

REDUCTION OF MOLYBDENUM OXIDE FROM STEELMAKING SLAGS BY PURE LIQUID IRON

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Abstract

The effects of reaction temperature, slag basicity and FeO concentration on the reduction of molybdenum oxide from steelmaking slags by pure liquid iron were investigated experimentally. The reduction kinetics of molybdenum oxide by liquid iron was analysed. The reaction models were developed based on the condition that diffusion of [Mo] in liquid iron and CaMoO₄ in slag is the control steps, respectively. These reaction models were tested using data from a series of experiments. The results indicate that under the present experimental conditions, the temperature and the FeO content, other than slag basicity, have some effects on the reduction of molybdenum oxide from steelmaking slags by pure liquid iron. Both the molybdenum oxide reduction rate and final reduction ratio increase with an increase of temperature and a decrease of FeO content. The diffusion of CaMoO₄ in slag which dominated overall reduction process is the only one rate-controlling step with its apparent activation energy 294 kJ/mol. The reduction of molybdenum oxide used directly as alloy additive can be further enhanced by strong stirring in the converter practice.

Keywords: Reduction kinetics; Molybdenum oxide; Steelmaking slags; Liquid iron; Direct alloying

1. Introduction

Molybdenum oxide employed directly as alloy additive in steelmaking may eliminate the process of ferro-molybdenum smelting and reduce the cost of molybdenum alloying.

When molybdenum oxide is added into the converter for direct alloying, it is likely that a fraction of molybdenum oxide, which was not in time reduced by [C] in liquid steel, still exists in converter slag after [C] decreases to lower content. Thus, the total

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molybdenum yield would be subjected to the effect of further reaction between molybdenum oxide and liquid iron in the converter. However, the reduction kinetics of molybdenum oxide from steelmaking slags by liquid iron has not been reported in detail up to now [1]. Furthermore, in the presence of stronger reducing agents such as [C] or [Si] in liquid steel, the reduction capability of liquid iron to molybdenum oxide could not be individually reflected in previous studies [2-6]. The present study was attempted to investigate the reduction of molybdenum oxide from steelmaking slags by pure liquid iron in the laboratory and expected to provide a foundation for molybdenum oxide direct alloying in the converter.

2. Experimental

Materials. Commercial grade pure iron with chemical compositions shown in Table 1 and analytical-grade MoO_3 powder were employed in each experiment. The master slag was prepared by the way of mixing analytical-grade CaO, MgO, SiO_2 and CaF_2 , as well as new-made FeO by heating ferrous oxalate at 850°C for 1 hour under an Ar atmosphere. The master slag was prepared according to the composition of the converter final slag shown in Table 2. The amount of MoO_3 used in each experiment was calculated, supposing all the MoO_3 were reduced, by molybdenum concentration in target steel. The slag was added according to slag-metal mass ratio of 10%.

Methods. A quantity of pure iron was fed into a high purity MgO crucible with 52 mm inner diameter (ID) and 100 mm height. The MgO crucible was put into a graphite crucible,

Table 1. Compositions of commercial grade pure iron (w_B , %)

| C | Si | Mn | Al | Cu | Ni | Mo |
|--------|--------|-------|--------|-------|-------|--------|
| <0.002 | 0.0021 | 0.004 | 0.0025 | 0.035 | 0.008 | 0.0026 |

Table 2. Chemical compositions of master slag (w_B , %)

| CaO | MgO | SiO_2 | FeO | CaF_2 |
|-----|-----|----------------|-----|----------------|
| 51 | 8.5 | 12.5 | 25 | 3 |

Note: Primary basicity $B = w_{\text{CaO}} / w_{\text{SiO}_2} = 4.1$

and the graphite crucible was placed in the constant temperature zone of a vertical electric resistance furnace, the furnace was equipped with 70 mm ID and 1000 mm length alumina working tube. The whole experiments were carried out under the protection of purified nitrogen with 500 mL/min introduced through the hole in the bottom plug of the furnace. The furnace was programmed to heat at a rate of $5^\circ\text{C}/\text{min}$ to the desired temperature and held constant temperature throughout the experiment. The master slag powders mixed well with MoO_3 powder were packed in paper and quickly put onto the surface of liquid iron in the MgO crucible. And this moment was taken as the initial time of the reduction reaction. A silica tube with 4 mm ID was employed to take metal samples for molybdenum analysis at different times during experiment. An iron rod was used to dip into the final slag for molybdenum analysis. Based on the results of chemical analysis, the actual molybdenum oxide reduction ratio at any time was estimated according to the following equation (1):

$$\eta = \frac{m_{\text{Fe}} \cdot w_{\text{Mo}}}{m_{\text{S}} \cdot w_{(\text{Mo})}^{\text{F}} + m_{\text{Fe}} \cdot w_{\text{Mo}}^{\text{F}}} \times 100 \quad (1)$$

