Kinetic Analysis of Aluminum and Oxygen Variation of G20CrNi2Mo Bearing Steel during Industrial Electroslag Remelting Process

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Kinetics of slag-metal reactions was investigated in order to elucidate the mechanism of Al-oxidation and oxygen increase during industrial electroslag remelting (ESR) process. G20CrNi2Mo bearing steel was utilized as the consumable electrode and remelted using a 2 400-kg industrial ESR furnace. It was found that with the content of FeO in the slag increasing from 0.20 wt% to 0.45 wt%, the content of oxygen increased from 12 ppm in electrode to 16 ppm, 21 ppm in the ingot while Al decreased from 0.040 wt% in the electrode to 0.031 wt%, 0.019 wt% in the ingot. Based on penetration and film theories, a kinetic model has been developed. The model indicates that Al in the electrode is mainly oxidized by FeO at the metal film. Increase of soluble oxygen mainly occurs during the time of droplet formation and falling. The content of soluble oxygen occupies about fifty percent of the total oxygen. The rate-determining step of Al-oxidation is the mass transfer of Al at metal side, whereas oxygen increase lies in the mass transfer of FeO at slag side. With the content of FeO increasing from 0.20 wt% to 0.45 wt%, the mass transfer resistance of FeO decreases obviously, thus would result in an increase of Al-oxidation and total oxygen. In order to improve the cleanliness of refined ingot, it is more effective to decrease the oxygen potential of slag pool to a minimum level, or decrease the time of droplet formation and the temperature of slag pool to some extent, rather than improve the Al content in the electrode.

KEY WORDS: bearing steel; ESR; slag-metal reaction; kinetic analysis; oxygen variation.

1. Introduction

G20CrNi2Mo, equal to SNCM420 in Japan and AISI 4320 in US, is one of the typical carburized bearing steels, widely used in the bearing of railway wagon in China due to its good surface hardness, high contact fatigue strength and mechanical property.1) With the railway speed-up and heavier load of the train, a higher requirement for the superior quality of G20CrNi2Mo has been put forward. Electroslag remelting (ESR) is widely employed for producing the high-performance steels by means of chemical refinement and controlled solidification.2,3) Therefore, the steel plants in China generally utilize this technology to produce G20CrNi2Mo. However, oxygen increase cannot be avoided during ESR process due to the existence of unstable slag components such as FeO, MnO, which is detrimental to the fatigue life of bearing steel. Therefore, it is imperative to well understand the variation mechanism of Al and oxygen of G20CrNi2Mo from consumable electrode to the refined ingot.

Several scholars have made efforts to investigate the influence of slag-metal reactions on the control of oxygen during ESR process. Mitchell et al.4) found that reactions between FeO and deoxidant predominate at high oxygen potential while at low oxygen potential exchange reactions between deoxidant and slag components control the inclusion composition. F. R. Carmona et al.5) indicated that FeO offered a very narrow deoxidation range due to its high activity coefficient. Shi et al.6) indicated that original oxide scale on the electrode surface would result in an increase of oxygen potential of slag pool. Iron oxide played an important role in transporting oxygen to the metal phase. The authors7) established a thermodynamic model of designing the slag compositions balanced with the electrode in order to decrease the degree of slag-steel reactions, further to decrease the content of oxygen in the ingot. However, study about the oxygen increase of bearing steel during ESR process from kinetics has been less reported until now.

The current work focuses on the influence of slag composition on the variation of Al and oxygen from kinetics. Firstly, an industrial experimental was carried out using a 2 400-kg industrial ESR furnace. Then, a kinetic model on the basis of penetration and film theories was developed in order to better elucidate the variation mechanism during ESR process. This practice is also expected to provide...
some guidance for the commercial ESR production of G20CrNi2Mo bearing steel.

2. Experimental

2.1. Experimental Procedure and Sampling

An industrial experimental was carried out using a furnace with a capacity to refine 2400 kg ingot, as shown in Fig. 1. The bloom with the specification of 2200 mm*250 mm*280 mm was utilized as the consumable electrode with the chemical composition listed in Table 1. The water-cooled copper mold had a height of 2000 mm and a diameter of 470 mm. Before arcing, 75 kg slag pre-melted by Fe–Al electrode was added into the mold. High-purity argon with a flow of 100 L.min\(^{-1}\) was introduced into the mold to isolate the air from outside. The height of slag pool was about 140 mm. The alternate current and secondary voltage applied during the normal refining was 9000 A and 60 V, respectively. No deoxidizer was added into the slag pool during the refining process. The average melting rate was about 6.30 kg/min and total refining process lasted about 380 min.

One slag sample was taken from the slag pool at the beginning while another was sampled at the end of normal refining. After the ingot cooling, two slices with a height of 20 mm were cut from the position where they were 70 mm from bottom and 50 mm from the top of ingot. The sampling position of the ingot corresponded with the time of slag sampling. Then two steel cuttings were cut from the edge and 1/2 radius position of the slice, respectively, while one was sampled from the center, as shown in Fig. 2.

