In-situ Synthesis of an Auxiliary Electrode of Solid Electrochemical Sulfur Sensor by CaAl$_4$O$_7$ Coating

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A novel auxiliary electrode CaAl$_4$O$_7$+Al$_2$O$_3$+CaS used for solid electrochemical sulfur sensor, was synthesized by the in-situ reaction of CaAl$_4$O$_7$ coating on the surface of the ZrO$_2$(MgO) electrolyte tube by: CaAl$_4$O$_7$+[S]=CaS+2Al$_2$O$_3$+[O]. The CaAl$_4$O$_7$ coating was synthesized using aluminum nitrate solution and calcium hydroxide solution as raw materials and then was fabricated on the surface of the ZrO$_2$(MgO) electrolyte tube using solid sintering technology at 1500 °C. The microstructure of the coating was dense and well combined with the ZrO$_2$(MgO) electrolyte. The solid electrochemical sulfur sensor Fe[[S]$_{Fe}$][CaAl$_4$O$_7$]ZrO$_2$(MgO)|Cr+$Cr_2$O$_3$|Mo was assembled and tested in the carbon-saturated molten iron at 1500 °C. The results showed that the sensor had a good stability and accuracy, and the CaAl$_4$O$_7$ coating was converted to CaAl$_4$O$_7$+Al$_2$O$_3$+CaS when the sulfur sensor was inserted into the molten iron. The phase composition and microstructure of the synthetized auxiliary electrode were investigated after the sulfur sensor was tested, indicating that the auxiliary electrode coating with a thickness of 40-50 μm was synthetized. The empirical formula of the sulfur sensor was obtained as follows:

$$E(\text{mV}) = 45.891n[\text{wt}\% \text{S}] + 24.39$$

Keywords: Coating; Auxiliary electrode; Sulfur sensor; Solid electrolyte; In-situ synthesis

1. INTRODUCTION

Sulfur is a deleterious element for the iron and steel. In order to remove the sulfur element from the iron and steel, some techniques have been adopted such as hot metal desulphurization and secondary refining. For better understanding the desulfurization process, it is necessary to monitor the sulfur content and its change in this process. Using a solid electrochemical sulfur sensor is considered to be an effective method for quickly and simply measuring the sulfur content in the molten iron and steel.
In recent years, the sulfur sensor with an auxiliary electrode was developed and applied to measure the sulfur content in the molten iron and steel [1-5]. The auxiliary electrode comprised of sulfides was coated on the surface of the oxide electrolyte uniformly, and the sulfur sensor could be assembled as follows by using the auxiliary electrode.

\[
\text{lead 1}[[S]_n|B_{m}S_n|\text{Oxide electrolyte}|M+M_xO|\text{lead 2}} (1)
\]

where \([S]_n\) is the sulfur content in the molten iron and steel, \(B_{m}S_n\) is the sulfide which is the coating of the auxiliary electrode on the surface of the oxide electrolyte, and \(M+M_xO\) is the reference electrode composed of metal M and its oxide.

The \(\text{ZrO}_2(\text{MgO})\) is often used as the oxide electrolyte for the sulfur sensor due to its excellent ionic conductivity and high temperature stability. The sulfide coating has mainly included \(\text{ZrS}_2\), \(\text{CaS}\) and \(\text{MgS}\) [4, 5], which have been prepared by the sintering, plasma spraying, flame spraying, screen printing and laser cladding. The sulfide coatings could satisfy the requirements in terms of ionic conductivity and high temperature properties. However, there were some disadvantages such as difficult to sinter and easy to oxidize, which will seriously affect the stability of the auxiliary electrode.

For resolving the above problems, the \(\text{CaAl}_4\text{O}_7\) was synthetized and fabricated on the surface of the \(\text{ZrO}_2(\text{MgO})\) electrolyte tube as the electrode coating. A novel auxiliary electrode comprised of \(\text{CaAl}_4\text{O}_7+\text{Al}_2\text{O}_3+\text{CaS}\) compound was synthesized on the surface of \(\text{ZrO}_2(\text{MgO})\) electrolyte tube by in-situ reaction of the \(\text{CaAl}_4\text{O}_7\) coating \(\text{CaAl}_4\text{O}_7+[S]=\text{CaS}+2\text{Al}_2\text{O}_3+[O]\) during the sulfur measurement and the synthesized compound could play the same role as that of the sulfide coating in the traditional auxiliary electrode.

