Viscosity Property and Melt Structure of CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO Slag System

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For the purpose to describe the change of the viscosity properties of the converter slag during smelting reduction process using aluminum ash as reductant and provide basis for technology development, the viscosity of CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO slag system at a fixed basicity of 3 was measured with the various ratio of $A/(A+F)$ ($w(Al_2O_3)/w(Al_2O_3+FeO)$) by the cylinder method, and the structural of the melt was analyzed based on the FTIR and Raman spectroscopy to further explain the evolution behavior of viscosity. The results showed that viscosity of the slag was increased with increasing the ratio of $A/(A+F)$. When this ratio increased from 0.17 to 0.5, the simple network units of the molten slag were polymerized into more complex network structure, resulting in a slow increase in viscosity from 0.65 dPa·s to 0.91 dPa·s at 1 873 K. With further increasing this ratio to 1.0, the main structure was converted from silicate structure to aluminate structure. In addition, the polymerization degrees of aluminate units and silicate units both increased, which eventually led to an rapid increase in the viscosity from 0.91 dPa·s to 1.94 dPa·s.

KEY WORDS: quinary slag system; smelting reduction; viscosity; structure; polymerization degree.

1. Introduction

Steel slag as byproduct of the steelmaking process, its discharge occupies much land and often causes circumstance problem, and therefore, the utilization of steel slag has been causing much attentions during past several decades all over the word. But owing to the poor grindability performance and tendency to pulverization, the utilization ratio of steel slag is very limited. It is reported the generation of the steel slag has already exceeded 13 billion tons until 2014 in China, but its utilization ratio is only around 10%. With the development of environmental protection policy, the requirement for utilization of steel slag are becoming very urgent.

As well known, converter steel slag contains some available component like iron, manganese, and phosphorus coming from hot metal refining processing using basic oxygen converters. For the purpose to emission reduction and resource recovery, the treatment of steel slag by carbothermal reduction or metallothermic reduction to recovery of valuable elements and dephosphorization has been studied. Li et al. investigated the recycling of iron element and depshrophorization at around 1 923 K and 2 073 K, respectively. Though the depshrophorization rate is 95%, vast energy supply to maintain high temperature is an adverse factor for carbothermal reduction. In addition, the formation of CO gas facilitate to form forming slag which restrict the deep reduction of FeO in the slag. For metallothermic reduction, the cost problem caused by the expensive metal aluminum is considered to be a restrictive factor. It is well known, aluminum ash as a byproduct generated in electrolytic aluminum or casting aluminum alloy, its main composition contains Al$_2$O$_3$, SiO$_2$ and Al, and the content of Al often ranges from 22.0% to 32.5%. Owing to the low price of aluminum ash and without formation of forming slag, it is considered that that the treatment of steel slag using aluminum ash as reductant facilitate to avoid the disadvantage of the present carbothermal or metallothermic reduction methods, and is considered to be better method for treatment of steel slag.

It is known the basic composition of converter slag is CaO–MgO–SiO$_2$–FeO system, with small amount of MnO, P$_2$O$_5$ and so on. While treating converter slag using aluminum ash as reductant (as listed in Table 1), the basic composition of the slag system would transfer from CaO–MgO–SiO$_2$–FeO system to CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO system and further to CaO–MgO–SiO$_2$–Al$_2$O$_3$–P$_2$O$_5$ system with the reduction process proceeding, and during this process, the viscosity of the melting slag would change. It is known that the viscosity of the slag acts important roles during the smelting reduction process, and it is important for determination of operating parameters in practical production. Hence, it is very important to know the viscosity properties of CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO system with the composition of the reduction process. And furthermore, to understanding the effect mechanism of slag composition on its viscosity properties, the study on structure of the melting slag is necessary. But so far, many studies mainly focused on the structures or physicochemical properties of the CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO slag system with composition of BF slag system. Wang et al. found the alumina behaved as an acidic oxide in CaO–SiO$_2$–Al$_2$O$_3$–MgO–FeO melts even for the slags...
containing 24.42 mass% Al₂O₃. They reported that Al³⁺ behaved as [AlO₄]-tetrahedra (network former) whereas Fe³⁺ might play two roles that majority of Fe³⁺ acted as network former ([FeO₄]-tetrahedra) and the remaining Fe³⁺ acted as network modifier ([FeO₆]-octahedra). Park et al.⁶ clarified that Al₂O₃ behaved as an amphoteric oxide at in CaO–SiO₂ (–MgO)–Al₂O₃ slag system. Their results indicated the alumina behaved as a network former up to about 10 mass% Al₂O₃, while a network modifier in the composition greater than 10 mass% Al₂O₃. Kim et al.⁷ explored that the viscosity was not significantly changed with varying MgO content and the viscosity increased with increasing Al₂O₃ content at a fixed basicity (C/S = CaO/SiO₂) and MgO content. According to the results of the study from Gao et al.⁸ the complex network structure of the slag melt was depolymerized into simpler network units with increasing basicity or MgO content, resulting in a continuous decrease in viscosity of the slag. For BOF slags, Seok et al.⁹ studied the effect of basicity and the composition content on slag viscosity. The results turned out that the slag composition might change to the liquid-solid coexisting region and basicity had significant effect on increasing slag viscosity. Wright et al.¹⁰ characterized viscosities of the CaO–MgO–Al₂O₃–SiO₂ melts containing spinel particles of different sizes at 1646 K. Although these studies described the relationship between viscosity and the structure in a certain range, the melt compositions in the previous studies were different that of the present area (as listed in Table 2). Therefore, considering the condition of the smelt reduction of converter slag using aluminum ash as reductant, the viscosity of the CaO–MgO–SiO₂–Al₂O₃–FeO slag system with the different ratio of A/(A+F) at a fixed basicity (C/S) of 3 was investigated in this work, and the mechanism of the viscosity evolution was also revealed by melt structure analysis. The purpose of this work is to provide information about structural variation and its relationship with viscosity of the present slag system, and to provide theoretic basis for melting reduction using aluminum ash.

