FEASIBILITY STUDY ON HIGH TEMPERATURE ELECTROLYTIC DESULFURIZATION IN HOT METAL PRETREATMENT

Hot metal pretreatment desulfurization is an important way in metallurgical industry, and Mg as a desulfurizer is widely used in the steel industry. In this paper, magnesite based desulfurizer that the ratio is 63 % MgF_2, 12 % CaF_2, 18 % NaF and 7 % MgO is used and at the molten iron temperature, magnesite based desulfurizer molten salt system is electrolyzed and the counter electromotive force and cell voltage is measured. The results of X-ray diffration(XRD) analysis of the desulfurization reaction products show that the counter electromotive force and the cell voltage of the magnesite desulfurizer is linear with current; MgO is electrolyzed and generated Mg, but other substances are not electrolyzed; The generated Mg is successfully desulfurized. All those indicated that it is feasible for magnesite based desulfurizer electrolytic desulfurization at the temperature of molten iron.

Key words: magnesite , desulfurization, high temperature , electrolytic process , X-ray diffration (XRD)

INTRODUCTION

Hot metal pretreatment desulfurization is an important way in the metallurgical industry, and Mg as a desulfurizer favored by the majority of iron and steel enterprises [1]. However, electrolyzes magnesium oxide to produce magnesium and magnesium passivation are high cost, furthermore, the utilization of magnesium is also low at present [2]. Therefore, developing an energy-saving, environmentally friendly and efficient desulfurizer is very important [3]. At present, some iron and steel enterprises carry out pretreatment desulfurization process by the method of blowing magnesium based desulfurizer [4], which is the mixture of passivated magnesium granules and CaO, CaC_2 and so on [5]. Magnesite is an important material for the production of magnesium elemental, and this provides an feasibility for the hot metal pretreatment desulfurization [6].

ELECTROCHEMICAL THEORY BASIS of MAGNESITE BASED DESULFURIZER

In this paper, magnesite based desulfurizer is used as the material, and electrolysis desulfurization reaction is carried out at the **hot metal** temperature. In the process of electrolyzing magnesite based desulfurizer, the characteristics of counter electromotive force are studied mainly. When the electrolytic cell voltage is greater than the theoretical decomposition voltage, the magnesite based desulfurizer electrolysis reaction occurs[7].

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And the theoretical decomposition voltage is the minimum voltage value that allows the products to be generated at the cathode and anode, and it is equal to the potential difference between the anode and cathode. The formula is (1).

$$E_T^\theta = \varphi^{\theta+} - \varphi^{\theta-} \qquad (1)$$

In the above formula:
E_T^θ – The theoretical decomposition voltage value / V;
$\varphi^{\theta+}$ – Anode potential / V;
$\varphi^{\theta-}$ – Cathode potential / V;

Because the electric energy that material decomposition required is equal to the difference of Gibbs free energy, so we can get the formula of theoretical decomposition voltage. It is showed in formula (2).

$$G_T^\theta = -E_T^\theta nF \qquad (2)$$

$$E_T^\theta = -\Delta G_T / nF \qquad (3)$$

So:

$$\Delta G_T = \Delta G_T^\theta + RT \ln \frac{\alpha_{\text{product}}}{\alpha_{\text{the original content}}} \qquad (4)$$

In the above formula:
ΔG_T – The change value of free enthalpy when the compound generated;
G_T – The change value of free enthalpy at constant pressure;
α – Substance activity;
R – Avogadro constant, 8.314 J/mol·K;
F – Faraday constant,96500.