2. EXPERIMENTAL

2.1 Synthesis of \(\text{CaAl}_4\text{O}_7\)

Calcium aluminates have been synthetized by co-precipitation technology in the past studies [6-8]. On the basis of this, \(\text{CaAl}_4\text{O}_7\) used as the coating material in this study was synthesized by the same method. Aluminum nitrate solution and calcium hydroxide solution were used as the raw materials. The mixed solution with a proportion of \(X_{\text{Al}^3+/X_{\text{Ca}^{2+}}}=4.1\) was prepared using the above two solutions based on the phase diagram of \(\text{CaO-Al}_2\text{O}_3\) [9-11], and then the pH value of the mixture solution was adjusted by adding the ammonia to get the precipitation. Filtrating and drying the precipitate to obtain powder and then sintered it at 1000 °C to form \(\text{CaAl}_4\text{O}_7\).

2.2 Fabrication of coating

The \(\text{CaAl}_4\text{O}_7\) coating was fabricated on the surface of the \(\text{ZrO}_2(\text{MgO})\) tube by solid sintering technology. The surface of the \(\text{ZrO}_2(\text{MgO})\) tube was first treated by 40% of hydrofluoric acid first, and then the \(\text{CaAl}_4\text{O}_7\) added with epoxy resin and curing agent was coated on the surface of the above \(\text{ZrO}_2(\text{MgO})\) tube. After dried at 150 °C for 4 hours, the \(\text{ZrO}_2(\text{MgO})\) tube coated with the \(\text{CaAl}_4\text{O}_7\) was sintered at 1500 °C for better adhesion.
2.3 Assembly and test of the sulfur sensor

The (Cr+Cr₂O₃) mixture was used as the reference electrode material and filled in the above ZrO₂(MgO) tube. The Mo wire was embedded inside the reference electrode mixture as the electrode lead and the high alumina cement was used to seal the tube. The counter electrode was the molten iron that was electrically connected by Fe bar embedded inside a quartz tube.

After assembly, the sulfur sensor was used to measure the sulfur content in the carbon-saturated molten iron at 1500 °C and formed a concentration cell as follows.

\[ \text{Fe}[\text{S}]_{\text{Fe}}|\text{CaAl}_4\text{O}_7|\text{ZrO}_2(\text{MgO})|\text{Cr}+\text{Cr}_2\text{O}_3|\text{Mo} \] (2)

About 1.0 kg of industrial pure iron was melted in a graphite crucible to make the carbon-saturated molten iron in a MoSi₂ furnace at 1500 °C. A stable flow of highly purified argon (99.99%) was used as shielding gas. Iron sulfide was used to adjust the sulfur content in the molten iron.

2.4 Analysis and detection

The phase composition of the synthesized powder was analyzed by using X-ray diffraction (XRD). The microstructure of the coating was observed by using field emission scanning electron microscopy (FESEM), the distribution of element was analyzed with energy dispersive spectrum analysis (EDS).

For the test of the sulfur sensor, when the sulfur sensor was inserted into the molten iron, the electromotive force (EMF) was measured with Keithley Model 2450 Source Meter®. The metal specimens were taken with a quartz tube for chemical analysis before each measurement. After the test, the phase composition and microstructure of the synthesized auxiliary electrode on the surface of the solid electrolyte was detected using X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), the distribution of element was analyzed with energy dispersive spectrum analysis (EDS).

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction of the synthesized powder. From Fig. 1, it could be clearly seen that the phase composition of synthesized powder was entirely CaAl₄O₇ phase as compared with the calcium dialuminate standard (JCPDS card no. 00-023-1037). The CaAl₄O₇ was chosen as the coating material because the CaAl₄O₇ showed a strong ability to chemically react with dissolved sulfur in the molten iron and steel and was a solid phase under the operation condition of the sulfur sensor [9, 12-15].

Fig. 2 presents the SEM micrograph of the cross-section of the fabricated coating on the surface of the ZrO₂(MgO) solid electrolyte and the EDS microanalysis for two different locations on the micrograph. From the SEM micrograph, it could be clearly seen the grain sizes of the coating are
bigger than the electrolyte substrate and its crystalline grain was uniform. The EDS analysis of the prepared coating (location 2) was presented the stoichiometric composition near to ZrO$_2$+CaAl$_4$O$_7$, with the thickness of about 50-60 μm, and well combined with the ZrO$_2$(MgO) solid electrolyte because of the inter diffusion of elements through the interface as shown in the EDS result of Fig. 2. It should be noted that the fabricated coating was not the auxiliary electrode for the prepared sulfur sensor. The basic requirement of the auxiliary electrode was that it must contain elements to be measured [16]. For sulfur sensors, the auxiliary electrode should be sulfide. Thus, the fabricated coating was used as a medium for synthesizing the sulfide auxiliary electrodes in situ at high temperature.

