity

3.1.1. Comparison with other data

Fig. 3 shows the viscosity changes of $\text{SiO}_2\text{-CaO-MgO-}$

9wt% Al_2O_3 slags with temperature at different basicities. As expected, the viscosity decreases smoothly with increasing temperature, in the fully liquid region of all the slags. These results were comparable to those of the $\text{SiO}_2\text{-CaO-MgO-}$ Al_2O_3 slag system of similar compositions reported in Refs. [1, 11, 23]. Furthermore, Fig. 4 shows the effect of basicity on the isothermal viscosity of the slags. It can be seen that the viscosity values obtained in the present work are in good agreement with previously reported data of the slag system with a higher basicity [11, 23–24]. However, these results are higher than those reported by Machin *et al.* [1] and lower than those reported by Kawai [10]. The viscosity measurement at high temperature is rather complicated and a systematic process that involves several steps could cause errors. These factors include temperature, composition, spindle/crucible material and geometries, and the experimental setup [11, 25–26]. Given these limitations, it is highly difficult to identify reasons for the observed discrepancies in viscosity measurements, based on limited experimental information given in previous publications. Considering experimental uncertainties associated with viscosity measurements, the viscosity testing method proposed in the present work can be considered reliable and the viscosity values obtained can be assumed reasonable.

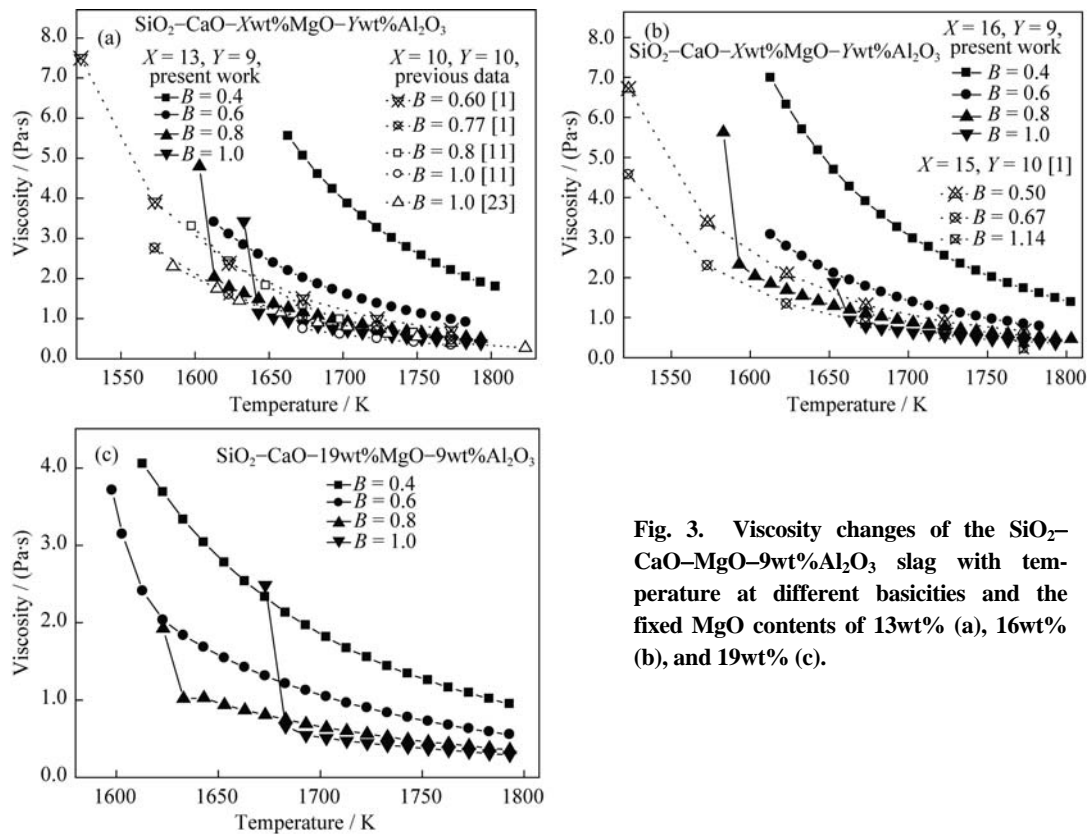


Fig. 3. Viscosity changes of the $\text{SiO}_2\text{-CaO-MgO-9wt\%Al}_2\text{O}_3$ slag with temperature at different basicities and the fixed MgO contents of 13wt% (a), 16wt% (b), and 19wt% (c).

