Research of unpolluted deoxidization technology with applied electric field

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Abstract. A commercial experiment system of unpolluted deoxidization with applied electric field is designed and fabricated based on laboratory and pilot research. A simulation model for the electrochemical deoxidization system between molten steel and slag with direct current electric field is found and calculated. A series of research work has been carried out in order to explore the influence of the various technology parameters on the electrochemical deoxidization efficiency. The effects and influences of the electric field parameters, the electrode parameters, the properties of the molten slag and molten steel on the distribution of the current density in the electrochemical deoxidization system are analyzed according to the simulation experiments and the commercial experiments. The simulation results are verified based on experiments. The result shows that the oxygen transfers from the molten slag into the molten steel without electric field because of the high oxidizing slag. And the electrochemical deoxidization can be carried out effectively with the application of electric field. The maximum deoxidization rate can reach to 11.3×10⁻⁶·min⁻¹ and the deoxidization rate can be improved by increasing oxygen ion current. Increasing both of the mass transfer coefficient and the reaction interface area can increase the oxygen ion current between the steel and slag.

1. Introduction
In refining process, the deoxidizer is added into the molten steel directly with the traditional deoxidization methods [1]. It results in the formation of nonmetallic inclusions in the steel and the quality of the product can be affected. In 1970s, in order to prevent the molten metal from being unpolluted, the deoxidizer of H₂, CO and other active metals--all these deoxidizers and their products of H₂O, CO₂ and oxide could not be contacted with molten metal by the methods of electrolytic and galvanic. Thus the oxygen in molten metal has been decreased without pollution [2,3]. A concept of controlled oxygen flow metallurgy technology was proposed by Zhou G Z in 1980s. Based on the electrochemistry, the oxygen ion moving direction could be controlled and then the oxygen could be transferred out of the molten steel. Unpolluted deoxidization technique had been studied with applied electric field between slag and molten steel or Cu melt by Lu, Zhang and Li [4-6], the oxygen content in molten steel or Cu melt was decreased rapidly and effectively with this method. The kinetic model with electrochemical characteristic representing oxygen ion immigration had been worked out, and the theoretical results were in good agreement with experiments. The electrochemical research on oxygen transfer process of CaO-MgO-Al₂O₃ slag and Steel was carried out by Li [7], and the results showed...
that under the experimental conditions, the oxides in the slag decomposed in the electric field. The electrode electrochemical reactions were controlled by the voltage parameters and ion concentration of the slag and steel.

In Iron & Steel Research Institute of Ansteel, the laboratory equipment of the deoxidization experiment with DC field with 500 kg molten steel was exploited in 2010. A series of unpolluted deoxidization experiments were carried out [8,9]. In order to research the deoxidization effect continuously, the commercial research equipment of the deoxidization experiment was set up based on 100t ladle. The experimental processes and the results are introduced in this paper.

2. Experimental

2.1. Theory

Molten slag is a kind of electrolyte that includes oxygen ion, various positive metal ions and mult-ion groups, which can be used as a passage for the oxygen ion elimination. The moving direction and reaction velocity can be controlled by applying DC field. The following steps occur during the process.

1. Oxygen ion is transferred from the molten steel to the interface
2. Cathode reaction in the steel-slag interface: \([O] + 2e \rightarrow (O^2-)\)
3. Oxygen ion is transferred into the slag with the application of DC field
4. Anode reaction in the interface of the slag and anode: \((O^2-) \rightarrow 1/2O_2 + 2e\)

Based on the electrochemistry theory, the positive charge is accumulated on the steel-slag interface with the step ②. With step ④, the negative charge is accumulated on the slag-anode interface. So the electric field is formed between the two interfaces and the transport of the oxygen ion will be prevented. Thus the deoxidization process is prevented. In order to maintain the deoxidization process, an electric field should be imposed to eliminate the original electric field between the two interfaces.

2.2. Equipment

The equipment system includes: 100t ladle, DC source, anode (graphite, diameters of the two anodes are 400 mm and 150 mm respectively), cathode (inner is graphite and the diameter is 80 mm, exterior is the insulated material that prevents the erosion from the steel and slag, and diameter is 150 mm), clamps and elevators for the electrodes, control room and stirring system, as shown in figure 1.