When the substance activity is approximately 1, we can get the formula $\Delta G_T = \Delta G_T^\theta$ and formula (5)

$$E_T^\theta = -\frac{\Delta G_T^\theta}{nF} \qquad (5)$$

The counter electromotive force value is equal to the sum of the theoretical decomposition voltage and over-

voltage, and its value not only reflects the over-voltage in the cathode and anode, but also reflects the mass of the electrolyte, composition, pole distance and other information. In the electrolysis process, metal is reduced at the cathode and the voltage at this time is actual voltage, which also known as counter electromotive force. If the voltage applied to the electrolytic cell is less than the counter electromotive force, the entire electrolytic cell output voltage. So, the counter electromotive force can be expressed as the formula (6).

$$E_2 = E_T^\theta + \eta_a + \eta_c \qquad (6)$$

In the above formula:

E_2 – The counter electromotive force / V;

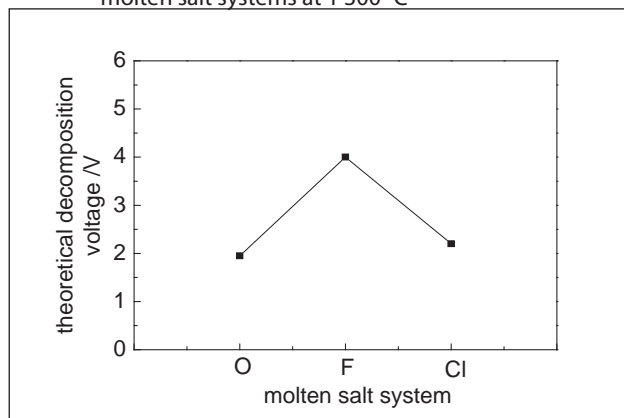E_T^θ – Theoretical decomposition voltage / V;

η_a, η_c – Over-voltage of cathode and anode / V;

The magnesite based desulfurizer contains sodium fluoride, magnesium fluoride, calcium fluoride and magnesium oxide. The theoretical decomposition voltage of fluoride at the molten iron temperature are shown in Figure 1 and Figure 2.

As can be seen from Figure 1, in the fluoride system, the electronegativity of calcium ions and sodium ions is relatively large, and the theoretical decomposition voltage of magnesium ions is lower than that of calcium ions and sodium ions. Therefore, the electrolysis of magnesium fluoride takes precedence over calcium fluoride and sodium fluoride. As can be seen from Figure
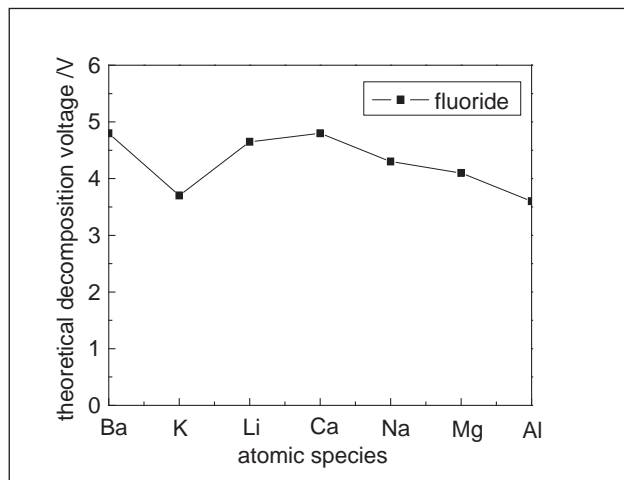
Figure 1 The theoretical decomposition voltage of different molten salt systems at 1 300 °C

Figure 2 The theoretical decomposition voltage of magnesium ions at 1 300 °C

2, the theoretical decomposition voltage of oxide molten salt system is lower than that of fluoride molten salt system. In summary, the electrolysis of magnesium oxide priors to other substances. In addition, because the desulfurizer contains only magnesium oxide, so it is magnesium oxide electrolyzed before the anode effect[8] occurs. After the anode effect happened, the fluoride system begins to be electrolyzed. In this study process, the critical current density at which the anode effect occurs be measured firstly, and then let the current density below this value in the whole experiment[9] to ensure that magnesium oxide is electrolyzed but fluoride is not electrolyzed. The counter electromotive force that critical current density corresponded is equal to the actual decomposition voltage.

EXPERIMENTAL PART
Experimental reagents and devices

In order to ensure the accuracy of the experimental results, all are analytic reagents. The experimental reagents are shown in Table 1.