Figure 1. X-ray diffraction of the synthesized CaAl$_4$O$_7$ powder

Figure 2. EDS analysis of the coated sample (2)
**Figure 2.** SEM micrograph of the cross-section of the fabricated coating on the surface of the ZrO$_2$(MgO) solid electrolyte and the EDS microanalysis of two different locations

**Figure 3.** SEM images of the surface of the (a) ZrO$_2$(MgO) solid electrolyte and (b) fabricated coating.

Fig. 3 shows the SEM images of the surfaces of the ZrO$_2$(MgO) solid electrolyte and fabricated coating. As seen in Fig. 3b, it was known that the crystal of the surface of the fabricated coating developed well without crack. Contrast Fig. 3a with Fig. 3b, the crystal grain of coating was in the form of flake or other irregular shapes different from ball structure of electrolyte substance, and the grain size was bigger than the electrolyte substrate. It indicated that the more dense surface of the fabricated coating could present the high bond strength. The results matched with the above analysis of the cross-section of the coating.

**Figure 4.** (a) Typical responses of the sulfur sensor and (b) relationship between sensor EMF and sulfur content in the molten iron at 1500 °C.

Fig. 4 shows the response of the sulfur sensor and the relationship between the sensor EMF and sulfur content in the carbon-saturated molten iron at 1500 °C.

Fig. 4a shows typical responses of the sulfur sensor at a contents of 0.022 and 0.035 wt%S in the carbon-saturated molten iron at 1500 °C. As seen in Fig. 4a, it could be understood that the response time of the sulfur sensor was about 10 seconds, and the signal platform was stable and could
continue more than 40 seconds. Compared with the previous sulfur [1-5, 17], this sulfur sensor still showed great superiority in the response time and signal platform. In the Fig. 4a, the red line and the blue line all correspond to the response of the sulfur sensor at the 0.022 wt%S content in the molten iron, the signal platforms from them were almost overlapped, it meant that the EMF of the sulfur sensor remained nearly constant in the same sulfur content of the molten iron. From the comparison of the blue line of 0.022 wt%S content and the black line of 0.035 wt%S content, the EMF changed obviously with the changes of sulfur content in the molten iron. This indicated that the sulfur sensor showed a good stability and accuracy in the measurement. It is important to point out that the prepared sulfur sensors took longer time to obtain a stable EMF than commercial oxygen sensors applied in steelmaking due to the fact that the CaAl$_4$O$_7$ coating had to in-situ synthesize the auxiliary electrode and come to equilibrium with the sulfur in molten iron, a species not present in the electrolyte.

Fig. 4b shows the relationship between the sensor EMF and sulfur content in the molten iron, where the EMF of the sensor is plotted against sulfur content acquired via chemical analysis, and the solid line represents the regression curve. As seen in Fig. 4b, the relationship between EMF and ln[w t% S] was linear, the sulfur sensor was very sensitive to the variation of the sulfur content and the accuracy was satisfactory. The measurement results had strong regularity and the points with larger measurement deviations did not appeared compared the previous sulfur sensor. That was because that the coating was not easy to fall off from the surface of the solid electrolyte, and the sulfide auxiliary electrode was synthesized in situ in the molten iron, greatly reducing the possibility of being oxidized. The EMF of the sulfur sensor could be expressed as the following empirical equation.

$$ E(\text{mV}) = 45.89 \ln[\text{wt}\% \text{S}] + 24.39 \quad R = 0.99 $$

Using the above equation, the sulfur content of the molten iron could be easily obtained by the EMF of the sulfur sensor.