3. Thermodynamic Considerations

The common molybdenum oxide additives contain substances such as MoO_3 , MoO_2 , CaMoO_4 . According to the phase diagram, the melting point and boiling point of MoO_3 is 795°C and 1155°C , respectively, the melting point of MoO_2 is above 2200°C [7], and that of pure CaMoO_4 is $1445\pm 5^\circ\text{C}$ [8]. In paper [9] and the literature [10], as the thermodynamic analysis on molybdenum oxide reduction during steelmaking process was performed in more detail, so a brief description on the reduction thermodynamics of molybdenum oxide only by pure liquid iron is given as follows.

The Gibbs energy changes of the molybdenum oxide reduction at the standard state are presented at Fig.1. It can be seen from the figure all three kinds of molybdenum oxide can be reduced by liquid iron, the reduction of MoO_3 is the easiest and that of CaMoO_4 is relatively difficult. That molybdenum oxide can be reduced by liquid iron is helpful not only to decrease the influence of oxygen-blowing on the

reduction during steelmaking process, but also to improve the final molybdenum yield.

As is well known, MoO_3 is the most convenient source of molybdenum compound. However, it is possible for adding directly MoO_3 into the bath of molten steel to produce a great deal of intense smoke, a jet of hot gas or explosive noise due to its high vapour pressure beyond the melting point of MoO_3 [11]. This would result in not only valuable element loss, but also the serious problems of environmental protection. Therefore it is necessary to change the way of addition MoO_3 to molten metal [12, 13]. Taking economic reason into account, the conversion of MoO_3 into more stable molybdates *in situ* would be highly desirable. Furthermore, in order to simulate the reduction of molybdenum oxide in the converter final slags by pure Fe(l) in this study, the mixture of MoO_3 with the master slag powders mentioned above was added onto the surface of liquid iron to slagging. And it is also necessary to determine the existence state of molybdenum in molten slag phase in order to further examine the reduction process of molybdenum oxide.

The relevant investigations in the literature [12-15] showed MoO_3 may react, except SiO_2 , with the basic oxide such as CaO , MgO , FeO , to form corresponding molybdates. Chychko [12] performed thermodynamic calculations to analyze the relevant stabilities of different molybdates toward MoO_3 evaporation. It could be concluded that CaMoO_4 possesses the highest stability among three kinds of molybdate for CaMoO_4 , MgMoO_4 , FeMoO_4 . Chychko et al [14] confirmed that the formation of CaMoO_4 from the mixture of

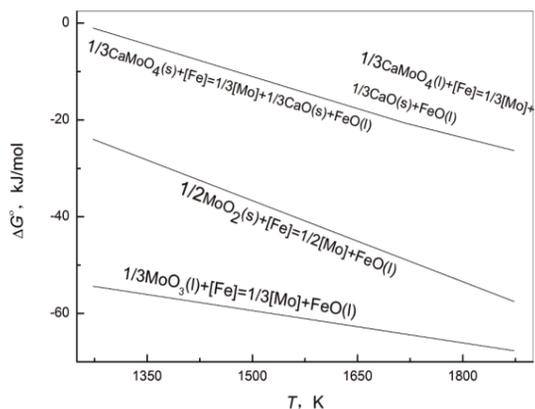


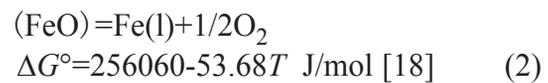
Fig. 1. The Gibbs energy changes of the molybdenum oxide reduction by liquid iron at the standard state

MoO₃ with CaO starts even at 600°C and is completed around 700°C by means of high temperature X-ray diffraction studies, which precedes the beginning of evaporation of MoO₃. They also found that the formation of corresponding molybdates goes much faster than the evaporation of pure MoO₃ by means of non-isothermal thermogravimetric studies. Therefore, MoO₃ can be very easily transformed to CaMoO₄ in the presence of lime [10,12,14]. In view of the present experimental methods, it may also be deduced CaMoO₄ can be formed *in situ* from the mixture of MoO₃ with the master slag powders containing CaO even before the slag melts. And that, the melting point and viscosity of slags can be reduced since CaMoO₄ formed has a low melting point.