![Figure 1. Schematic of applied electrical field steel refining equipment.](image_url)

3. Simulation
3.1. Model
Based on the experiment system, a simulation model is set up by the finite element software. Molten steel and slag are the two main parts, one anode in the slag and another cathode in the steel, as shown in figure 2. The diameter of the anode and cathode are 400 mm and 150 mm respectively. The slag thickness is 100 mm and anode is inserted in the slag with 50 mm depth. The cathode is inserted in the steel with the depth of 100 mm.

Simulation parameters are: 5 V imposes in the anode and 0v in the cathode. Others are shown in table 1.

| Simulation parameter | Height | Diameter | Resistivity | Inductive capacity |
|----------------------|--------|----------|-------------|-------------------|
| Molten steel         | 3 m    | 3 m      | $1.4\times10^{-6}$ Ω·m | 1000              |
| Molten slag          | 100 mm | 3 m      | 0.2 Ω·m     | 6                 |

3.2. Simulation results
The current density in the steel and slag interface is shown in figure 3. It can be seen that the maximum current density under the anode is 258 A/m² when the anode diameter is 400 mm and the current in this area is almost 32 A. The total current is higher than 50 A in the steel-slag system when adding the current around the anode. When the anode diameter is 150 mm, the maximum current density is 53.5 A/m², which is lower than that with the bigger anode. So in practice, a bigger anode should be adopted to achieve a better result.

![Figure 2. Schematic of simulation model and net mesh.](image)

![Figure 3. Comparison of current density at the steel-slag interface of different simulation.](image)

![Figure 4. The result of experiments.](image)
4. Experiment

4.1. Experimental scheme

Q235B is selected as the experimental steel. Tapping temperature is higher than 1710°C, and the slag is pushed off when tapping in order to control the slag content strictly. Lime and refining slag are added into the ladle in the final stage of tapping. Oxygen content is checked after 2 minutes of large amount Argon bottom blowing. Then the electrodes are descended by the elevators respectively. Anode is immerged in the molten slag and cathode is immerged in the molten steel. An electric field is provided by a DC source. The experimental scheme is shown in table 2.

Table 2. Experimental scheme.

| No. | Condition | DC field | Reaction, min |
|-----|-----------|----------|---------------|
| Exp.1 | no electrodes | None | 20 |
| Exp.2 | anode diameter: Φ400mm, distance to the steel surface: 50mm | None | 15 |
| Exp.3 | anode diameter: Φ150mm, distance to the steel surface: 50mm | 3~5V, 30~50A | 15 |
| Exp.4 | anode diameter: Φ400mm, distance to the steel surface: 50mm | 3~5V, 30~50A | 20 |
| Exp.5 | anode diameter: Φ400mm, distance to the steel surface: 30mm | 3~5V, 50~80A. | 20 |

4.2. Results and discussion

In the experiments, the effects of the electrode diameter, the current and the immersion depth are researched respectively.

4.2.1. Results and analysis without DC field. In order to validate the deoxidization effect, the contrast experiments 1 and 2 are carried out firstly. Figure 4 shows the results. It can be seen that the oxygen content increases from $853 \times 10^{-6}$ to $972 \times 10^{-6}$ in 20 mins without electrode and DC field in exp 1. The oxygen content increases from $510 \times 10^{-6}$ to $538 \times 10^{-6}$ in 15 mins with electrode while without DC field in exp. 2.

Table 3 shows the composition and content of the steel before and after the contrast test. The slag content and components before the test are shown in table 4.

Table 3. Content and composition of the steel (wt,%).

| Stage | C  | Si  | Mn  | P   | S   |
|-------|----|-----|-----|-----|-----|
| Initial | 0.0252 | <0.01 | 0.020 | 0.0050 | 0.026 |
| End   | 0.0248 | <0.01 | 0.020 | 0.0062 | 0.027 |

Table 4. Content and composition of the slag (wt,%).

| CaO  | SiO2 | MgO | Al2O3 | MnO | P2O5 | TFe | FeO | Fe2O3 |
|------|------|-----|-------|-----|------|-----|-----|-------|
| 38.00 | 12.15 | 6.80 | 11.40 | 0.99 | 21.75 | 19.04 | 9.94 |