2.2. Chemical Analysis

The chemical analysis was performed at National Analysis Center for Iron and Steel (NACIS), China. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for the determination of soluble Al, Si, Mn, Cr, Ni and Mo in the steel. The contents of total oxygen, sulfur and carbon were measured by the inert gas fusion-infrared absorptiometry while nitrogen content was determined by an inert gas fusion-thermal conductivity method.

The contents of total Ca, MgO, MnO, SiO\(_2\) and Al\(_2\)O\(_3\) in the slag sample were determined by wavelength dispersion X-ray fluorescence spectrometry while FeO was measured by potassium dichromate volumetric method. The EDTA method was used for the determination of fluorine content. The CaF\(_2\) in the molten slag existed in the form of Ca\(^{2+}\) and F\(^-\). Therefore, the content of CaF\(_2\) could be determined by the content of measured fluorine. Then, the Ca existed in the CaO form could be obtained by subtracting the Ca in the CaF\(_2\) from total Ca.

3. Experimental Results

Table 2 shows the slag compositions at the beginning and end of normal refining, respectively. From Table 2, the content of Al\(_2\)O\(_3\) and CaF\(_2\) decreases while CaO shows a rising trend, mainly due to the reaction of CaF\(_2\) with Al\(_2\)O\(_3\) yielding AlF\(_3\), as shown in reaction (1):

\[
3(CaF_2) + (Al_2O_3) \rightarrow 3(CaO) + 2AlF_3 \quad (1)
\]

The content of SiO\(_2\) and MnO has a pick-up mainly due to the continuous oxidation of Si and Mn during the refining process. As the reactions proceed, the content of FeO also shows a growth trend. The mechanism is not yet completely understood, the main source may be the scale which is formed by oxidation with air or the current leakage through the mold wall.\(^{6,8}\)

The average contents of C, Si, Mn, Al, N and O at bottom and top of the ingot were measured, as listed in Table 3.
Combining Tables 1, 2 and 3, it can be seen that slag composition exerts a significant influence on the variation of Al and oxygen. The content of oxygen increased from 12 ppm in electrode to 16 ppm, 21 ppm in the ingot while Al decreased from 0.040 wt% in the electrode to 0.031 wt%, 0.019 wt% in the ingot with the content of FeO in the slag increasing from 0.20 wt% to 0.45 wt%.

4. Discussions

4.1. Kinetic Model of Slag-Metal Reactions

In order to better clarify the variation mechanism, the slag-metal reactions were investigated from the viewpoint of kinetics. The ESR system is a complex metallurgical process involving different reaction interfaces, electrode-tip-slag interface, droplet-slag interface, metal pool-slag interface, respectively. The kinetic model is based on mass transfer control across the slag-metal interface at which equilibrium is maintained during ESR process. The following assumptions are considered in this model:

1. At each reaction position, the slag-metal system is considered to consist of two semi-infinite systems.
2. In the two phases of slag and metal, the initial concentrations of reactants and products are evenly distributed.
3. The coupled reactions at the slag-metal interface occur quickly, and reach up to a total chemical equilibrium state. The rate of reactions is controlled by the diffusion of reactants and products through a boundary layer at the reacting interface.
4. The effective segregation coefficient at liquid pool/ingot interface is equal to one and no further chemical refining occurs after solidification.

The coupled reactions occurred at different slag-metal interfaces are expressed as Eqs. (2)–(5):

\[
\begin{align*}
[\text{Al}] + 1.5[\text{O}] &= (\text{AlO}_1.5) \quad \text{(2)} \\
[\text{Si}] + 2[\text{O}] &= (\text{SiO}_2) \quad \text{(3)} \\
[\text{Mn}] + [\text{O}] &= (\text{MnO}) \quad \text{(4)} \\
[\text{Fe}] + [\text{O}] &= (\text{FeO}) \quad \text{(5)}
\end{align*}
\]

The expressions of standard equilibrium constants of Eqs. (2)–(5) are given as Eqs. (6)–(9):

\[
\begin{align*}
\lg K_{\text{Al}}^i &= \frac{32000}{T} - 10.29 \quad \text{(10)} \\
\lg K_{\text{Si}}^i &= \frac{30410}{T} - 11.59 \quad \text{(11)} \\
\lg K_{\text{Mn}}^i &= \frac{15015}{T} - 6.664 \quad \text{(12)} \\
\lg K_{\text{Fe}}^i &= \frac{6320}{T} - 2.734 \quad \text{(13)}
\end{align*}
\]

All the reactants and products can be classified into four systems Al+Al₂O₃, Si+SiO₂, Mn+MnO, Fe+FeO. During the refining process, the concentration of different components changes continuously, with the corresponding material flow across the slag-metal interface, as shown in Fig. 3.