On the other hand, the valence state of molybdenum cations in molten slags would depend on the basicity of the slags as well as the oxygen potential [16]. Farges et al [15] investigated the coordination chemistry of molybdenum in nine series of synthetic silicate glasses using electron paramagnetic resonance (EPR) and X-ray absorption fine structure (XAFS) spectroscopies. The molybdenum mass fraction of these glasses ranges from 300 ppm to 3%. They found that molybdenum is present primarily as molybdate moieties [Mo(VI)O₄²⁻] in most of the glass compositions prepared at partial pressure values of oxygen ranging from 1 atm to 10⁻¹² atm (temperatures ranging from 1100 to 1700°C). At the same time, no evidence for second-neighbor Si around Mo was found in any of the glasses, confirming that molybdate moieties are not connected to the tetrahedral framework silicate, suggesting that Mo-silicate phases would

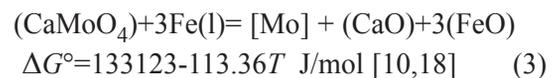
not be important in glass melts. This is agreement with the observation of Muthupari et al [17] on glasses of the ternary MoO₃-SiO₂-P₂O₅ system using Si K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Therefore it is unlikely that MoO₃ could combine with SiO₂ in the present study.

According to the following slag-metal equilibrium, the partial pressure of oxygen estimated in the present molten slags is about 3.4×10⁻¹⁰ atm at 1600°C.



where the standard state for FeO in molten slag are chosen as the pure liquid FeO. Since the mass fraction of FeO was 25% at different temperatures in this experiment, its corresponding activity a_{FeO} is determined as 0.40 in accordance with phase diagram [19].

From the above analysis, it can be ascertained molybdenum existed in basic steelmaking slags is mainly dissolved in the form of CaMoO₄ though the molybdenum oxide added is MoO₃. Hence, the reduction reaction discussed in this investigation may be expressed as follows:



where the standard state for CaMoO₄ in molten slag is chosen as the pure liquid CaMoO₄, that for CaO is the pure solid oxide and for [Mo] in liquid iron is the 1 mass-percent solution.

4. Experimental Results

The effect of temperature. The

reduction of molybdenum oxide by Fe(l) at three temperatures of 1550 °C, 1575 °C and 1600 °C is shown in Fig. 2. It can be observed that within the range studied, the temperature has some effects on the reduction rate and final reduction ratio of molybdenum oxide, and both of them increase or show a tendency to increase with an increase of temperature. Since the reduction of CaMoO_4 by liquid iron is an endothermic reaction, it moves easily along positive reaction with an increase of temperature. And simultaneously the molybdenum oxide final reduction ratio can also make further advance.

The effect of slag basicity. The slag basicity plays an important role on desulfurization and dephosphorization in the blowing process of converter. So the influence of slag basicity on the molybdenum oxide reduction by Fe(l) was investigated in the present study and the results are shown in Fig. 3. For a given ratio of other components in slag, the basicities, defined by the ratio $B = w_{\text{CaO}} / w_{\text{SiO}_2}$, were selected for 3.6, 4.1 and 4.6, respectively. As one can see, the

reduction rate and final reduction ratio of molybdenum oxide are the same with different basicities. This is because the amount of MoO_3 addition in each experiment was very small and the initial content in slags was about 3.5%, while the basicity B was higher, i.e. there was higher lime addition to slags. The most of MoO_3 in slags was easily transformed into CaMoO_4 at high temperatures and high basicities according to the above-mentioned analysis. There is not much change of the activities of CaMoO_4 in molten slags with high basicities. Besides, the basicity has only a limited effect on kinetics properties of the related components in slag phase. Therefore, the elementary conditions of the molybdenum oxide reduction in each experiment were almost the same, and the slag basicity had no effect on the reduction rate and final reduction ratio of molybdenum oxide.