### 2. Experimental Procedures

#### 2.1. Starting Materials

Reagent grade oxides powders of CaCO₃ (> 99.50 mass%), SiO₂ (> 99.50 mass%), FeC₂O₄ (> 99.50 mass%), Al₂O₃ (> 99.50 mass%), MgO (> 99.50 mass%) were used as raw material. CaCO₃ powder was calcined for 5 h at 1 273 K to make CaO, and other kind powders were dried at 473 K for 4 h in a drying oven to remove moisture, then were well mixed by the ball-mill (polyurethane jar), using corundum balls as milling media, in the required proportion according to practical components of converter slag as shown in Table 3. Considering the decrease of FeO and the increase of Al₂O₃ during smelting reduction, the ratio of A/(A+F) was defined as different slag samples in the present study. Then the mixed powders were pressed into tablet samples and firstly held at 873 K for 2 h to decarburize FeC₂O₄, then further heated at 1 923 K for 2 h in molybdenum crucible to prepare pre-melted slag under high purified (HP; 99.999 pct) Ar (0.35 L/min) atmosphere in a vertical MoSi₂ furnace. Finally, the samples were quenched in water, dried, crushed and ground under 200 mesh for further use.

#### 2.2. Viscosity Measurement

The viscosity measurements were carried out by a rotat-
ing cylinder Brookfield digital viscometer. The schematic illustration of the apparatus and dimensions of the crucible and bob are shown in Fig. 1. For measuring the viscosity of CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO slag system, 150 g of the pre-melted sample was put inside a molybdenum crucible and heated in a rotary viscometer under the high purified Ar atmosphere (0.35 L/min) to prevent the oxidation of the spindle and slag. When the temperature reached the desired temperature and held for more than 30 min to homogenize the slag melt, the molybdenum spindle, connected to the viscometer by an alumina shaft, was then immersed in liquid slag for 10 mm above the crucible base and rotated at a fixed speed of 200 r/min, then the viscosity was measured at different temperatures (with temperature step of 5 K) during temperature dropping process.$^{11,12}$

### 2.3. Characterization

Melt structure analysis was studied using Raman scattering and FTIR measurements. The pre-melted slag was melted again in a D10 mm×10 mm zirconia crucible at 1873 K for approximately 4 hours under the same Ar atmosphere (0.35 L/min), and then rapidly quenched in water to obtain quenching sample.$^{13}$ The dried slag was crushed and ground into powders to analyze the structural properties by Raman and FTIR spectroscopy. Furthermore, the ratio of Fe$^{2+}$ to Fe$^{3+}$ was measured by titration method in the both experiments.$^{14,15}$ with the results shown in Table 4. It indicates that the content of Fe$^{3+}$ was very few in the studied slag system and thus the effect of Fe$^{3+}$ on this slag system could be ignored.