3.1.2. Effect of basicity on the viscosity

As can be seen in Fig. 4, the viscosity of the slag decreases with increasing basicity for given MgO contents and temperatures. Comparing the slope of the viscosity-to-basicity plot in the regions of 0.4 to 0.6 and 0.8 to 1.0, it can be inferred that the effect of basicity becomes less pronounced at a higher basicity. This can be explained on the basis of the fact that the absolute amount of SiO₂ (acidic component) decreases and the absolute amount of CaO (basic component) increases with increasing basicity, as the basicity is defined as the mass ratio of CaO/SiO₂. It is well known that the depolymerization of the slag structure results in a lower viscosity. For a higher basicity, the availability of free oxygen ions (O²⁻) increases due to CaO dissociation. The free oxygen ions, in turn, can react with the bridged oxygen (O⁰) in the aluminosilicate network structures to form non-bridging oxygen (O⁻). The relative amounts of the complex network structures within the slag decrease with the increase in the formation of non-bridged oxygen. Thus, the subsequent slag viscosity decreases with the depolymerization of the aluminosilicate structures [11]. However, when excess free oxygen ions are supplied in the slag with a higher basicity, many of the existing complex network structures have already been depolymerized into simpler and smaller network units for viscous flow. Therefore, further depolymerization is less pronounced with increasing basicity due to the lack of complex network structures in the more basic slag melt [11].

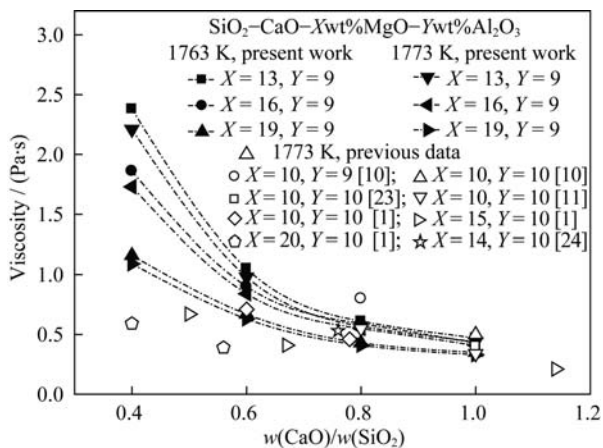


Fig. 4. Effect of basicity on the viscosity of the SiO₂-CaO-MgO-9wt%Al₂O₃ slag at given MgO contents and temperatures.

On the other hand, increasing the basicity shows an increasing trend of the liquidus temperature of the slag (Table 1) due to the excessive formation of CaO with high melting point. This results in a decrease of the superheat degree of the slag melt, which in turn can increase the viscosity in case of the slag with a higher basicity [13]. Hence, the increase of

basicity does not necessarily decrease the viscosity, as too high basicity can also result in a higher viscosity. Further the increase in basicity of the slag from 0.8 does not have a significant effect on the viscosity, in which case the decrease in viscosity is relatively lower. It is believed that the decrease of viscosity with increasing slag basicity can even be canceled out by the increase of viscosity with increasing CaO content. This situation tends to maintain the viscosity value unchanged at a given temperature. However, this phenomenon was not observed in the present experimental conditions.

The depolymerization of slag structures can also occur at higher temperatures, where the excess thermal energy can provide sufficient energy to break the existing complex network structures, thereby decreasing the viscosity. Thus, at high temperatures of the order of 1773 K, the increase of basicity does not have a significant effect on the depolymerization, as many of the existing complex network structures have already been broken due to the higher thermal energy at 1773 K compared to 1673 K, as shown in Fig. 3.