The effect of FeO concentration. Since FeO was a component of original slag phase, and also a reaction product of the molybdenum oxide reduction by liquid iron, it was necessary to understand the

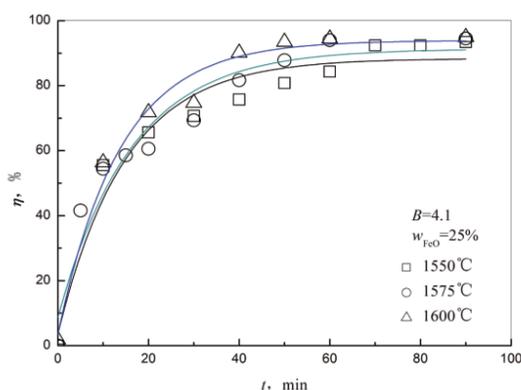


Fig. 2. The effect of temperature on the reduction of molybdenum oxide

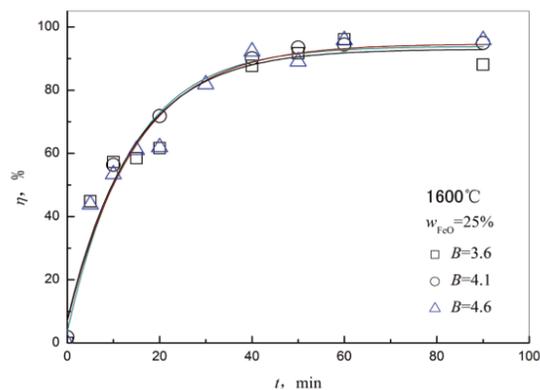


Fig. 3. The effect of basicity on the reduction of molybdenum oxide

effect of the FeO concentration on the reduction of molybdenum oxide. For a given ratio of other components in slags, the reduction of molybdenum oxide by Fe (l) was investigated with the FeO mass fractions of 20%, 25% and 30% in slags, respectively. The results are shown in Fig.4. It can be seen the FeO concentration has a few effects on the reduction of molybdenum oxide. The molybdenum oxide reduction rate decreases obviously and final reduction ratio also shows a trend to decrease with an increase of the FeO content. The calculation had shown in the literature [20] the FeO concentration had few effects on the activity of CaMoO_4 in original slags. However, FeO, which acted as the product, retarded certainly the interfacial reaction of the molybdenum oxide reduction by Fe (l) and resulted in the decrease of molybdenum oxide reduction rate and final reduction ratio. Therefore, too high FeO content in slags should be avoided in the converter practice, and this would be helpful to increase the reduction rate and final reduction ratio of molybdenum oxide.

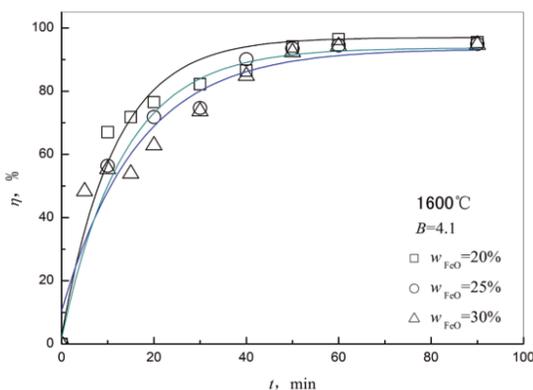


Fig. 4. The effect of FeO content on the reduction of molybdenum oxide

5. Determination of the Rate-controlling Step

5.1 Analysis of the kinetics steps for the reduction reaction

Based on the reduction reaction equation (3), the overall reaction process can be divided into six elementary steps in series as follows: ①transport of the reactant Fe(l) to the slag-metal reaction interface, ②transport of the reactant CaMoO_4 in slag phase to reaction interface, ③the interfacial chemical reaction, ④transport of the product [Mo] into liquid iron, ⑤transport of the product FeO into slag phase, and ⑥transport of the product CaO into slag phase.

