

Electrochemical Characteristic of Decarburization Reaction

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Abstract: The electrochemical mechanism of the reaction between Fe-C melts and CaO-SiO₂-Al₂O₃-FeO_x slag systems has been carried out. The experimental results suggest that the final content of carbon in melt increases as the partial oxygen pressure of gas decreases no matter whether there is electronic conductor or not. However, the final content of carbon in the system with electronic conductor is much lower than that without electronic conductor. It can be deduced that the transfer ability of oxygen in slag is dominated by electrons. When an electronic conductor exists, an easy pathway for the electrons is provided and the oxygen transfer rate is accelerated.

Key words: melt-slag reaction; decarburization; electrochemistry; electronic conductor

There have been several studies on the investigation of the behaviour of metal droplet with CaO-SiO₂-Al₂O₃-FeO_x slags [1~3]. The important information from these previous investigations is that the reaction is controlled by the transfer of electron in slag. The rate and the extent of reaction could be increased by altering the electrochemical factors of system. However, all of these studies were carried out in closed system, in which it is impossible to provide oxygen from atmosphere for reduction reaction. Therefore, in opening or circulating system, it is believed that oxygen can be enhanced to transport through liquid slag from gas phase to an underlying phase of liquid metal and the rates of reduction reaction will also be increased by connecting the two phases with electronic conductor. The objective of the present work is to examine the electrochemical mechanism of reduction of the melt with slags.

1 Experimental

A schematic diagram of the experimental apparatus is shown in **figure 1**.

An Al₂O₃ crucible was used to hold the metals that contain different contents of carbon and was placed at a constant temperature zone. The furnace was purged with argon during metal melting. As the temperature was heated to the level of experimental temperature, the prefabricated slag was charged into the alumina crucible. The method for preparing slag has been reported elsewhere [4]. $w(\text{CaO}) : w(\text{SiO}_2) : w(\text{Al}_2\text{O}_3)$ (w stands for mass fraction) in all the slags used in the

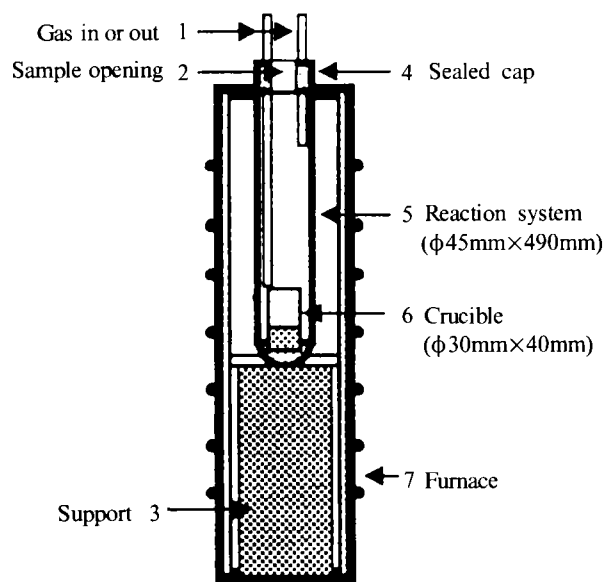


Figure 1 Diagram of experimental apparatus for circulating reaction system

experiments was 50:40:10, and the concentration of FeO_x in slag was determined in experimental condition. The slag could be melted in quite a short time (about 1 min) because of the large amount of metal melts.

The mixture of argon and air was driven through the reaction system. While keeping the flow of air constant, the partial oxygen pressure of the system was controlled by adjusting the flow of argon. After the first metal sample had been obtained, the subsequent samples were taken at predetermined time inter-

vals. By analyzing the variation of the carbon content with time of metal samples, the reaction process can be recorded. Taking sample will not affect the experiment because of the small weight of the sample.

The experimental installation for the reaction with electronic conductor is nearly the same as that without electronic conductor, the only change is that one electrode (electronic conductor) is placed in the system to short-circuit the gas / slag and slag / metal interfaces.

The initial attempt to use metal Mo thread connecting metal and slag failed because the Mo thread dissolved in Fe-C melt during the experimental process. However, molybdenum ceramic was found the satisfactory electrode material. The molybdenum ceramic was made by heating 50 mm×10 mm×5 mm strips which were squeezed with 50% ZrO₂ + 50% Mo powder under the deoxidizing gas at 1600 °C for 2 h. It was found that the molybdenum ceramic was not attacked by metal melts and / or slags.

2 Results and Discussions

2.1 Effect of temperature and concentration of FeO

In the opening system (the oxygen partial pressure was 21273 Pa), the curves for the reactions of Fe-C melt containing 3.2% carbon with slags having 8.17% FeO at different temperatures and with various concentrations of FeO in the slag at 1500 °C are shown in figure 2 and figure 3 respectively.