Table 1 **Experimental reagents**

Name	Specifications	Manufacturer
MgO	Analytic Reagents	Disney's Aladdin
MgF$_2$	Analytic Reagents	Mclean
CaF$_2$	Analytic Reagents	Chinese Medicine Reagent
NaF	Analytic Reagents	Chinese Medicine Reagent

The experimental device includes the molten salt electrolysis equipment and monitoring equipment. The monitoring equipment uses method of continuous pulse computer. When the single-phase alternating current is rectified, the computer shows a periodic half-sine wave and its minimum value is the actual decomposition voltage.

The process of magnesite based desulfurizer electrolytic experiment

The magnesite based desulfurizer used in this experiment is the mixture of MgF$_2$, CaF$_2$, NaF and MgO. The four components are ground and placed into the hot air oven of 3 00 °C for two hours. Then, compound the desulfurizer according to the percentage of mass. Their proportions are MgF$_2$ is 63 %, CaF$_2$ is 12 %, NaF is 18 % and MgO is 7 %, and the total mass is 200 g.

Firstly, the desulfurizer is mixed and placed into the corundum crucible.Secondly, put the corundum crucible into the high temperature furnace and open its heating program. Finally, set the heating rate is less than or equal to 5 °C/min. The furnace is heated gradually to 1 300 °C and keep the temperature constant. Set the heating time is two hours. In the condition of no pig iron is added, tested the counter electromotive force and the cell voltage of the magnesite based desulfurizer using the desulfurization experimental device.
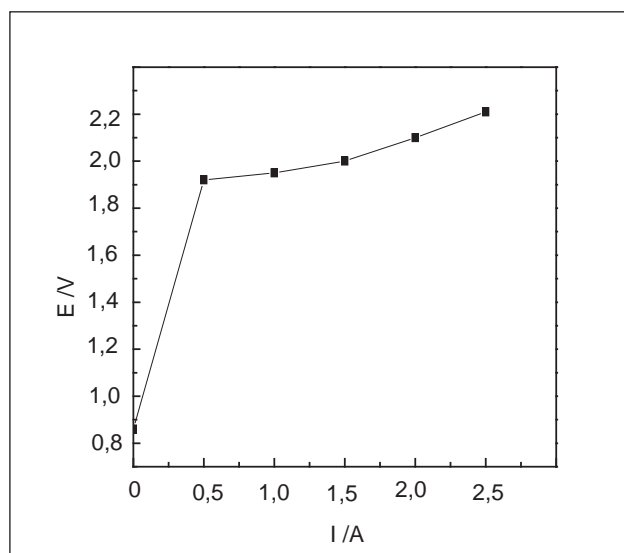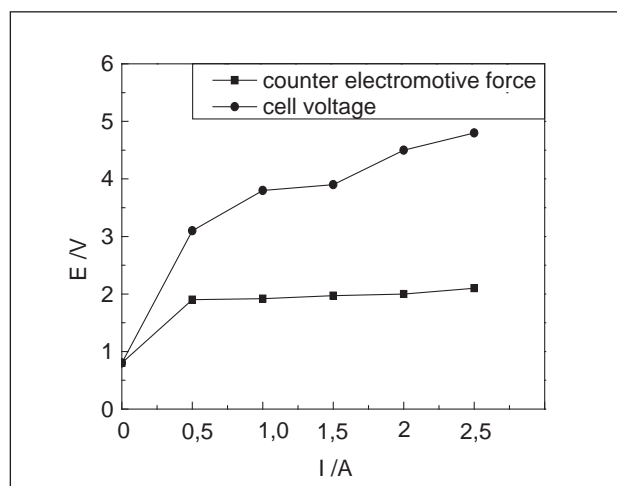
Figure 3 The curve of counter electromotive force changed with current intensity
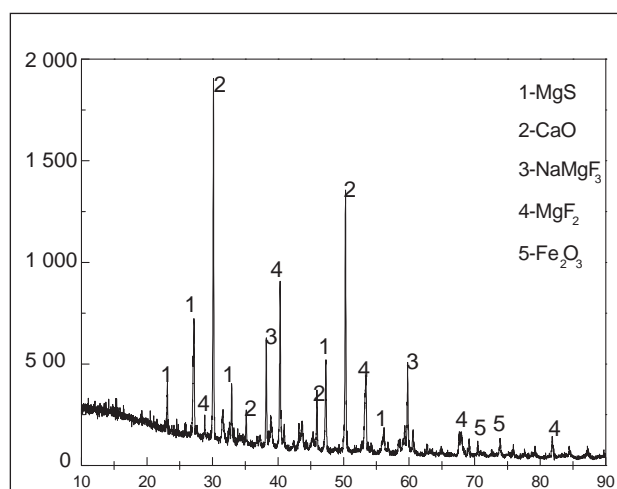