Since the reaction (3) takes place between Fe(l) and slag, step ① cannot be a rate-controlling step. The interface chemical reaction at high temperatures is very fast in general and step ③ is also not a rate-controlling step. At the same time, in the experiment the FeO mass fraction in slag was relatively high by 25%, while the initial mass fraction of reactant CaMoO_4 converted by the amount of MoO_3 addition was only 5% or so, the FeO concentration difference between slag bulk and reaction interface may be negligible, step ⑤ should not be a rate-controlling step. Under the condition of high basicity slag, step ⑥ has no effect on the overall kinetics process according to the experimental results as shown in Fig. 3. Therefore, the rate-controlling step can but be step ② and/or ④ among the above mentioned steps. On the assumption that steps ② and ④ are defined as limited by only one step respectively, the kinetics models can be derived and further confirmed with correlative experimental data below.

5.2 Equation derivation of the rate-controlling step

Assuming that CaMoO_4 transfer in slag is the rate-limiting step for the reduction of molybdenum oxide from basic slag by Fe(l), the reaction rate may be described by the equation

$$-\frac{dw_{\text{CaMoO}_4}}{dt} = \frac{\beta_{\text{CaMoO}_4}}{h_s} (w_{\text{CaMoO}_4} - w_{\text{CaMoO}_4}^*) \quad (4)$$

The equilibrium constant for reaction equation (3) may be written as the ratio of the respective activities

$$K = \frac{a_{\text{Mo}}^* a_{\text{FeO}}^{*3} a_{\text{CaO}}^*}{a_{\text{CaMoO}_4}^* a_{\text{Fe}}^3} \quad (5)$$

Both the FeO and CaO contents in original slag phase were higher, their concentrations changed very little before and after the reaction takes place in this study, so the activities of FeO and CaO may be taken for the constant throughout the experiment. As mentioned earlier, the FeO activity a_{FeO} is 0.40. Owing to high slag basicity, the CaO content in slag is also high and its activity a_{CaO} may be assumed approximately to unity [21]. Since the concentrations of both [Mo] in liquid iron and CaMoO_4 in liquid slag phase are very low, their activity coefficients remain constant over the small change in composition involved in an experiment and are also assumed as unity, respectively. Then a new equilibrium constant, K_1 , can be defined as:

$$K_1 = \frac{w_{\text{Mo}}^*}{w_{\text{CaMoO}_4}^*} = \frac{1}{a_{\text{FeO}}^3} \frac{1}{M_{\text{CaMoO}_4}} \sum \frac{w_{\text{B}}}{M_{\text{R}}} K \quad (6)$$

The equilibrium constant, K , is available from the standard Gibbs free energy change

ΔG° for the reaction (3), and K_1 can be calculated from the right-hand side of equation (6) for a given slag composition.

When only CaMoO_4 transfer in the slag is the limiting step, [Mo] transfer is very fast, w_{Mo}^* and is equal to w_{Mo}^* . So equation (7) may be obtained from equation (6):

$$w_{\text{CaMoO}_4}^* = \frac{w_{\text{Mo}}}{K_1} \quad (7)$$

In accordance with the mass balance, equation (8) is given:

$$w_{\text{CaMoO}_4} = w_{\text{CaMoO}_4}^0 - w_{\text{Mo}} \frac{m_{\text{Fe}}}{m_{\text{S}}} \cdot \frac{M_{\text{CaMoO}_4}}{M_{\text{Mo}}} \quad (8)$$

Combining equations (4), (7), (8), equation (9) can be obtained:

$$\begin{aligned} & \frac{m_{\text{Fe}}}{m_{\text{S}}} \frac{M_{\text{CaMoO}_4}}{M_{\text{Mo}}} \\ & \int_{w_{\text{Mo}}^0}^{w_{\text{Mo}}} \frac{dw_{\text{Mo}}}{w_{\text{CaMoO}_4}^0 - \left(\frac{m_{\text{Fe}}}{m_{\text{S}}} \cdot \frac{M_{\text{CaMoO}_4}}{M_{\text{Mo}}} + \frac{1}{K_1} \right) w_{\text{Mo}}} \quad (9) \\ & = \frac{\beta_{\text{CaMoO}_4}}{h_s} t \end{aligned}$$

In case of $\frac{m_{\text{Fe}}}{m_{\text{S}}} \frac{M_{\text{CaMoO}_4}}{M_{\text{Mo}}} \gg \frac{1}{K_1}$ and $w_{\text{Mo}}^0 \approx 0$ (note that it is valid for the present study), the equation (9) can be simplified to:

$$\ln \frac{w_{\text{CaMoO}_4}^0}{w_{\text{CaMoO}_4}^0 - \frac{m_{\text{Fe}}}{m_{\text{S}}} \frac{M_{\text{CaMoO}_4}}{M_{\text{Mo}}} w_{\text{Mo}}} = \frac{\beta_{\text{CaMoO}_4}}{h_s} t \quad (10)$$