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Raman scattering measurements are performed with a multichannel modular triple Raman system (Horiba Jobinyvon HR800) with excitation wavelength of 633 nm and the laser power of 2 mw at room temperature in the frequency range of 50–2000 cm$^{-1}$. Then the spectra of Raman was fitted by assuming Gaussian line shapes for the peaks of different structural units.$^{16}$ FTIR measurements are recorded in the scanning range of 4000–400 cm$^{-1}$ using a Fourier transform infrared spectrometer equipped with a KBr detector (Bruker, Tensor27, USA)$^{17–19}$.

The phase compositions of the prepared slag samples were determined by X-ray powder diffraction (XRD; X’pert PRO, PANalytical, Netherlands) using Cu Kα radiation (λ=1.5406Å) with a step of 0.02° (2θ) and a scanning rate of 2°/min from range of 10° to 90°. The microstructures of the quenched slags were observed using scanning electron microscopy (SEM; SSX-50, Shimadzu, Japan).

### 3. Results and Discussion

#### 3.1. Phase Compositions and Microstructure

Figure 2 shows glassy phase of the slags with different ratio of A/(A+F) at 1873 K. This indicates that the slags were completely molten with the ratio of A/(A+F) increasing 0.17 to 1.0 at 1873 K. Therefore, the glassy samples obtained this way were used to carry out the viscosity and structure analysis.

| Sample No. | Viscosity measurement | Structure analyses |
|------------|----------------------|-------------------|
| 1          | 0.91                 | 0.92              |
| 2          | 0.93                 | 0.88              |
| 3          | 0.89                 | 0.94              |
| 4          | 0.92                 | 0.90              |
| 5          | 0.95                 | 0.89              |
| 6          | –                    | –                 |

#### Table 4. The ratio of Fe$^{2+}$ to Fe$^{3+}$ of the studied slag system in the both experiments.

Fig. 2. XRD pattern and SEM image of the quenched samples: (a) XRD pattern; (b) SEM image of Sample 4.
### 3.2. Viscosity Property of CaO–SiO$_2$–Al$_2$O$_3$–FeO–MgO Slag System

Figure 3 shows the effect of temperature and the ratio of A/(A+F) on the viscous behavior of the CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO slag system. From Fig. 3(a) it is observed that the viscosity of all the samples first decreased and then decreased slowly with increasing of temperature, and it finally reached to different constant values. It was about 0.65 dPa·s for sample S1 at temperature above 1 823 K, about 0.76 dPa·s for sample S2 at temperature above 1 833 K, about 0.91 dPa·s for sample S3 at temperature above 1 843 K, while for sample S4 to S6 at temperature above 1 853 K, 1 863 K, and 1 873 K, the viscosity value is 1.14 dPa·s, 1.44 dPa·s, 1.95 dPa·s, respectively. It is also observed that the inflection points of viscosity curve, defined as crystallization temperature, decreased from 1 713 K to 1 693 K with the ratio of A/(A+F) increasing from 0.17 to 0.5, whereas increased to 1 753 K with further increase of this ratio to 1.0. This difference in crystallization behavior for slag was existed because of the different regions of designed compositions in the equilibrium phase diagram and the change of the primary crystal-line regions. From Fig. 3(b), it is found that the viscosity slowly increased with increasing the ratio of A/(A+F) from 0.17 to 0.5 and then significantly increased with further increasing this ratio to 1.0. Specifically, this change was considered due to solid precipitation when temperature was below 1 823 K.

Figure 4 shows the temperature dependence of the viscosity for the present study. The activation energy values were calculated from slope of linear fitting of the natural logarithm of the viscosity (ln $\eta$) with reciprocal temperature ($1/T$) according to the following equation:

$$\ln \eta = \ln A + E_A / T$$

where $\eta$ (Pa·s) is the viscosity, $A$ is constant, $T$ (K) is the absolute temperature, and $E_A$ (kJ·mol$^{-1}$) is the activation energy of viscous flow, as displayed in Table 5. It is observed that the activation energy of viscous flow ($E_A$) was increased 4.396 to 28.994 kJ·mol$^{-1}$ for sample S1 to S6. Compared with the values obtained by other studies (35–180 kJ·mol$^{-1}$), the corrected activation energy was still relatively low due to the low amount of silicate structure but the high amount of non-bridging oxygen. It is well known that the change of the slag structure was represented by the variation of activation energy, and the value of activation energy was varying for different component content due to the change of characteristics of the primary structural units. Therefore, the increase of Al$_2$O$_3$ content along with decreasing FeO content to the slags resulted in an increase of the activation energy. This indicates the rise of energy barrier for viscous flow and formation of some more complex structural units in molten slags were consisted with the viscosity behavior.