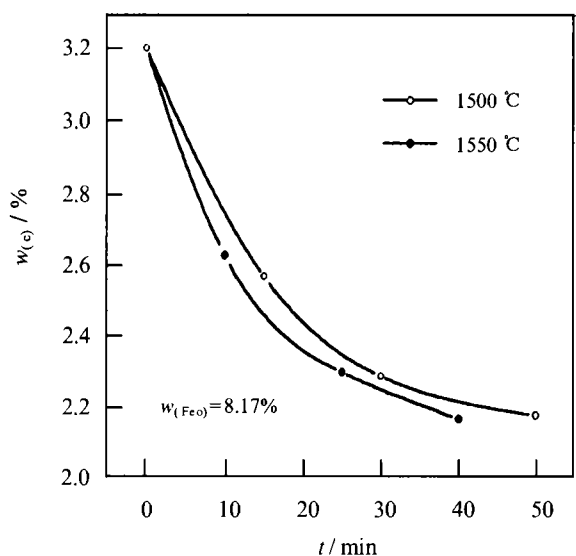


Figure 2 Relations of the carbon content in melts with reaction time for different temperatures

Figure 2 shows that the rates of reaction increased slightly as temperature rose and the temperature had little effect on the reaction. In figure 3, it is shown that the rates of reaction and the final carbon in melt

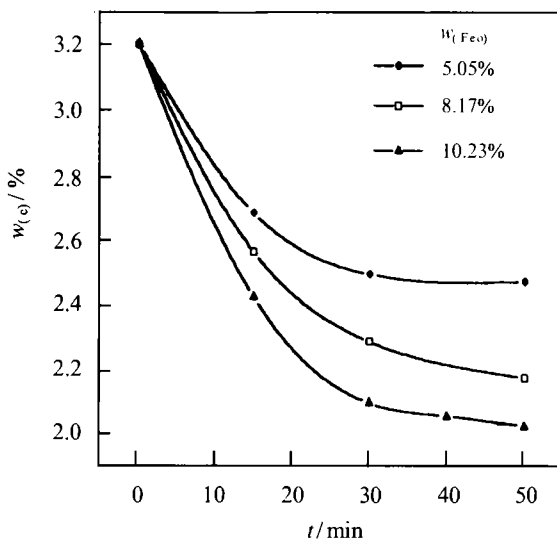


Figure 3 Relations of the carbon content in melt with reaction time for different content of FeO in slag

changed appreciably as the content of FeO in slag changed. The effect of temperature and the content of FeO on reaction is different. It has been reported in reference [5] that the permeability and diffusion coefficients of oxygen were $3 \times 10^{-8} \sim 3 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ and $1 \times 10^{-5} \sim 1 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$ respectively in the experimental slag system. The effect of the content of slag was more prominent than that of temperature on the permeability and diffusion coefficients of oxygen. The experimental results have proved this viewpoint.

2.2 Effect of oxygen partial pressure and electronic electrode

As mentioned above, the objective of the present work is to examine the electrochemical mechanism of the reaction of melt with slags. Therefore, the reactions in different flows of argon under the condition of with or without electronic conductor were carried out. The reaction curves are shown in figure 4. From

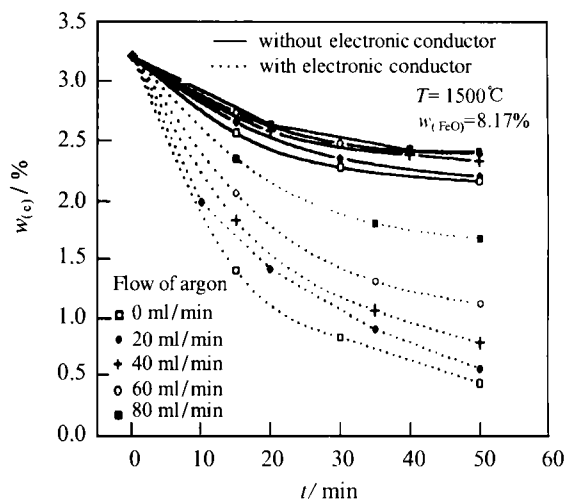


Figure 4 Relations between the carbon content and reaction time in different flows of Ar under the condition of with or without electronic conductor

figure 4 it is clearly seen that the rates and the extent of reaction can be influenced distinctly as electronic conductor exists.

The rates of reaction and the mass fraction of carbon w_c (final) in melt at different Ar flows are listed in table 1.

Table 1 Rates of reaction and the w_c (final) in melt

Flows of argon/ $\text{ml} \cdot \text{min}^{-1}$	Without electronic conductor		With electronic conductor	
	w_c (final)/%	Decarburization rate/ $\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$	w_c (final)/%	Decarburization rate/ $\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$
0	2.18	0.089	0.47	0.25
20	2.22	0.073	0.59	0.23
40	2.35	0.068	0.81	0.19
60	2.41	0.061	1.14	0.15
80	2.43	0.060	1.70	0.11

Note: $T=1500^\circ\text{C}$, $w_{(\text{FeO})}=8.17\%$, $t_{\text{total}}=50$ min.