The left-hand side of equation (10) is a function of [Mo] concentration in liquid iron, letting the left as $F_1(w_{\text{Mo}})$. The relationship between $F_1(w_{\text{Mo}})$ and time t may be obtained from the figure plotted based on the experimental data. If the diffusion of CaMoO_4 in slag is single rate-controlling step, the relationship should show a line with

its slope as $\beta_{\text{CaMoO}_4} / h_s$.

Assuming that [Mo] transfer in liquid iron is the limiting step, one can go through the same steps as for the diffusion of CaMoO_4 in slag, and using the same basic relationships, the final rate equation can be yielded:

$$\int_0^{w_{\text{Mo}}} \frac{dw_{\text{Mo}}}{K_1 w_{\text{CaMoO}_4}^0 - \left(\frac{m_{\text{Fe}}}{m_s} \cdot \frac{M_{\text{CaMoO}_4}}{M_{\text{Mo}}} K_1 + 1 \right) w_{\text{Mo}}} = \frac{\beta_{\text{Mo}}}{h_{\text{Fe}}} t \quad (11)$$

The left-hand side of equation (11) is also defined as $F_2(w_{\text{Mo}})$, which integral operation can be carried out by means of computer numerical software. The relationship between $F_2(w_{\text{Mo}})$ and time t may also be obtained from the figure plotted based on the experimental data. If the diffusion of [Mo] in liquid iron is a rate-controlling step, the

relationship should show a line with its slope as $\beta_{\text{Mo}}/h_{\text{Fe}}$.

5.3 Discussion and analysis

In order to examine the above kinetic models, some experimental data for the same slag system is presented in Table 3, where the mass fractions of [Mo] in liquid iron resulting from the reduction of CaMoO_4 in slag are shown at different temperatures and times. Table 4 lists corresponding experimental conditions. Substituting equations (10) and (11) with the parameters in Tables 3 and 4 for calculation, one can plot the relationship between $F(w_{\text{Mo}})$ and time t in the two cases, as shown in Fig.5 and 6, respectively. Linear relationships can be observed for $F_1(w_{\text{Mo}})-t$ and $F_2(w_{\text{Mo}})-t$ at

Table 3. Mass fractions of [Mo] in liquid iron at different temperatures and times (w_{Mo} , %)

| Time, min | 10 | 20 | 30 | 40 | 50 | 60 | 70 |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| Temperature, °C | | | | | | | |
| 1550 | 0.11 | 0.13 | 0.14 | 0.15 | 0.16 | 0.167 | 0.183 |
| 1575 | 0.106 | 0.118 | 0.135 | 0.159 | 0.171 | 0.183 | - |
| 1600 | 0.117 | 0.149 | 0.155 | 0.187 | 0.194 | 0.196 | - |

Table 4. Parameters of kinetic experiments

| | | | |
|---|-------|-------|-------|
| Temperature, °C | 1550 | 1575 | 1600 |
| Liquid iron mass, g | 512.7 | 486.7 | 502.7 |
| Slag mass, g | 51.27 | 48.67 | 50.27 |
| Liquid iron density [22], g/cm ³ | 7.1 | 7.08 | 7.06 |
| Slag density [23], g/cm ³ | 3.5 | 3.5 | 3.5 |
| Liquid iron height h_{Fe} , $\times 10^{-2}\text{m}$ | 3.4 | 3.24 | 3.35 |
| Liquid slag layer height h_s , $\times 10^{-3}\text{m}$ | 6.9 | 6.5 | 6.8 |
| Initial mass fraction of CaMoO_4 , % | 5.03 | 5.03 | 5.03 |

Note: MgO crucible of 52 mm in inner diameter.