3.1.3. Effect of basicity on the break temperature of the slag

In this study, basicity was found to have a significant effect on the break temperature of the slag. In theory, break temperature [27–28] is defined as the temperature at which there is a significant change of viscosity during the cooling cycle, and it can separate the fully liquid region from the solid-liquid co-existing region. The viscosity of the slag with a lower basicity exhibits the behavior of a glassy slag, of which the viscosity gradually increases with decreasing temperature. Hence, the viscosity-to-temperature curve of the slag with a lower basicity of 0.4 did not exhibit a pronounced break. However, the viscosity of the slag with a higher basicity rises sharply, as the slag was cooled down to the break temperature. The viscosity-to-temperature curves of the slags with higher basicities of 0.8 and 1.0 were found to exhibit correspondingly a pronounced break, as shown in Fig. 3. This indicates that the solid precipitates are formed below the break temperature, in case of the slag with a higher basicity. In general, the break temperature increases with increasing slag basicity, which is a similar tendency to that of the liquidus temperature from the phase diagram (Table 1). However, the break temperature does not correspond to the liquidus temperature. Instead, the break temperature associated with the degree of supercooling is lower than the liquidus temperature. It is speculated that the difference between the break temperature and the liquidus temperature is related to thermodynamic driving force by which the solid phases can be precipitated from the molten slag [16, 23].

3.1.4. Effect of basicity on the slag structure

The slag melt quenched in water was further analyzed by using FTIR, in order to understand the relationship between the viscosity and the slag structure. Characteristic transmittance peaks in the FTIR spectra for silicate systems can be observed in the wavenumber region between 1200 and 400 cm^{-1} [3, 11, 29]. This region generally represents the symmetric Si–O stretching vibration bands of the $[\text{SiO}_4]^-$ tetrahedral at about 1200–750 cm^{-1} [23–24, 29–32], the asymmetric stretching vibrations of the $[\text{AlO}_4]^-$ tetrahedral (which behaves as a network former) at about 750–630 cm^{-1} [23–24, 29, 33], and the symmetric Si–O–Al bending vibration bands at about 630–400 cm^{-1} [3, 12, 14, 24, 33], etc. As a typical result, Fig. 5 shows the FTIR spectra of the SiO_2 –CaO–16wt%MgO–9wt% Al_2O_3 slags with different basicities, obtained by quenching of the molten slag from 1763 K.

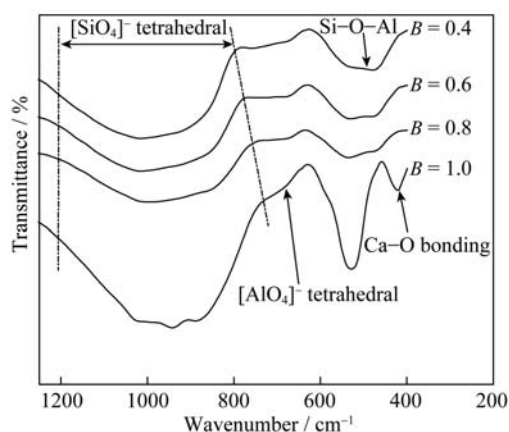


Fig. 5. Effect of basicity on the FTIR spectra of the as-quenched SiO_2 –CaO–16wt%MgO–9wt% Al_2O_3 slag from 1763 K.

As can be seen in Fig. 5, the lower limit of the $[\text{SiO}_4]^-$ tetrahedral bands at about 1200–750 cm^{-1} shifts to a lower wavenumber from about 790 to 730 cm^{-1} with an increase in basicity of the slag from 0.4 to 1.0. Furthermore, the broadening of the width of the $[\text{SiO}_4]^-$ tetrahedral bands suggests an increase in distance between Si and O. In other words, the silicate network structures in the slag melt are depolymerized with an increase in basicity of the slag [3, 32]. In addition, the trough of $[\text{AlO}_4]^-$ tetrahedral at about 750–630 cm^{-1} [23, 24, 29] dampens with increasing basicity, and almost disappears at the basicity of 1.0. This indicates that the aluminate network structures in the slag melt are also depolymerized with increasing basicity [11, 14, 23, 28, 34]. It seems reasonable to consider that the band groups observed at about 500 cm^{-1} are the Si–O–Al bending vibrations [3, 14, 23–24, 33, 35]. Furthermore, a new peak of Ca–O bonding at about 420 cm^{-1} [13, 29] appears at the basicity of 1.0.