The following equation represents the flux of metal element i into the slag, as the form of iOₐ:

\[
J_i = \frac{k_{i,m} M_{iO}}{100 M_i} \left( \frac{[\% i]}{[\% i]^*} \right) \quad \text{(10)}
\]

Where \( J_i \) is the molar flow, mol.cm⁻².s⁻¹. \( k_{i,m} \) and \( k_{i,s} \) represent the mass transfer coefficient for component in molten steel and slag, cm.s⁻¹. \( M_i \) and \( M_{iO} \) is molecular weight of steel and slag components, g.mol⁻¹. \( \rho_m \) and \( \rho_s \) is the density of steel and slag, 7.20 g.cm⁻³ and 2.65 g.cm⁻³, respectively. A symbol with superscript (*) represents an interfacial concentration.

According to Eq. (10), the equilibrium concentration of metal element at the interface can be re-arranged as follows:

\[
\frac{k_{i,m} M_{iO}}{M_i k_{i,s} \rho_s} \left( \frac{[\% i]^*}{[\% i]} \right) + \frac{k_{i,m} \rho_m M_{iO}}{M_i k_{i,s} \rho_s} \left( \text{FeO}^* \right) = B_i \left( \text{FeO}^* \right) \quad \text{(11)}
\]

Where \( B_i \) is the apparent equilibrium constant, which is expressed as Eq. (12):

\[
B_i = \frac{\left( \frac{[\% i]^*}{[\% i]} \right)}{\left( \frac{[\% i]^*}{[\% i]} \right) + \sum \left( \frac{[\% iO]}{[\% iO]} \right) \frac{M_{iO} \gamma_{iO}}{M_{iO} \gamma_{iO}}} \quad \text{(12)}
\]

Where \( [\% i]^* \) is the oxygen activity at the interface. \( K_M \) is the equilibrium constant, \( \gamma_{iO} \) is the Henry activity coefficient. \( \gamma_{iO} \) is the Raoult activity coefficient of slag component which are given as Eqs. (13)–(16):

\[
\lg \gamma_{iO} = \frac{11800}{T} \left( (N_{\text{CaO}} + N_{\text{MgO}})(N_{\text{SiO}_2} + 0.25N_{\text{Al}_2\text{O}_3}) \right) + \frac{4916}{T} N_{\text{MnO}} N_{\text{SiO}_2} + \frac{3562}{T} N_{\text{AI}_2\text{O}_3} N_{\text{SiO}_2} + \frac{123}{T} N_{\text{MnO}} N_{\text{Al}_2\text{O}_3} \quad \text{(13)}
\]
\[
\begin{align*}
\lg \gamma_{\text{MgO}} &= \lg \gamma_{\text{FeO}} - \frac{4.916}{T} N_{\text{SiO}_2} - \frac{123}{T} N_{\text{AlO}3} \quad \ldots (14) \\
\lg \gamma_{\text{SiO}_2} &= \lg \gamma_{\text{FeO}} - \frac{11,800}{T} (N_{\text{CaO}} + N_{\text{MgO}}) \\
&\quad - \frac{4.916}{T} N_{\text{MgO}} - \frac{3.562}{T} N_{\text{AlO}3} \quad \ldots (15) \\
\lg \gamma_{\text{AlO}3} &= \lg \gamma_{\text{FeO}} - \frac{2.950}{T} (N_{\text{CaO}} + N_{\text{MgO}}) \\
&\quad - \frac{3.562}{T} N_{\text{SiO}_2} - \frac{123}{T} N_{\text{MgO}} \quad \ldots (16)
\end{align*}
\]

Here, \( N_i \) is the mole fraction of component \( i \) in the molten slag.

The reaction rate of respective component can be given as Eq. (17):
\[
-\frac{d[\% i]}{dt} = \frac{A \cdot k_{i,m}}{V_m} \frac{1}{100 M_i} \left( [\% i] - [\% i]^* \right) \quad \ldots (17)
\]

\( A, V_m \) are the reaction area, \( \text{cm}^2 \) and volume of molten steel, \( \text{cm}^3 \). Combining Eqs. (11), (12) and (17), the final expression of reaction rate can be re-arranged as follows.

\[
-\frac{d[\% \text{Al}]}{dt} = \frac{A}{W_m} k_{\text{Al}} \left( [\% \text{Al}] - \frac{(\% \text{AlO}3)}{B_{\text{Al}} (\text{AlO}3)^3} \right) \quad \ldots (18)
\]

\[
\frac{1}{k_{\text{Al}}} = \frac{1}{\rho_{m,k_{\text{Al,m}}} \cdot B_{\text{Al}} (\text{AlO}3)^3 k_{\text{AlO}3}} \quad \ldots (19)
\]

\[
-\frac{d[\% \text{Si}]}{dt} = \frac{A}{W_m} k_{\text{Si}} \left( [\% \text{Si}] - \frac{(\% \text{SiO}2)}{B_{\text{Si}} (\text{SiO}2)^2} \right) \quad \ldots (20)
\]

\[
\frac{1}{k_{\text{Si}}} = \frac{1}{\rho_{m,k_{\text{Si,m}}} \cdot B_{\text{Si}} (\text{SiO}2)^2 k_{\text{SiO}2}} \quad \ldots (21)
\]