It can be seen that the oxidizability of the slag is very high because the total content of FeO and MnO is higher than 20%. The $a_{FeO}$ is used to characterize the oxidizability of the slag and Fe$_2$O$_3$ is another supporter for the slag oxidizability except for FeO. According to the oxygen contain:

$$w(FeO) = w(FeO) + 1.35w(Fe_2O_3)$$

There is a balance for Ferous oxidizing:
\[ K_{\text{FeO}}^\infty = \frac{a_{\text{FeO}}}{(a_{\text{Fe}})_{\text{FeO}}} = \exp(2.303 \times \left(\frac{6320}{T} - 2.734\right)) \] (2)

In the molten steel, \( a_{\text{Fe}} \approx 1 \), so

\[ a_{\text{FeO}} = \frac{a_{\text{FeO}}}{K_{\text{FeO}}} \] (3)

The oxygen active coefficient can be calculated with the interaction coefficient in the molten steel.

\[ \lg f_{\text{O}} = e_C^O w[C] + e_O^O w[O] + e_S^O w[Si] + e_M^MN w[Mn] + e_P^O w[P] + e_S^S w[S] \] (4)

where, \( e_C^O = -0.45, \) \( e_O^O = -0.20 \) (or 0.30), \( e_S^O = -0.131, \) \( e_M^MN = -0.021, \) \( e_P^O = 0.07 \) (or 0.006), \( e_S^S = -0.18 \) (or -0.133) [10] (Annotation: the interaction coefficients are various from the different materials.)

The steel components are substituted into equation (4), then \( f_{\text{O}} \) can be calculated.

\[ f_{\text{O}} = 0.95 \] (5)

When temperature is 1600°C, \( K_{\text{FeO}}^\infty \) equals to 4.369. From figure 5, \( a_{\text{FeO}} \) is 0.7 according to the slag composition in table 4, as shown the red area in figure 5. Then the oxygen content in the steel should be:

\[ w[O]^\infty = \frac{a_{\text{FeO}}}{f_{\text{O}} \cdot K_{\text{FeO}}} = 0.168\% \] (6)

It is much higher than the total oxygen that of molten steel. So the oxygen ions will transport into the steel if there is no DC field. In exp. 2 the oxygen content increases slowly. It exhibits that the electric field balance between steel and slag is destroyed because of the immersion of the electrodes. More oxygen ions move into the slag and react with the electrodes and the oxygen transport ratio is reduced.

![Figure 5. FeO activity in the slag [11].](image1)

![Figure 6. The transformation of applied electric field in exp. 5 during the reaction.](image2)

4.2.2. Analysis of the deoxidization experiment with DC field. The effect of the various diameter and immersion depth of the anode on the deoxidization are tested. The results are shown in figure 4. In exp. 3, the anode diameter is 150 mm and the distance to the steel and slag interface is 50 mm. The
oxygen content decreases from $881 \times 10^6$ to $795 \times 10^6$ in 15 mins and the deoxidization rate is $5.73 \times 10^6 \cdot \text{min}^{-1}$. In exp. 4, the anode diameter is 400 mm and the distance is 50 mm also. The oxygen content decreases from $795 \times 10^6$ to $650 \times 10^6$ in 20 mins. The deoxidization rate is $7.25 \times 10^6 \cdot \text{min}^{-1}$. So the deoxidization rate can be improved by increasing the reaction interface area. The difference between exp. 4 and exp. 5 is the immersion depth of anode. In exp. 5, the distance between anode end to the interface of steel and slag is 30 mm. With DC field, the oxygen content decreases from $868 \times 10^6$ to $642 \times 10^6$ in 20 mins. The deoxidization rate is $11.30 \times 10^6 \cdot \text{min}^{-1}$.