There exists excess of Ca^{2+} over ions that acted as charge-balancing for Al^{3+} . This indicates that many of the complex anion groups in the aluminosilicate melt have already been depolymerized into simpler and smaller network units for viscous flow. The above mentioned variations in the structure of the slag melt with increasing basicity can explain the decrease of slag viscosity in the present work, as shown in Fig. 4.

3.2. Effect of MgO on the viscosity

Fig. 6 shows the viscosity changes in the SiO_2 –CaO–MgO–9wt% Al_2O_3 slag with temperature, plotted as a function of MgO content. Fig. 7 shows the effect of MgO content on the viscosity at a given temperature. As can be seen from Figs. 6 and 7, the viscosity of the slag melt decreases with increasing MgO content at all basicities. This implies that MgO behaves as a network modifier [2, 10, 12, 13, 23, 32]. This can be a common behavior of basic oxides, such as CaO, in the viscous flow of the slag. At a lower basicity of 0.4, MgO content have significant effect on the viscosity. However, at higher basicities of 0.8 and 1.0, as the basic components (CaO and MgO) in the slag outweigh the acidic component (SiO_2) with increasing MgO content (Table 1), many of the network structures have already been depolymerized into simpler polymer type units, such as dimer or monomer [3]. Therefore, the effect of MgO content on the slag viscosity is not much pronounced. It is considered that the effect of MgO content on the viscosity tends to diminish with increasing basicity. Similar results have been reported by H. Kim *et al.* [3], W.H. Kim *et al.* [12], and J.R. Kim *et al.* [14] in slags with similar compositions. On the other hand, the increase in MgO content also shows an increasing trend of the liquidus temperature of the slag (Table 1). Hence, the increase of MgO content, similar to basicity, also has two characteristics in influencing the viscosity. In this slag system, MgO not only behaves as a basic oxide to modify the slag network structure, but also increases the viscosity at significantly higher contents.

As can be seen from Fig. 4, the increase in basicity is much more effective in decreasing the slag viscosity at a lower MgO content than at a higher MgO content. Similarly, the increase of MgO content is more effective at a lower basicity than at a higher basicity, as shown in Fig. 7. These results suggest that the increase of basicity or MgO content is more effective in decreasing the slag viscosity at lower basicity and MgO content than at higher basicity and MgO content. This indicates that the viscosity can be strongly influenced by the synergistic action of basic oxide components in the slag.