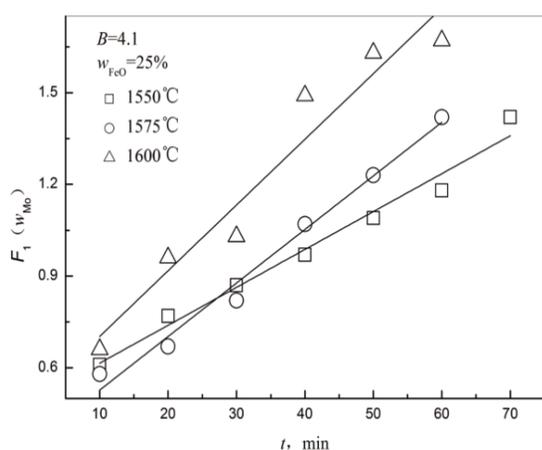


Fig. 5. Relationship between $F_1(w_{Mo})$ and time t

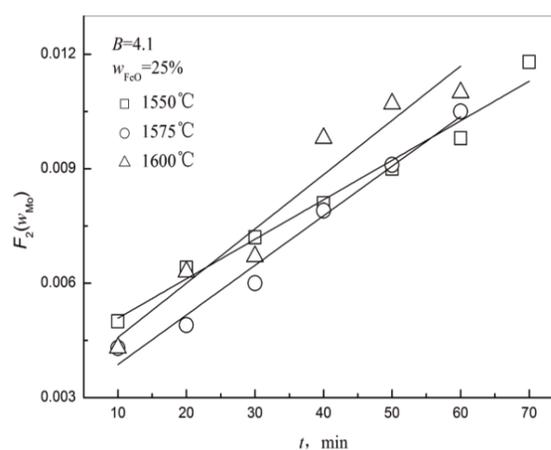


Fig. 6. Relationship between $F_2(w_{Mo})$ and time t

different temperatures and the regression coefficients of both cases from low temperature to high are 0.98, 0.98, 0.93 in turn, which suggests that either the diffusion of CaMoO_4 in slag or $[\text{Mo}]$ in liquid iron be the likely rate-controlling step. In order to decide dominating limiting step, further analysis can be made by means of the rationality of the mass transfer coefficients and the activation energy acquired.

The values of the mass transfer coefficient obtained from the above straight lines in the two cases are summarized in Table 5. The value of diffusion coefficient of $[\text{Mo}]$ in liquid iron is about $5.5 \times 10^{-10} \text{m}^2/\text{s}$ according to the literature [24], the component diffusion coefficient in liquid slag is

commonly of the order of $10^{-10} \sim 10^{-11} \text{m}^2/\text{s}$, the thickness of boundary layer is about the order of $10^{-4} \sim 10^{-5} \text{m}$. According to the well known equation $\beta = D/\delta$, the value of the mass transfer coefficient of $[\text{Mo}]$ in liquid iron is about the order of $5.5 \times (10^{-5} \sim 10^{-6}) \text{m/s}$ and the component in liquid slag is about $10^{-5} \sim 10^{-7} \text{m/s}$. From Table 5 it is thus clear that the values of the mass transfer coefficient of CaMoO_4 in liquid slags are reasonable and the $[\text{Mo}]$ mass transfer coefficients in liquid iron are relatively small by at least two orders of magnitude as compared with the above common data from the literature, which indicates the solely rate-controlling step for the kinetics process of the reduction of molybdenum oxide by Fe(l) is the

Table 5 Mass transfer coefficients at different temperatures

| | Temperature, °C | 1550 | 1575 | 1600 |
|-------------------|--|------|------|------|
| $F_1(w_{Mo}) - t$ | Slope of straight line, $\times 10^{-2}/\text{min}$ | 1.24 | 1.75 | 2.15 |
| | Mass transfer coefficient of CaMoO_4 $\beta_{\text{CaMoO}_4} \times 10^{-6} \text{m/s}$ | 1.43 | 1.9 | 2.43 |
| $F_2(w_{Mo}) - t$ | Slope of straight line, $\times 10^{-4}/\text{min}$ | 1.04 | 1.3 | 1.42 |
| | $[\text{Mo}]$ mass transfer coefficient, $\beta_{\text{Mo}} \times 10^{-8} \text{m/s}$ | 5.9 | 7.02 | 7.93 |

diffusion of CaMoO_4 in slag and not [Mo] in liquid iron. It can be noted that Guo et al [10] found the rate-controlling step for the kinetics process of the reduction of MoO_3 from slag by [Si] or [C] in molten steel was the diffusion of CaMoO_4 in slags. However, Chen et al [2] found the rate-controlling step for the reduction of MoO_3 from slags by carbon-saturated iron melt was the diffusion of molybdenum in slag at 1440~1500°C and [Mo] in metal at 1500~1590°C.