Figure 4 The curves of counter electromotive force and cell voltage changed with current intensity

Figure 5 X-ray diffraction diagrams

The results of magnesite based desulfurizer electrolytic experiment

The counter electromotive force and cell voltage of magnesite based desulfurizer are measured under the conditions of temperature is 1 300 °C and anode surface area is 10 cm^2 and without pig iron is added. Changing the current every 0,5A. The results are shown in Figure 3 and Figure 4.

As can be seen from Figure 3, when the current changes from 0,5 A to 2,5 A, the counter electromotive force changes from 1,93 V to 2,27 V, and its value is greater than the theoretical decomposition voltage value but less than that of magnesium fluoride. When the current is 2,5 A, the anode effect occurs, and the corresponding critical current density is 0,25 A/cm^2. Therefore, the current be controlled below 2,5 A and the actual decomposition voltage of magnesium oxide at this time is 2,27 V. As can be seen from Figure 4, both the cell voltage and the counter electromotive force increase with the increase of current intensity. When the current intensity changes from 0A to 2,5 A, the cell voltage changes from 0,86 V to 5,0 V, and the counter electromotive force from 0,86 V to 2,27 V. This indicates that only magnesium oxide is electrolyzed before the anode effect occurs at the molten iron temperature. From the formula (5) can we know that the theoretical decomposition voltage doesn't change with the current intensity at a certain temperature, so when the current changes from 0,5 A to 2,5 A, Mg^{2+} across the double layer and separates out on the cathode. Then Mg^{2+} reacted with (S) in the molten steel and finally formed MgS. In the anode, the oxygen-containing complex ions reacted at the anode surface. It lost the electrons to produce carbon dioxide and then the carbon dioxide leaved the anode. When a large amount of carbon dioxide is aggregated, they overflow the electrolyte in the form of bubble. When the current increases, the current density increases, and the anode polarization voltage increases.

Therefore, when the current changes from 0 A to 2,5 A, the change of counter electromotive force is mainly caused by the increase of anode polarization voltage.

The products of magnesite based desulfurizer are detected by XRD and the results are shown in Figure 5.

As can be seen from Figure 5, only MgS is included in the generated sulfide, which indicates that MgO is successfully electrolyzed and the generated Mg achieved the effect of desulfurization. However, the other substances in the magnesite based desulfurizer are not electrolyzed.

CONCLUSION

(1) When the magnesite based desulfurizer is melted, metal compounds distributed in the crucible in the form of ions and the ions generated the complex ions, which reduced the melting point of MgO. And this provides the conditions for electrolysis of MgO at the molten iron temperature.

(2) With the increase of the current intensity, the counter electromotive force and the cell voltage increase linearly. When the current intensity increases from 0

A to 2,5 A, the counter electromotive force increases from 0,86 V to 2,27 V.

(3) In the electrolysis process, the anode current occurs when the current is 2,5 A, and the corresponding current density is 0,25 A / cm^2, and the actual decomposition voltage is 2,27 V.

(4) In the electrolysis system of magnesite based desulfurizer, MgO is successfully electrolyzed and the generated Mg achieved the effect of desulfurization but other substances in the magnesite based desulfurizer are not electrolyzed.

Acknowledgments

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