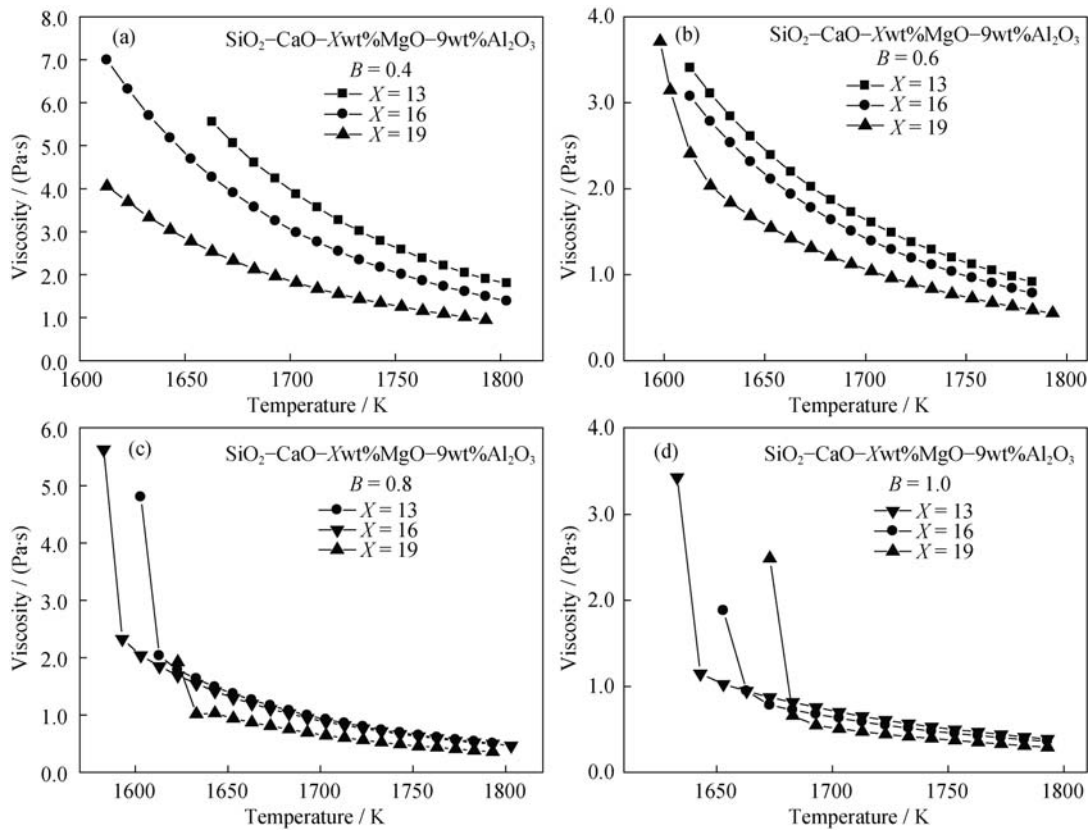


Fig. 6. Viscosity changes of the SiO₂-CaO-MgO-9wt%Al₂O₃ slag with temperature at different MgO contents and the fixed basicities of 0.4 (a), 0.6 (b), 0.8 (c), and 1.0 (d).

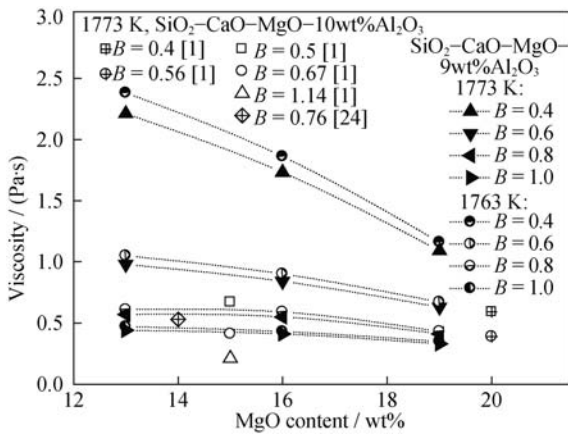


Fig. 7. Effect of MgO content on the isothermal viscosity of the SiO₂-CaO-MgO-9wt%Al₂O₃ slag at given temperatures and basicities.

The ability of basic oxide in decreasing the viscosity of the slag is strongly related to the basicity of oxides, namely, its tendency to offer O²⁻ ions. As the ionic radius of Mg²⁺ ions (0.65×10^{-10} m) is much smaller than that of Ca²⁺ ions (1.06×10^{-10} m), the Z/r^2 value (where Z is the valency and r is the radius of the cation) of Mg²⁺ ($Z/r^2 = 3.08$) is much higher than that of Ca²⁺ ($Z/r^2 = 1.89$). Thus, the polarizing power of Mg²⁺ is stronger than that of Ca²⁺. And, Mg²⁺ ex-

hibits a stronger electrostatic interaction with other ions [36]. Therefore, the ability of MgO to offer O²⁻ ions is considered to be relatively weaker than that of CaO. Consequently, the network breaking ability of MgO is not as high as that of CaO [10, 19].

Analogous to the trend observed in basicity, the effect of MgO on the depolymerization is comparatively lower at higher temperatures than that at lower temperatures. In addition, it exhibits a pronounced effect on the break temperature of the slag, as shown in Fig. 6. In this study, the break temperature was found to increase with an increase in MgO content of the slags, except for the composition of 16wt% MgO with the basicity of 0.8.

Fig. 8 shows the FTIR spectra of the SiO₂-CaO-MgO-9wt%Al₂O₃ slags with the basicity of 0.6 obtained by quenching of the molten slag from 1763 K, plotted as a function of wavenumber at different MgO contents. With an increase in MgO content from 13wt% to 19wt%, the lower limit of the [SiO₄]⁻ tetrahedral bands at about 1200-750 cm⁻¹ slightly shifts to a lower wavenumber from about 780 to 765 cm⁻¹. In addition, it can be observed that the trough of the [AlO₄]⁻ tetrahedral at about 750-630 cm⁻¹ becomes slightly narrow with increasing MgO content [12, 23].