\[
-\frac{d[\% \text{Mn}]}{dt} = \frac{A}{W_m} k_{\text{Mn}} \left( [\% \text{Mn}] - \frac{(\% \text{MnO})}{B_{\text{Mn}} (\text{MnO})} \right) \quad \ldots (22)
\]

\[
\frac{1}{k_{\text{Mn}}} = \frac{1}{\rho_{m,k_{\text{Mn,m}}} \cdot B_{\text{Mn}} (\text{MnO}) k_{\text{MnO}}} \quad \ldots (23)
\]

\[
-\frac{d[\% \text{O}]}{dt} = \frac{A}{W_m} k_{\text{O}} \left( [\% \text{FeO}] - \frac{(\% \text{O})}{B_{\text{Fe}}} \right) \quad \ldots (24)
\]

\[
\frac{1}{k_{\text{O}}} = \frac{1}{\rho_{m,k_{\text{O,m}}} \cdot B_{\text{Fe}} (\text{FeO}) k_{\text{FeO}}} \quad \ldots (25)
\]

Here, \( W_m \) is the mass of molten steel, \( k_i \) is the overall mass transfer coefficient. The oxygen activity at the interface can be determined on the basis of the mass balance of elements across the interface.

\[
\frac{1.5}{M_{\text{Al}}} \frac{d[\% \text{Al}]}{dt} + \frac{2}{M_{\text{Si}}} \frac{d[\% \text{Si}]}{dt} + \frac{1}{M_{\text{Mn}}} \frac{d[\% \text{Mn}]}{dt} - \frac{1}{M_{\text{O}}} \frac{d[\% \text{O}]}{dt} = 0 \quad \ldots (26)
\]

The Eqs. (18)–(26) are applicable at all the slag/metal interfaces. When the oxygen activity at interface and mass transfer coefficients are given, the reaction rate of respective component can be obtained.

4.1.1. Mass Transfer Coefficient

The penetration theory is used to calculate the mass transfer coefficient both in molten steel and slag which assumes that interface is continuously renewed by eddies of fresh material from bulk liquid. Figure 4 shows the schematic diagram of flow of fluid element at the metal side.

1. Mass Transfer at the Metal Film/slag Interface

At the metal film side, the mass transfer coefficients of metal element can be calculated by Eq. (27):

\[
k_i = 2 \frac{D_i}{\pi \tau_e} \quad \ldots (27)
\]

Where \( D_i \) is the diffusion coefficient, \( \text{cm}^2 \cdot \text{s}^{-1} \), \( \tau_e \) is the time that an eddy is in contact with the interface which can be obtained through Eq. (28).

\[
\tau_e = 3.35 \left( \frac{2 \pi \cos \theta}{3 Q_m} \right)^{2/3} \left( \frac{\mu_m}{8 \rho_m \sin \theta} \right)^{1/3} \left( \frac{R_e}{\rho_m \sin \theta} \right)^{5/3} \quad \ldots (28)
\]

Where \( \theta \) is angle of cone. \( Q_m \) is the rate of volumetric melting, \( \text{cm}^3 \cdot \text{s}^{-1} \). \( R_e \) is the equivalent radius of electrode, \( \mu_m \) is the viscosity of metal in 0.005 Pa.s.15) In order to determine the cone angle, the electrode was quickly lifted during the refining process, as shown in Fig. 5(a). It can be seen that there are several small droplets generate simultaneously at the electrode tip. It is assumed that the time of every small droplet stay at the electrode tip is the same. The cone angle is set as 10°, as shown in schematic diagram of the electrode tip Fig. 5(b). After being calculated, the contact time during the droplet formation is about 2.89 s.

The behavior of mass transfer has a strong dependence of temperature. It has been reported that the temperature of metal film at electrode tip is close to the liquidus temperature of steel (1 785 K, calculated by Thermo-Calc software), and its superheat cannot exceed 20–30 K.16,17) Thus, the temperature of metal film is supposed to be 1 815 K more or less. It was assumed that the diffusion coefficient \( D_i \) has an identical value of 6.10 \( \times \) 10^{-5} \( \text{cm}^2 \cdot \text{s}^{-1} \) while \( \rho_m \) and \( \sin \theta \) are the density of metal element from bulk liquid.8) Combining Eqs. (25) and (26), the time that an eddy is in contact with the interface which can be obtained through Eq. (28).

The penetration theory is used to calculate the mass transfer coefficient both in molten steel and slag which assumes that interface is continuously renewed by eddies of fresh material from bulk liquid. Figure 4 shows the schematic diagram of flow of fluid element at the metal side.

Fig. 4. Schematic diagram of flow of metal element.
4.00 × 10⁻⁵ cm².s⁻¹. Therefore, k₁ is 0.0037 cm.s⁻¹ for Al₂O₃ and SiO₂, 0.0074 cm.s⁻¹ for MnO and FeO.