![XRD pattern of the auxiliary electrode after the test of the sulfur sensor](image)

**Figure 5.** XRD pattern of the auxiliary electrode after the test of the sulfur sensor
Fig. 5 shows the XRD pattern of the synthesized auxiliary electrode on the surface of the ZrO$_2$(MgO) electrolyte after the test of the sulfur sensor. It could be learnt from the pattern that the auxiliary electrode was comprised of CaAl$_4$O$_7$, Al$_2$O$_3$ and CaS. During the measurement, when the prepared sulfur sensor was inserted into the molten iron, the ZrO$_2$(MgO) solid electrolyte tube with the CaAl$_4$O$_7$ coating was firstly contacted with the molten iron and react with sulfur component in the molten iron according to the following equation.

$$\text{CaAl}_4\text{O}_7 + [\text{S}] = \text{CaS} + 2\text{Al}_2\text{O}_3 + [\text{O}] \quad (4)$$

Based on the above reaction, the coating material was changed to the mixture of CaAl$_4$O$_7$, Al$_2$O$_3$ and CaS, which worked as the auxiliary electrode for the sulfur sensor, improving the stability of the sulfur sensor. The existence of iron phase is due to the attachment to the surface of auxiliary electrode during the cooling process of the molten iron, which has no effect on the formation of the auxiliary electrode.

Fig. 6 presents the SEM-EDS analysis of the cross-section of the synthesized auxiliary electrode after the test of the sulfur sensor. As shown in the SEM analysis of Fig. 6, the synthetized auxiliary electrode had the three-layer structure of electrolyte substrate-auxiliary electrode-Fe layer. The middle auxiliary electrode achieved good densification which adhered to the ZrO$_2$(MgO) electrolyte firmly, and its average thickness was about 40-50 μm. From the EDS analysis in Fig. 6, it was clearly that zone 1 showed the analysis of ZrO$_2$(MgO) electrolyte, and the elemental proportion agrees approximately with the original ZrO$_2$(MgO) stoichiometry; zone 2 showed the analysis of the synthesized auxiliary, presenting near stoichiometric composition CaAl$_4$O$_7$+Al$_2$O$_3$+CaS. Zone 3 showed the analysis of Fe attached to the surface of auxiliary electrode during the cooling of the molten iron. As discussed above, the existence of the iron has no effect on the formation of the auxiliary electrode.
Therefore, the sulfur sensor used actually for the measurement was obtained as follows.

\[ \text{Fe}[\text{S}]_2/\text{CaAl}_2\text{O}_7+\text{Al}_2\text{O}_3+\text{CaS}/\text{ZrO}_2(\text{MgO})/\text{Cr}+\text{Cr}_2\text{O}_3]/\text{Mo} \]  

Once the auxiliary electrode of CaAl$_2$O$_7$+Al$_2$O$_3$+CaS was formed, the measurement process would be affected by the reaction (4). Next, the measurement mechanism of the sulfur sensor could be discussed as below.

When the reaction (4) reached thermodynamic equilibrium, the following relation should be established.

\[ K = \frac{a_O a_{\text{Al}_2\text{O}_3} a_{\text{CaS}}}{a_{\text{CaAl}_2\text{O}_7}} \]  

where \( K \) is the equilibrium constant for the reaction (4), \( a_O \) and \( a_S \) are the activities of oxygen and sulfur in the molten iron, respectively, \( a_{\text{CaAl}_2\text{O}_7} \), \( a_{\text{Al}_2\text{O}_3} \) and \( a_{\text{CaS}} \) are the activities of the CaAl$_2$O$_7$, Al$_2$O$_3$ and CaS on the surface of the auxiliary electrode.

Assuming \( a_{[S]}=[\text{wt} \% \text{ S}]f_S \), and taking logarithm for both sides, the equation (6) could be converted as the following form.

\[ \ln[\text{wt} \% \text{ S}] = \ln a_O + \ln \frac{a_{\text{CaAl}_2\text{O}_7}}{a_{\text{CaAl}_2\text{O}_7}} - \ln K - \ln f_S \]  

\( \ln a_O \) could be expressed as a function related to \( E \) and \( T \), namely, \( \ln a_O = f(E, T) \). Therefore, the relation between the \( \ln[\text{wt} \% \text{ S}] \), \( E \) and \( T \) which would be measured by the sulfur sensor is given as the following equation.

\[ \ln[\text{wt} \% \text{ S}] = f(E, T) + \ln \frac{a_{\text{CaAl}_2\text{O}_7}}{a_{\text{CaAl}_2\text{O}_7}} - \ln K - \ln f_S \]  