Overall, the above mentioned changes in the structure of the slag indicate the depolymerization of some of the complex anion groups in the aluminosilicate melt into simpler structural units. This results in a decrease of slag viscosity at the basicity of 0.6, as shown in Fig. 7. It can be noted that the modifying effect of MgO content on the aluminosilicate network structures is not so pronounced under the present experimental conditions. Moreover, comparing Figs. 5 to 8, it can be found that the changes in the structure of the slag melt is more pronounced with increasing basicity than that with increasing MgO content. This can explain the fact that the increase in basicity is more effective than MgO content in decreasing the slag viscosity.

3.3. Activation energy for viscous flow

According to the Arrhenius-type relationship, the temperature dependence of the viscosity for the Newtonian fluid can be expressed by

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \quad (1)$$

where η is the viscosity, Pa·s; η_0 is the pre-exponent factor, Pa·s; E_η is the activation energy for viscous flow, J·mol⁻¹; R is the ideal gas constant, 8.314 J·(mol·K)⁻¹; and T is the absolute temperature, K.

Fig. 9 shows the temperature (above the break tempera-

ture) dependence of the viscosity for the SiO₂-CaO-MgO-9wt%Al₂O₃ slag system with different basicities and MgO contents. It can be seen that the natural logarithm of viscosity ($\ln \eta$) is proportional to the reciprocal of temperature ($1/T$) in the fully liquid region of the slag system above the break temperature of each slag composition. The activation energy, which represents the change of the frictional resistance for viscous flow, can be calculated from the slope of $\ln \eta$ plotted as a function of $1/T$. Variations in the activation energy can suggest a change in the structure of the slag melt, or

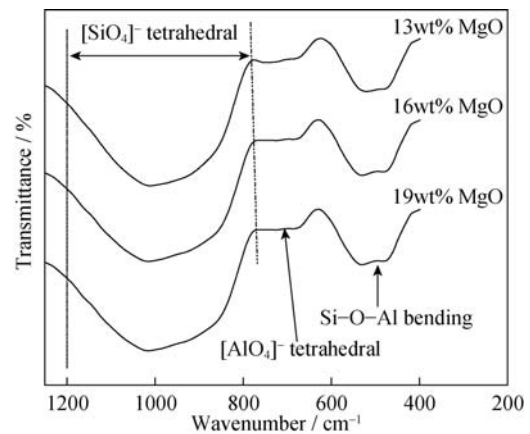


Fig. 8. Effect of MgO on the FTIR spectra of the as-quenched SiO₂-CaO-MgO-9wt%Al₂O₃ slag with the basicity of 0.6 from 1763 K.