As mentioned above, the droplets generate in several sites, in this case, the composition of metal film will be rather uniform and close to that of droplets at the electrode tip except the soluble oxygen, for that the droplet was heated continuously to a high temperature about 1 973 K by the molten slag within 2.89 seconds. Therefore, the solvability of oxygen will increase obviously. It is assumed that the mass transfer coefficient of oxygen at metal side is 0.030 cm. s⁻¹.

(2) Mass Transfer at the Falling Droplet/slag Interface

The average temperature of slag pool and metal pool/slag interface is determined by commercial software Meltflow-ESR. All the related parameters including the properties of slag and steel, refining time, secondary voltage and alternate current used in the experimental are input as shown in Fig. 6. After calculation, the results can be output by Tecplot Focus. Figure 6(a) shows the velocity and temperature fields. The black line in the slag pool represents the velocity. The more intensive the line, the higher the velocity is. The average temperature of 437 points in Fig. 6(b) is utilized to evaluate the temperature of slag pool. The white vector represents the slag/metal pool interface. Extract the temperature of “Path 1” (slag pool/metal pool interface), then, take the average. The average temperature of slag pool and metal pool/slag interface is 2 020 K, 1 957 K, respectively.

At the metal side, the diffusion coefficient of Al, Si, Mn and O at 2 020 K is 1.93 × 10⁻³ cm².s⁻¹ while 1.34 × 10⁻³ cm².s⁻¹ at 1 957 K. The velocity of droplet falling is set as 61 cm.s⁻¹, and the time of droplet falling is about 0.23 s. According to the penetration theory, k₂ is 0.10 cm.s⁻¹ at the droplet and 0.018 cm.s⁻¹ in the metal pool.

At the slag side, the diffusion coefficient of Al₂O₃, SiO₂ is 9.00 × 10⁻⁵ cm².s⁻¹ at 2 020 K, 7.00 × 10⁻⁵ cm².s⁻¹ at 1 957 K, while MnO and FeO is 1.20 × 10⁻⁴ cm².s⁻¹ at 2 020 K, 1.00 × 10⁻⁴ cm².s⁻¹ at 1 957 K. After calculation, k₃ is 0.022 cm.s⁻¹ for Al₂O₃ and SiO₂, 0.026 cm.s⁻¹ for MnO and FeO during the falling of droplet, while 0.0042 cm.s⁻¹ for Al₂O₃ and SiO₂, 0.0050 cm.s⁻¹ for MnO and FeO at the slag side.

4.1.2. Area/Volume Ratio Estimates

(1) Area/volume Ratio of Metal Film

At the metal film/slag interface, the area and volume of metal film is estimated from Eqs. (29) and (30):

\[ A_{\text{Film}} = \frac{\pi R^2_e}{\cos \theta} = 731.42 \text{ cm}^2 \] (29)

\[ V_{\text{Film}} = \frac{\pi R^2_e \delta}{3} = 10.59 \text{ cm}^3 \] (30)

Where \( \delta \) is the average thickness of metal film, which can be calculated from Eq. (31):

\[ \delta = \left[ \frac{3 \mu_m Q_m}{2 \pi (\rho_m - \rho_e) g \sin \theta \cos \theta} \left( \frac{1 - x^2 \cos^2 \theta}{R^2_e} \right) \right]^{1/3} \] (31)

(2) Area/volume Ratio of Droplet and Metal Pool

During the time of droplet falling, because of the oscillation effect, it was assumed that area/volume ratio is about 24.0. The metal pool is constituted of a cylinder and cone, as shown in Fig. 6(a). The depth of cylinder \( h_1 \) is 2.5 cm and the cone \( h_2 \) is 12.5 cm. Thus, the area and volume of metal pool can be obtained as follows.

\[ A_{\text{Metal Pool}} = \pi R^2_m = 1 734 \text{ cm}^2 \] (32)

\[ V_{\text{Metal Pool}} = V_{\text{Cylinder}} + V_{\text{Cone}} = \pi R^2_m h_1 + \frac{\pi R^2_m h_2}{3} = 11 560 \text{ cm}^3 \] (33)

Where \( R_m \) is the radius of mold, cm.

In light of the above analysis, all the necessary parameters for use in the model have been detailed, as listed in Table 4. Table 5 shows the apparent equilibrium constants of reactions (2) and (5) at the beginning of refining. It indicates that the value of \( B_{Al} \) is several orders of magnitude higher than \( B_{Fe} \). Table 6 shows the mass transfer resis-
tance of element in steel and slag. It can be seen that the rate-determining step of Al-oxidation is on the metal side while oxygen increase lies in the slag phase transport, which is closely related with the value of $B_{M}$. The mass transfer resistance includes $B_{M}$ in the denominator. With the value of $B_{M}$ decreasing, the resistance shows a rising trend. Therefore, the high mass transfer resistance of FeO is mainly due to the low value of the apparent equilibrium constant $B_{Fe}$. In addition, with the temperature increasing, the mass transfer resistance of all elements decreases obviously.