### 3.3. Structural Analysis of Slag by FTIR and Raman Spectroscopy

It is well known that the three types of oxygen exist in the molten slag: the bridging oxygen connecting elements with two oxygen bonds, non-bridging oxygen connecting elements with one oxygen bond, and free oxygen without oxygen bond. Reticular complex structures such as [Si$_2$O$_6$]$^4$-ring will be decomposed into [Si$_2$O$_7$]$^6$-dimer and [SiO$_4$]$^4$-monomer by the non-bridging oxygen ion and the
free oxygen ion with adding the basic oxides (CaO, MgO and FeO) into the silicate melt. In consequence, the reason for the reduction of slag viscosity is depolymerization of network structure into short polymer units such as monomer or dimer with the concentration of basic oxides more than acidic oxides and the non-bridging oxygen ion continues to destroy the long chain after entering into the network structure. For amphoteric oxides such as Al₂O₃, Al³⁺ either is combined with [SiO₄]⁴⁻ to form more complex silicate network or disintegrate complex silicate structure to balance charge, just as Ca²⁺ or Mg²⁺. The effect of Al³⁺ in the melt slag is determined by the Al₂O₃ content and basicity. Song et al. explored Al₂O₃ could behave as a network-forming oxide in Al₂O₃–CaO–MgO–SiO₂ system in the highly basic region.

Figure 5 shows the effect of the different ratio of A/(A+F)
of the quenched CaO–MgO–SiO2–Al2O3–FeO slag at fixed C/S of 3 by FTIR spectroscopy to analyze the structure of slag. In the [SiO4]4−tetrahedral symmetric stretching region, four major peaks for Si–O bands were found at about 840, 900, 980, 1 075 cm−1 which were assigned to NBO/Si=4, 3, 2, and 1 (NBO/Si: Non-Bridged Oxygen per Silicon Atom), respectively.7) The center of gravity of the [SiO4]4−tetrahedral bands at 1 200–800 cm−1 shifted from 880 cm−1 to 1 100 cm−1 with the ratio of A/(A+F)increasing from 0.17 to 1.0. It indicated that the degree of polymerization of silicate units increased with the FeO content decreasing from 25% to 0% and FeO as network modifier played an active role in reducing viscosity. In the [AlO4]5−tetrahedral stretching region, the major peak for Al–O was found at about 520 cm−1. The characteristic transmittance troughs of [AlO4]5− became less pronounced with increasing the ratio of A/(A+F) to 0.5 and the [AlO4]5− symmetric stretching troughs became deeper and broader with increasing this ratio from 0.5 to 1.0. These results indicate that the degree of polymerization of silicate units increased with the FeO content decreasing from 25% to 0% and FeO as network modifier played an active role in reducing viscosity. In the [AlO4]5−tetrahedral stretching region, the major peak for Al–O was found at about 520 cm−1. The characteristic transmittance troughs of [AlO4]5− became less pronounced with increasing the ratio of A/(A+F) to 0.5 and the [AlO4]5− symmetric stretching troughs became deeper and broader with increasing this ratio from 0.5 to 1.0. In Si–O–Al rocking region, the major peak for Si–O–Al band was found at about 700–640 cm−1. The characteristic transmittance troughs of [SiO4]3− became less pronounced with increasing the ratio of A/(A+F) from 0.17 to 0.5, while the depth of the troughs of Si–O–Al became less pronounced with increasing the ratio of A/(A+F) from 0.17 to 0.5 and the [AlO4]5− symmetric stretching troughs became deeper and broader with increasing this ratio from 0.5 to 1.0. In Si–O–Al rocking region, the major peak for Si–O–Al band was found at about 520 cm−1. The depth of the troughs of Si–O–Al became less pronounced with increasing the ratio of A/(A+F) from 0.17 to 0.5, while the depth of the troughs of Si–O–Al increased with increasing this ratio from 0.5 to 1.0. All the analysis of the structural units of Q2 decreased and the total of the silicate structural units were decreased with increasing this ratio from 0.5 to 1.0. Nevertheless, the all silicate structural units were decreased with increasing this ratio from 0.5 to 1.0. This change of the latter was attribute to the increase in the relative amount of all structural units with Al2O3 increasing. The aluminate structural units of Al2O3 worked as a network former to increase the degree of polymerization of silicate units and aluminate units as a function of the ratio of Al2O3 and FeO content (the A/(A+F) ratio) in this experiment. With increasing the ratio of A/(A+F) from 0.17 to 1.0, the degree of polymerization of silicate units and aluminate units increased, which lead to the increase of viscosity finally.