The experimental results suggest that the rates of the system with electrode are 2 ~ 3 times greater than that of the system without electrode. Another conclusion is that the rate of reaction has been affected little by varying the oxygen partial pressure only. Based on the results of studies [1~3], the advantage of electrochemistry nature of melt-slag reaction should be taken to increase the reaction rate.

As expected, increasing the contact area of electrode with the reaction system allowed more paths for oxygen to transfer resulting in an improvement of reaction rate.

At 1550°C in the air, the curves for slag in which $w_{(\text{FeO})}=8.17\%$ reacting with Fe-C melt in which $w_{(\text{C})}=3.2\%$ as the numbers of electronic conductor changed are shown in figure 5.

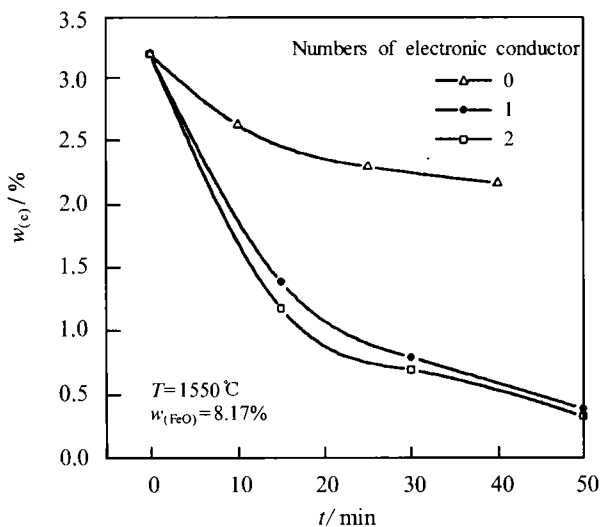


Figure 5 The content of carbon as function of time for experiments using different numbers of electronic conductor

Based on the experimental data, it was clearly seen that in the opening system, the final content of carbon in melt increased as the partial oxygen pressure of gas decreased no matter whether there was electronic conductor or not. However, the final content of carbon in the system with electronic conductor was much lower than that without electronic conductor.

It was the opinion of several investigators [6] that the transfer of oxygen was accomplished by oxidizing FeO in slag. In steelmaking process, the oxygen partial pressure or the content of FeO in slag must be increased to enhance the transfer ability of oxygen in slag, which would lead to a lot of wasting.

An illustrated summary of the transfer process for oxygen at gas / slag and slag / metal melt interface as electronic conductor existed is given in figure 6.

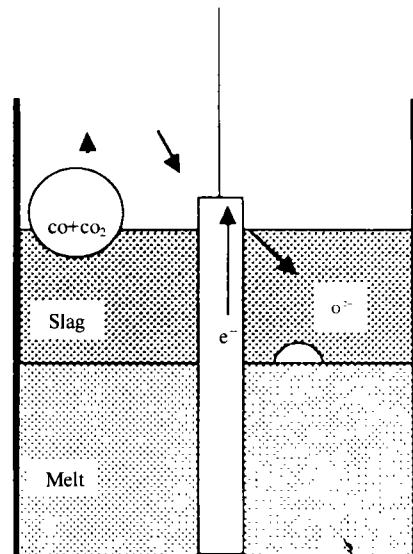


Figure 6 Schematic illustration of the oxygen transfer mechanism with electronic conductor in opening reaction system

At gas / slag interface:



At slag / metal melt interface:



In oxygen atmosphere:



In this process, the oxygen ions moving from the gas / slag interface to slag / metal melt interface were accompanied by electrons immigrating in the opposite direction through the electronic conductor.

The oxygen anions react with the carbon in melt to form carbon monoxide (or carbon dioxide, depending on the oxygen partial pressure) with the liberation of electrons. The carbon monoxide oxidizes in the oxygen-rich atmosphere to form carbon dioxide after percolating through the slag. So, the mass transfer of the oxygen anions is controlled by the conduction of electrons. The presence of electronic conductor provides an easy pathway for the electrons and the oxygen transfer rate is accelerated. In addition, increasing the perimeter of electrode or numbers of electrode also improve the oxygen transfer rate.

Based on the above analysis, the technique for increasing the electronic conduction of slag would enhance the oxygen transfer rate. This kind of method can be extended to steelmaking process, for example, the material with high electronic conduction can be used as the interior of converter and it is possible to increase the oxidizing rate and shorten the reaction time.

3 Conclusions

(1) In the opening system, the final content of carbon in melts increases as the partial oxygen pressure of gas decreases no matter whether there is electronic conductor or not. However, the final content of carbon in the system with electronic conductor is much lower than that without electronic conductor. The rates of the system with electrode were 2 ~ 3 times greater than that of the system without electrode.

(2) The transfer of oxygen is controlled by the conduction of electrons in slag. The presence of electronic conductor provides an easy pathway for electrons and the oxygen transfer rate is accelerated. In addition, increasing the perimeter of electrode or numbers of electrode also improve the oxygen transfer rate.

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