**Figure 7** shows the flow chart of the model. The volume element of liquid travels sequentially through various reaction regions, reacting during certain residence time. According to the penetration and film theories, the equilibrium oxygen activity, the content of Al and soluble oxygen with the changing of time at the metal film, droplet, metal pool/slag interface are calculated by Matlab software, respectively.

### 4.2. Kinetic Analysis

#### 4.2.1. Effect of Oxygen Potential of Slag on the Variation of Al and Soluble Oxygen

The rate-determining step of the oxidation of Al is the mass transfer of Al at the metal side, as shown in Table 6, and the oxidation rate of Al at different slag/metal interfaces can be deduced by the following equation.

$$\frac{d[\% Al]}{dt} = \frac{A \cdot k_{ Al, m } \cdot \rho_{m}}{V_{m}} \cdot \frac{\rho_{m}}{100 M_{Al}} \left( [\% Al] - [\% Al]^* \right) \quad \ldots \ldots (34)$$

From this equation, it indicates that the oxidation rate of Al depends on the Al concentration at the interface $[\% Al]^*$, which is determined by the activity of Al$_2$O$_3$ and the equi-

**Table 4.** The related parameters used in the model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Metal film</th>
<th>Droplet</th>
<th>Metal pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{Al}$ cm/s</td>
<td>0.0091</td>
<td>0.10</td>
<td>0.018</td>
</tr>
<tr>
<td>$k_{Al, O_{2}}$ cm/s</td>
<td>0.0037</td>
<td>0.022</td>
<td>0.0042</td>
</tr>
<tr>
<td>$k_{FeO}$ cm/s</td>
<td>0.0091</td>
<td>0.10</td>
<td>0.018</td>
</tr>
<tr>
<td>$k_{SiO_{2}}$ cm/s</td>
<td>0.0037</td>
<td>0.022</td>
<td>0.0042</td>
</tr>
<tr>
<td>$k_{MnO}$ cm/s</td>
<td>0.0091</td>
<td>0.10</td>
<td>0.018</td>
</tr>
<tr>
<td>$k_{Fe}$ cm/s</td>
<td>0.0091</td>
<td>0.026</td>
<td>0.0050</td>
</tr>
<tr>
<td>$k_{O_{2}}$ cm/s</td>
<td>0.0091</td>
<td>0.026</td>
<td>0.0050</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>1 815</td>
<td>2 020</td>
<td>1 957</td>
</tr>
<tr>
<td>$A_{Al}/V_{m}$</td>
<td>70</td>
<td>24</td>
<td>0.15</td>
</tr>
<tr>
<td>Residence time, s</td>
<td>2.89</td>
<td>0.23</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 5.** Apparent equilibrium constants of reactions (2) and (5) at the beginning of refining.

<table>
<thead>
<tr>
<th>Location</th>
<th>$B_{Al}$</th>
<th>$B_{Fe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal film</td>
<td>$6.53 \times 10^{5}$</td>
<td>314</td>
</tr>
<tr>
<td>Droplet</td>
<td>$3.73 \times 10^{7}$</td>
<td>178</td>
</tr>
<tr>
<td>Metal pool</td>
<td>$8.25 \times 10^{5}$</td>
<td>209</td>
</tr>
</tbody>
</table>

**Table 6.** Mass transfer resistance of element in steel and slag.

<table>
<thead>
<tr>
<th>Remelting stage</th>
<th>Location</th>
<th>Mass transfer resistance in steel</th>
<th>Mass transfer resistance of AlO$_{1.5}$</th>
<th>Mass transfer resistance of FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\frac{1}{\rho_{m} \cdot k_{m}}$</td>
<td>$M_{ AlO_{1.5} }$ ( B_{ Al } M_{ Al } \rho_{m} (\rho_{o}^*)^{-\frac{1}{2}} k_{ AlO_{1.5} } )</td>
<td>$M_{ FeO }$ ( B_{ FeO } M_{ FeO } \rho_{m} \rho_{o}^* k_{ FeO } )</td>
</tr>
<tr>
<td>Beginning</td>
<td>Metal film</td>
<td>9.09</td>
<td>0.084</td>
<td>3 942.95</td>
</tr>
<tr>
<td></td>
<td>Droplet</td>
<td>1.35</td>
<td>0.041</td>
<td>481.10</td>
</tr>
<tr>
<td></td>
<td>Metal pool</td>
<td>7.69</td>
<td>0.18</td>
<td>3 292.94</td>
</tr>
<tr>
<td>End</td>
<td>Metal film</td>
<td>9.09</td>
<td>0.036</td>
<td>2 240.80</td>
</tr>
<tr>
<td></td>
<td>Droplet</td>
<td>1.35</td>
<td>0.023</td>
<td>332.28</td>
</tr>
<tr>
<td></td>
<td>Metal pool</td>
<td>7.69</td>
<td>0.10</td>
<td>2 260.45</td>
</tr>
</tbody>
</table>
librium oxygen activity at the interface.