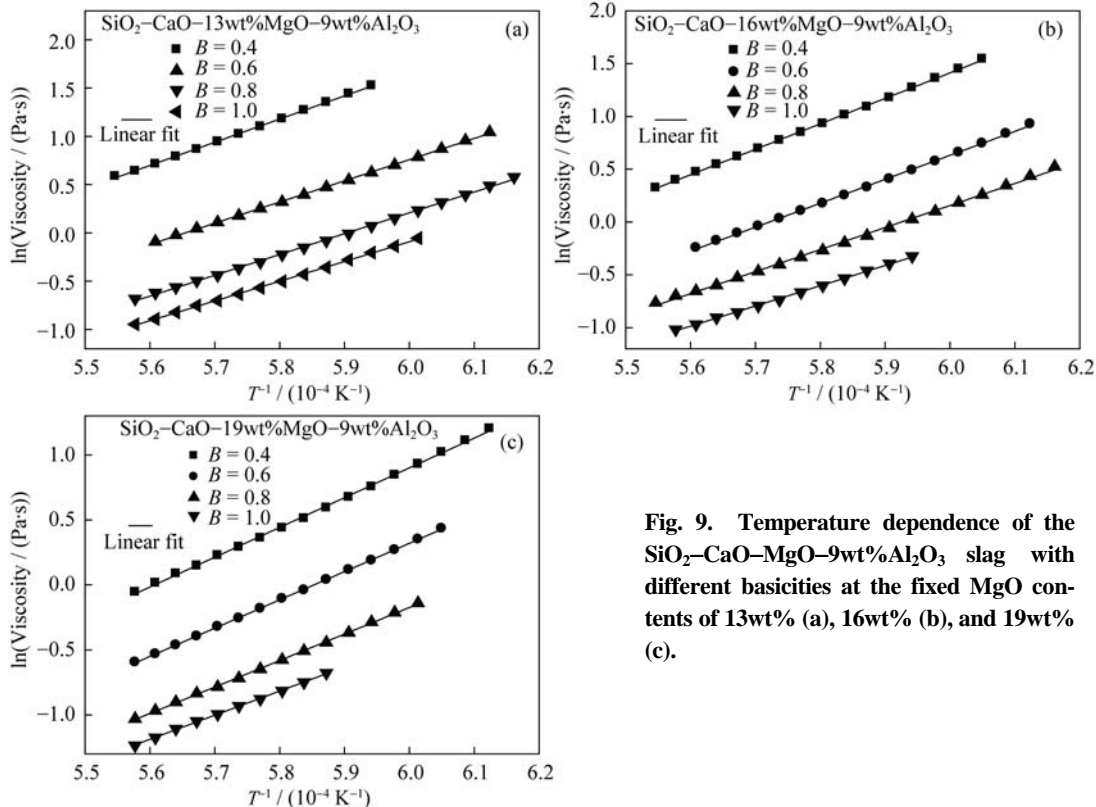


Fig. 9. Temperature dependence of the SiO₂-CaO-MgO-9wt%Al₂O₃ slag with different basicities at the fixed MgO contents of 13wt% (a), 16wt% (b), and 19wt% (c).

more directly, a change in the cohesive flow units comprising the slag structure. The values of the activation energy and the standard deviation from the linear regression are provided in Table 1. As expected, the activation energy decreases with increasing basicity from 0.4 to 1.0 for a fixed value of MgO content. Moreover, at the fixed higher basicities of 0.8 and 1.0, the activation energy also decreases with increasing MgO content from 13wt% to 19wt%. This is in agreement with the observed decrease in the viscosity value and also with the slag structure depolymerization due to the increase of basicity or MgO content. These values of the activation energy are relatively small when compared to previously reported values in the range of 230 to 280 kJ·mol⁻¹ for the SiO₂-CaO-MgO-10wt%Al₂O₃ slags with the constant basicity of 1.0 and the MgO content in the range of 5wt% to 13wt% [3]. Kim *et al.* [11] have also reported activation energy values of viscous flow in the range of 159 to 266 kJ·mol⁻¹ for the SiO₂-CaO-10wt%MgO-Al₂O₃ slags with the basicity in the range of 0.8 to 1.3 and the Al₂O₃ content from 0wt% to 20wt%. These values are comparable to those obtained in the present study.

4. Conclusions

The viscosity of the SiO₂-CaO-MgO-9wt%Al₂O₃ slag system has been determined by using the rotating cylinder method in the temperature range of 1573 to 1813 K. The results of the present work can be summarized as follows.

(1) FTIR analysis suggests that the complex network structures of the slag melt are depolymerized into simpler and smaller network units for viscous flow, with the increase in basicity or MgO content of the slag. This, in turn, results in a continuous decrease of slag viscosity. Increasing the basicity is found to be more effective in decreasing the slag viscosity than increasing the MgO content.

(2) The viscosity can be strongly influenced by the synergistic action of basic oxide components in the slag. At lower CaO and MgO contents, the degree of viscosity decrease with the increase of basicity or MgO content is higher than that at higher CaO and MgO contents. The effect of basicity on the viscosity at a lower MgO content is significant and becomes less pronounced with increasing MgO content from 13wt% to 19wt%. Similarly, the effect of MgO content on the viscosity at a lower basicity is also significant and becomes less pronounced with increasing basicity from 0.4 to 1.0.

(3) For all the slags, the viscosity decreases smoothly with increasing temperature, in the fully liquid region. The increase of basicity or MgO content does not appreciably

decrease the viscosity at higher temperatures, when compared to that at lower temperatures. The calculated activation energy of viscous flow is between 154 and 200 kJ·mol⁻¹, which decreases with increasing basicity from 0.4 to 1.0 at a fixed MgO content in the range of 13wt% to 19wt%.

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