The deoxidization experiments with DC field between the steel and slag were also carried on by Lu [6]. A kinetic model to describe the deoxidization process had been set up. As following:

$$O_m = O_{m,0} - \int_0^t \frac{I_{O^2-} \cdot M_O \times 10^6}{2FM_{\text{melt}}} d\xi$$

(7)

Where,

$$I_{O^2-} = I_{O^2-}^0 - \exp\left(-\frac{\alpha \rho_{\text{melt}} A}{M_{\text{melt}}} t\right)$$

(8)

The following equation can be obtained.

$$O_m = (O_0 - O_C) \cdot \exp\left(-\frac{\alpha \rho_{\text{melt}} A}{M_{\text{melt}}} t\right) + O_C$$

(9)

Where, $I_{O^2-}$ is the oxygen ion current, $t$ is time, $M_O$ is the mole mass of oxygen, $F$ is faraday constant, $M_{\text{melt}}$ is the weigh of the melt, $R$ is gas factor, $O_C$ is the balance oxygen concentration in the melt with the graphite, $\alpha$ is mass transfer coefficient, $\rho_{\text{melt}}$ is the melt density, $A$ is the area between the steel and slag, $O_m$ is the oxygen content in sometime and $O_0$ is the initial oxygen content in the steel.

From the kinetic model we can see that the deoxidization rate is mainly depend on the oxygen ion current between the steel and slag, the oxygen ion current is mainly influenced by mass transfer coefficient and reaction interface area of the steel and slag. It means that the oxygen ion current can be increased by increasing the mass transfer coefficient and the reaction interface area. Thus the reaction rate can be improved.

Compared exp. 3 and exp. 4, the deoxidization kinetic condition is improved because of increasing the reaction interface area and then the deoxidization rate can be improved. From exp.4 and exp.5, it can be seen that there will be some influences with the increase of the immersion depth, such as decrease of the slag resistance, increase of the oxygen ion current and then the deoxidization rate increases. It also can be obtained that deoxidization rate in the initial stage is higher than the terminal stage. In the initial 5 mins, the oxygen content decreases $93 \times 10^6$ and the deoxidization rate is $18.6x10^6 \cdot \text{min}^{-1}$, while in the terminal 5 mins, $28 \times 10^6$ oxygen is deoxidized and the deoxidization rate is $5.6 \times 10^6 \cdot \text{min}^{-1}$ in exp. 5.

The relationship between conductivity and viscosity of molten slag had been studied by Bockris [12] in 1980s. He found the electric conductivity of molten slag not only depend on ion concentration but also on the interaction force of plus or minus ion. The relationship between conductivity and viscosity expressed as follow equation:

$$K^n \cdot \eta = C$$

(10)

$K$ is conductivity of molten slag, $\eta$ is viscosity of molten slag, $n$ is an index ($>1$), $C$ is a constant.
The relationship between ion conductivity and diffusion coefficient had been studied by Goto [13] in 1980s. He found the relationship following the principle of Nernst-Einstein equation.

\[
D_i = \frac{RT}{F^2 z_i^2 c_i} K
\]  

(11)

\(D_i\) is the diffusion coefficient of ion, \(z_i\) is the electrovalence of ion, \(c_i\) is the concentration of ion, \(K\) is conductivity of molten slag.

The electric conductivity is mainly influenced by viscosity and diffusion coefficient according to their researches. At the beginning of experiments the mass transfer coefficient is relatively higher because of the high temperature of the steel and slag and lower viscosity of the slag. With the proceeding of the reaction, the viscosity of slag increases, the oxygen ion transports more difficult.

Figure 6 shows the variation of the DC field in the reaction process. It can be seen that the voltage is relatively stable in the process except for the fluctuation due to the slag flow. The system temperature decreases, the viscosity becomes higher and the resistance of the slag increases. All these lead to the reduction of the current. At the same time, the oxygen ion current decreases while the oxygen content of the steel and the oxygen ion transportation decrease during the process. Finally the system current also reduces.

5. Conclusions

- Unpolluted deoxidization can be carried out by applying a DC field between the steel and slag interface. The oxygen content in the molten steel can be decreased from 868×10^{-6} to 642×10^{-6} in 20 mins on the condition of voltage is 3–5 V, current is 50–80 A. The deoxidization rate reaches to 11.3×10^{-6}-min^{-1} and the initial ratio is higher than that of terminal one.
- Without DC field, oxygen ion must be transported into the steel due to the high oxidizability of the slag. The balance of the electric field between the steel and slag can be broken by the immersed electrode and the transfer rate of the oxygen ion can be restricted.
- The oxygen ion current can be improved by increasing both of the mass transfer coefficient and the reaction area between the steel and slag, and the deoxidization rate can be improved by optimizing the kinetic conditions.

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