Thus, the mass concentration of Al changing with time can be obtained by Eq. (35):

\[ \ln \frac{[\% Al]_0 - [\% Al]^*}{[\% Al]_1 - [\% Al]^*} = A \cdot k_{Al,m} \cdot \frac{\rho_m}{100M_{Al}} t \quad \ldots \ldots \ldots (35) \]

Figure 8 shows the calculated results of the variation of Al from metal film to metal pool, and the measured values in the ingot. The calculated result shows satisfactory agreement with the measured values. At the beginning of refining, the model predicts that the content of Al decreases from 0.040 wt\% in the electrode to 0.031 wt\% at the metal film, and slightly changed after the droplet detaching from the electrode tip. It is indicated that a very minor role is played by the droplets and metal pool in the overall contribution to the mass transfer of Al. This confirms the evidence of Wei et al.\(^{18}\) which indicates that the metal film was of significance in determining the overall rate of mass transfer.

Al is mainly oxidized by FeO at the metal film due to large area/volume ratio of 70.0, and relatively long contact time of 2.89 s. In order to verify the prediction, the characteristic of inclusions in the droplet as shown in Fig. 5(a) was investigated by SEM-EDS. The result shows that most of the inclusions are newly-generated Al\(_2\)O\(_3\) inclusions, which is different from the globular CaO–MgO–Al\(_2\)O\(_3\) inclusions in the electrode, providing evidence that Al-oxidation has occurred during the time of droplet formation.

At the end of refining, the model indicates that the content of Al decreases from 0.040 wt\% in the electrode to 0.021 wt\% at the metal film. That is because with the content of FeO in the slag increasing from 0.20 wt\% to 0.45 wt\%, the equilibrium oxygen activity at the interface increases apparently. Correspondingly, the content of equilibrium Al becomes low, thus enhancing the diffusion of Al from metal to the interface.

If the oxygen activity at interface is obtained, the rate of oxygen increase in the molten steel can be expressed as the following equation.

\[ \frac{d[\% O]}{dt} = A \cdot k_{O,m} \cdot \frac{\rho_m}{100M_O} ([\% O]^* - [\% O]) \quad \ldots \ldots \ldots (36) \]

The mass concentration of oxygen changing with time can be expressed as Eq. (37):

\[ \ln \frac{[\% O]^* - [\% O]_0}{[\% O]^* - [\% O]_f} = A \cdot k_{O,m} \cdot \frac{\rho_m}{100M_O} t \quad \ldots \ldots \ldots (37) \]

Figure 9 shows the calculated results of the variation of soluble oxygen at different locations. At the beginning of refining, the content of soluble oxygen in the droplet of electrode tip is supposed to be 4.30 ppm, about two twice the content at the metal film within 2.89 seconds. This can be explained by the fact that the temperature of droplet is much higher than that at the film. After the droplet detaching from the electrode tip, the content of soluble oxygen continues to rise from 4.30 ppm to 6.80 ppm within 0.23 s. During this period, the content of Al has no tendency to decrease, thus, the high temperature of slag pool is the key factor leading to the pick-up of soluble oxygen. After the droplet falling into the metal pool, the content of soluble oxygen varies little. It is rather difficult to measure the oxygen activity directly, but under such a high temperature, the equilibrium oxygen activity at the interface is definitely very high.

During the last stage of refining, the model indicates that the content of soluble oxygen increase from 6.40 ppm in the droplet of electrode tip to 9.86 ppm during the falling of droplet, much higher than that at the beginning of refining. This can be explained that with the content of FeO increases, the mass transfer resistance shows a downtrend, as shown in Table 5. Therefore, the equilibrium oxygen activity at the interface subsequently increases.

4.2.2. Effect of Al Content in the Electrode and Temperature of Slag Pool on the Variation of Soluble Oxygen

During the industrial ESR process, in order to prevent the excessive oxidation of Al, one method is to improve the Al content of the electrode. Figure 10 shows the effect of Al content in the electrode on the content of soluble oxygen.

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![Fig. 8. The variation of Al at different locations during ESR process.](image)

![Fig. 9. Variation of soluble oxygen at different locations during ESR process.](image)
From Fig. 10, with the content of Al in electrode increasing from 0.030 wt% to 0.050 wt%, the content of soluble oxygen in the metal pool has a limited decrease. Table 6 indicates that the rate-determining step of oxygen increase lies in the mass transfer of FeO at slag side, as given in Eq. (38).

\[ \frac{d\%O}{dt} = \frac{A}{W_v} k_{FeO} \left( (\%FeO) - B_{FeO} \right) \]  

That is to say, the content of soluble oxygen is influenced more by the oxygen potential. With the Al content increasing, the change of equilibrium oxygen activity is not obvious. From this view, compared to increase the Al content of electrode, it is more effective to decrease the oxygen potential of slag pool to a minimum level.

With different slag system, electric system and depth of slag pool, the temperature of slag pool will be of some difference. Figure 11 shows the effect of temperature of slag pool on the content of soluble oxygen. From Fig. 11, with the temperature of slag pool decreasing from 2 020 K to 1 960 K, the content of soluble oxygen at different locations all has an obvious decrease. The soluble oxygen can only precipitate during the process of cooling, which is an important source of total oxygen. Therefore, the temperature of slag pool should not be controlled too high.