In the general case, the sulfur content in the molten iron is far less than 1%, which could be regarded as a dilute solution and the activity coefficient \( f_S \) could also be assumed to be a constant. In addition, under the measuring condition, the equilibrium between the anions in the auxiliary electrode could be established, the sulfur and oxygen activity at the phase boundary of the molten iron and the auxiliary electrode depends on the above equilibrium. Meanwhile, the oxygen activity is also controlled by the reference electrode (Cr+Cr$_2$O$_3$). That means that the value of \( \ln \frac{a_{\text{CaS}}a_{\text{Al}_2\text{O}_3}}{a_{\text{CaAl}_2\text{O}_7}} \) does not change with the sulfur content and it can be considered to be a constant value. Therefore, the sulfur content in the molten iron could be expressed as follows.

\[ \ln[\text{wt} \% \text{ S}] = f(E, T) \]  

where \( E \) is the EMF of the sulfur sensor (V), \( T \) is the temperature of the molten iron (K). It should be noted that the experimental temperature in this study was fixed, 1500 °C, the effect of temperature on the sulfur would be discussed in next study. Therefore, the equation (9) could be expressed as follows used in this study.

\[ \ln[\text{wt} \% \text{ S}] = f(E) \]  

As discussed above, when the assembled sulfur sensor was applied to measuring the sulfur
content in the molten iron at 1500 °C, the value of the sulfur content could be obtained based on the EMF according to the equation (10) after the sulfur and oxygen reach equilibrium at the phase boundary of the molten iron and auxiliary electrode.

In the past few decades, there have been many investigations regarding the sulfur sensor. Initially, the sulfide electrolytes gained the attention in the fabrication of the sulfur sensor [18-20]. However, sulfide electrolytes have some disadvantages such as being difficult to sinter and easy to oxidize, and these seriously affect the stability of the solid electrolyte. With the advances in science and technology, this problem has been solved with the use of the auxiliary electrode on the surface of the electrolyte with sulfide [1-5]. The sulfide was easy to be oxidized, which made the preparation of the auxiliary electrode difficult and unstable. Thus, a more stable sulfur sensor was still needed. Compared with these previous sulfur sensors that the sulfide auxiliary electrode coated directly on the surface of the electrolyte, the prepared sulfur sensor in this study exhibited great superiority in stability. The prepared sulfur sensor was fabricated by ZrO$_2$(MgO) electrolyte and CaAl$_4$O$_7$ coating without sulfide, eliminating the instability of sulfide. The auxiliary electrode in this paper was synthetized in situ by the CaAl$_4$O$_7$ coating, always located in the interior of molten iron, not be oxidized. Meanwhile, the CaAl$_4$O$_7$ was stable in the air, which was the reason for the sulfur sensor to be kept for a long time.

Fig. 7 showed the changes of EMF with the kept time of the prepared sulfur sensor, where the sensor EMF was observed after the sulfur sensor kept for 7 days, 14 days, 21 days and 28 days. From Fig. 7, it showed little change in the sensor EMF after the sensor was kept for different time, and the sensor exhibited a good reproducibility, the deviation of sulfur sensor is less than 5 mV. It meant that the sulfur sensor prepared in this study had a good stability and accuracy, and the fabricated CaAl$_4$O$_7$ coating could be converted to the auxiliary electrode during the measurement, which made the sulfur and oxygen equilibrium established effectively at the phase boundary of the molten iron and auxiliary electrode to obtain the EMF. The above discussion has also proved that the sulfur sensor fabricated by the solid electrolyte without sulfide was practical.

![Figure 7. Changes of EMF with the kept time of the prepared sulfur sensor](image-url)
4. CONCLUSIONS

A novel auxiliary electrode comprised of CaAl$_4$O$_7$+Al$_2$O$_3$+CaS used for the sulfur sensor was synthesized by in-situ reaction of the CaAl$_4$O$_7$ coating on the surface of the ZrO$_2$(MgO) electrolyte: CaAl$_4$O$_7$+[S]=CaS+2Al$_2$O$_3$+[O], and its measurement mechanism was discussed. The CaAl$_4$O$_7$ coating was fabricated on the surface of the ZrO$_2$(MgO) electrolyte by solid sinter technology, the SEM results showed the coating had a CaAl$_4$O$_7$-rich structure and well combined with the ZrO$_2$(MgO) electrolyte. The solid electrochemical sulfur sensor was assembled and tested successfully in the carbon-saturated molten iron at 1500 °C. The sulfur sensor exhibited good stability and accuracy in the measurement and the empirical formula of the sulfur sensor was obtained as follows.

\[ E(\text{mV}) = 45.89\ln[\text{wt\% S}] + 24.39 \]

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