In view of $D = D_0 e^{-E_D/(RT)}$, if the thickness of diffusion boundary layer does not vary with temperature, one can rewrite

$$\ln \frac{D}{\delta} = \ln \frac{D_0}{\delta} - \frac{E_D}{RT}, \text{ i.e.,} \quad (12)$$

$$\ln \beta_{\text{CaMoO}_4} = \ln \frac{D_0}{\delta} - \frac{E_D}{RT}$$

The relationship of $\ln \beta_{\text{CaMoO}_4} - 1/T$ is plotted and shown in Fig. 7 by adopting the data in Table 5. The apparent activation energy calculated from the slope of the fitted straight line is found to be 294 kJ/mol, which is relative closer to 223 kJ/mol obtained by Chen [2] in similar cases. This further indicates that the diffusion of CaMoO_4 in slag is the only rate-controlling step.

Consequently, the reduction rate of

List of symbols

| Symbols | Meanings |
|----------------------|--|
| η | molybdenum oxide reduction ratio, % |
| w_B | Mass fraction of component B in liquid iron or slag bulk phase, % |
| $w_{(\text{Mo})}^F$ | The final mass fraction of (Mo) in slag phase, % |
| w_{Mo}^F | The final mass fraction of [Mo] in liquid iron, % |
| w_B^* | Mass fraction of component B at reaction interface, % |
| w_B^0 | Initial mass fraction of component B, % |
| K, K_1 | Equilibrium constant, respectively |
| ΔG° | Standard Gibbs free energy change, J/mol |
| $a_B - a_B^*$ | Activity of component B at bulk phase and interface, respectively, $\alpha_{Fe}=1$ |
| T | Absolute temperature, K |
| t | Time, s or min |
| m_{Fe}, m_S | Mass of liquid iron and slag mass, respectively, g |
| M_B | Molecular mass of component B, g/mol |
| β_B | Mass transfer coefficient of component B, m/s |
| h_{Fe}, h_S | Height of liquid iron and slag phase in the MgO crucible, respectively, m |
| δ | Thickness of diffusion boundary layer of component B, m |
| D | Diffusion coefficient, m^2/s |
| D_0 | Pre-exponential factor, m^2/s |
| R | Gas constant $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ |
| E_D | Activation energy, J/mol |

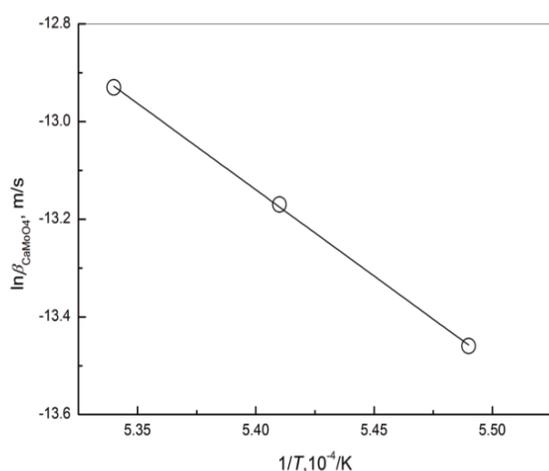


Fig. 7. Relationship between β_{CaMoO_4} and $1/T$

molybdenum oxide from steelmaking slags has something to do with several factors such as the mass transfer coefficient of $CaMoO_4$ in liquid slags and the reactive interface area of slag-metal. The action of a large amount of liquid iron can lower the influence of oxygen-blowing on the reduction of $CaMoO_4$ in the converter practice, where the reduction of $CaMoO_4$ should be further enhanced by strong stirring.

6. Conclusions

(1) Under the scopes of experimental study, the temperature and the FeO content have some effects on the reduction of molybdenum oxide from steelmaking slags by pure liquid iron, whereas the slag basicity has no effect. Both the reduction rate and final reduction ratio of molybdenum oxide increase or show a tendency to increase evidently with an increase of temperature and a decrease of FeO content.

(2) Within the range of experimental temperature, it is concluded that the rate-controlling step of the reduction reaction

process should be the diffusion of $CaMoO_4$ in slags, with apparent activation energy 294 kJ/mol.

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