It is noted that the total oxygen consists of soluble oxygen and the oxygen as a form of inclusions at the temperature of steelmaking.

\[ O_{Total} = [O]_{sol} + O_{inclusion} \]  

Figure 12 shows the content of soluble oxygen, and oxygen as a form of inclusions which mainly results from slag-metal reactions. The type of inclusions in the ingot is mainly small single Al2O3, low-MgO MgO-Al2O3, low MgO and low CaO CaO–MgO–Al2O3 which is different from that in the electrode, indicating that ESR process has an excellent ability to purify the molten steel. From Fig. 12, it can be seen that the oxygen generated from slag-metal reactions occupies about fifty percent of the total oxygen. As mentioned above, the oxidation of Al mainly occurs at the metal film of electrode tip, and Al2O3 would generate at the slag/metal interface, most of which will be absorbed by the molten slag while some will stay in the steel. The removal rate of the inclusions is related with the surface tension between slag, steel and inclusions, the depth of metal pool, etc., which is needed to be further studied.

In conclusion, Fig. 13 shows the mechanism of Al-oxidation and oxygen increase during ESR process. Al in the electrode is oxidized by the iron oxide at the metal film of electrode tip, Al2O3 will generate at the interface. The result indicates quasi-thermodynamic equilibrium can be attained at this position. With the low temperature about 1 815 K, the equilibrium oxygen activity at metal film is relatively low. However, during the time of droplet formation, the droplet of electrode tip is continuously heated by the molten slag to a high temperature. Thus, the content of soluble oxygen has an obvious pick-up. After the droplet detaching from the electrode tip, it is further to be heated by the molten slag, the equilibrium oxygen activity continues to increase, and the rate of FeO transfer to the slag/metal interfaces is large although the content of FeO is very low. After the droplet falling into the metal pool, the contents of Al and soluble oxygen vary little due to very low area/volume ratio. There
is no doubt some of the $\text{Al}_2\text{O}_3$ generated at the metal film will be transferred to the metal pool, some of which will float upward and be absorbed by the molten slag while some will be captured by the dendrite.

In light of previous analysis, the rate-determining step of oxygen increase is controlled by the transport of FeO. On one hand, the iron oxide is the main oxidizing agent for the oxidation of Al. Therefore, a feasible method is to add strong deoxidizer Al power into the slag pool for that the products will stay in the slag pool, or strengthen the protecting atmosphere to decrease the FeO-activity to a minimum level. The value of minimum oxygen potential from thermodynamics was calculated in our previous study.\(^7\) On the other hand, mass transfer coefficient is function of slag velocity. Therefore, to reduce the flow velocity seems to be beneficial from mass transfer point of view. A practical method is to enlarge the electrode/mold ratio, since the velocity is inversely proportional to the electrode radius.

In addition, the cone angle of electrode and temperature of slag pool also play a significant role in improving the cleanliness. With a relatively flat electrode, the time of droplet formation is longer, thus the superheat of droplet formation and falling. The rate-determining step of oxygen increase lies in the mass transfer of FeO at slag side. With the content of FeO increasing from 0.20 wt% to 0.45 wt%, the mass transfer resistance of FeO decreases obviously, thus would result in an increase of Al-oxidation and total oxygen. The model predicts that the soluble oxygen occupies about fifty percent of the total oxygen.

In order to improve the cleanliness, it is suggested to decrease the oxygen potential of slag pool to a minimum level, or decrease the time of droplet formation and temperature of slag pool to some extent, rather than improve the Al content in the electrode.

5. Conclusions

To elucidate the variation of Al and oxygen of G20CrNi2Mo bearing steel during industrial ESR process, a kinetic model was developed based on the penetration and film theory. The following conclusions are obtained.

1. With the content of FeO increasing from 0.20 wt% to 0.45 wt%, the content of oxygen increased from 12 ppm in electrode to 16 ppm, 21 ppm in the ingot while Al decreased from 0.040 wt% in the electrode to 0.031 wt%, 0.019 wt% in the ingot.

2. The Al in the electrode is mainly oxidized by FeO at the metal film. The rate-determining step of Al-oxidation lies in the mass transfer of Al in the molten steel. Increase of soluble oxygen mainly occurs during the time of droplet formation and falling. The rate-determining step of oxygen increase lies in the mass transfer of FeO at slag side. With the content of FeO increasing from 0.20 wt% to 0.45 wt%, the mass transfer resistance of FeO decreases obviously, thus would result in an increase of Al-oxidation and total oxygen. The model predicts that the soluble oxygen occupies about fifty percent of the total oxygen.

3. In order to improve the cleanliness, it is suggested to decrease the oxygen potential of slag pool to a minimum level, or decrease the time of droplet formation and temperature of slag pool to some extent, rather than improve the Al content in the electrode.

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REFERENCES