Figure 6 shows a part of the deconvolution of the Raman spectra at different ratio of A/(A+F) for various silicate and aluminate structural units of the quenched CaO–MgO–SiO2–Al2O3–FeO slag at 1 873 K. The strong peak of [SiO4]4− was disintegrate to Q0, Q1, Q2 and Q3 and the bands of [AlO4]5− and Al–O–Si were certain at the fixed Raman shift. The different Raman bands were related to the various silicate and aluminate structural units, as summarized in Table 6. The amount of the characteristic structural units was analyzed semi-quantitatively by the integrated area of the individual deconvoluted peaks in the melt. The fraction of structural units was defined by the ratio of the integrated areas of individual characteristic structural units over the sum of the integrated areas of all the characteristic structural units.

According to the integration of the deconvoluted spectra of the various structural units, the fraction of the silicate and aluminate structural units as a function of the ratio of A/(A+F) is showed in Fig. 7. When the ratio of A/(A+F) increased from 0.17 to 1.0, the total of the silicate structural units of Q0+Q1 decreased and the total of the silicate structural units of Q2+Q3 increased. Nevertheless, the all silicate structural units were decreased with increasing this ratio from 0.5 to 1.0. This change of the latter was attribute to the increase in the relative amount of all structural units with Al2O3 increasing. The aluminate structural units of Al2O3 and Al–O− had no obvious variation with the ratio of A/(A+F) increasing from 0.17 to 0.5 and suddenly increased with this ratio increasing from 0.5 to 1.0. Besides, the structural unit of Si–O–Al slowly increased with increasing this ratio from 0.17 to 1.0. All the analysis of the structural units were correlated well with the FTIR results. This result further indicated viscosity of the slag was affected by complicated structure units and degree of polymerization.

### Table 6. Assignments of Raman bands in spectra of CaO–MgO–SiO2–Al2O3–FeO slag system.

| A/(A+F) | 0.17 | 0.33 | 0.5 | 0.67 | 0.83 | 1 |
|---------|------|------|-----|------|------|---|
| Raman Shift (cm−1) | 515 | 542 | 599 | 521 | 522 | 544 |
| | 649 | 663 | 646 | 640 | 651 | 651 |
| | 758 | 761 | 748 | 752 | 752 | 770 |
| | 822 | 818 | 805 | 831 | 847 | 841 |
| | 901 | 913 | 912 | 925 | 912 | 925 |
| | 1 017 | 1 010 | 1 015 | 1 003 | 1 002 | 1 011 |
| | 1 113 | 1 114 | 1 095 | 1 087 | 925 | 912 |
| Raman bands | symmetric Al–O0 symmetric stretching vibration of [AlO4]3− | bending Si–O− vibration of [SiO4]2− | symmetric Al–O− vibration of [AlO4]3− |
| | 24–27 | 28, 29 | 30, 31 |
| | 30, 32 |
| | 28, 29 |
| | 28, 29, 33, 34 |
| | 24, 28, 29, 33, 34 |

### Fig. 7. Fraction of characteristic structure units with the various ratio of A/(A+F) from the deconvolution of the Raman spectra.
with various ratio of Al$_2$O$_3$/(FeO+Al$_2$O$_3$) were investigated and the following conclusions have been drawn;

1) The contents of Al$_2$O$_3$ and FeO had significant effect on the viscosity of the CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO slag system. The viscosity slowly increased from 0.65 dPa·s to 0.92 dPa·s with the A/(A+F) ratio increasing from 0.16 to 0.5, and then it obviously increased to 1.94 dPa·s with this ratio further increased to 1.0 at 1873 K.

2) FeO as a network modifier played the role of depolymerization in the present slag. With the FeO content ratio further increased to 1.0 at 1873 K, Q0 decreased in the silicate structure, and the polymerization degree of the silicate units steadily strengthened, which could increase viscosity of the CaO–MgO–SiO$_2$–Al$_2$O$_3$–FeO slag system.

3) Al$_2$O$_3$ served as a network former in the present slag. When the ratio of A/(A+F) increased from 0.17 to 0.5, the melt structure was based on the silicate structure and Al$^{3+}$ acted as a substitution for Si$^{4+}$ to strengthen the silicate network structure. With this ratio increasing to 1.0, the melt structure was converted from silicate structure to aluminate structure and the polymerization of aluminate units became increased. Meanwhile, the polymerization of silicate units also increased due to the decrease of the FeO content, which could significantly increase viscosity of the present slag.

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