Measuring the molten layer thickness of mold flux by electrode method

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Abstract. A feasible electrode method of measuring the molten layer thickness of mold flux was proposed to solve the limitations of the existing measuring methods. At first, the relationship between the conductivity and chemical compositions, as well as the temperature of mold flux was analysed theoretically. Then a simple measuring method was developed based on the former theoretical analysis. The measuring results were verified by the traditional method. It was shown that this measuring method was efficient and accurate, which could eliminate the interference of human factors and provide an effective guarantee for the continuous casting process.

1. Introduction
In the continuous casting production process, due to the effect of temperature gradient, the mold flux on the surface of the molten steel is a layered structure in the longitudinal direction. From top to bottom, the particle layer, the sintered layer and the molten layer are formed in sequence [1-6]. The molten layer plays a role of continuously supplying molten flux to the gap between the mold and the slab. During the entire casting process, the mold flux is melted to form a molten layer and flows as a liquid lubricant into the gap between the slab and the mold. Therefore, it is very important to maintain a sufficient thickness of molten layer [7].

The thickness of the molten layer is an important parameter of the properties of mold flux. Measuring the molten layer thickness timely and accurately is of utmost importance. At present, the method for measuring the molten layer thickness generally includes a manual measurement method and an on-line monitoring method. The manual measurement method is the most widely used in major steel plants, but only a rough measurement of the molten layer thickness. And for the slab mold, the molten steel temperature at each point of the section is inconsistent, so the measured molten layer thickness is also different [8]. This method not only increases the labor intensity of the steel-making workers, but also results in inaccurate measurements and large errors due to hand-shaking, mold vibrations, and fluctuations on the liquid level of molten steel. On-line monitoring methods include thermocouple method, ultrasonic method, and electromagnetic induction method. The thermocouple method judges the state of a substance based on the temperature measured by the thermocouple at different positions, and then obtains the thickness of the molten layer and the sintered layer, but the thermocouple protection sleeve is easily broken and causes the damage of the thermocouple.
Ultrasonic and electromagnetic induction methods can only measure the total thickness of mold flux \[8-9\]. In summary, it is necessary to develop a high-precision, low-cost, and new molten layer thickness measuring method.

By analyzing the conductive mechanism of mold flux, the boundary criterion of the conductivity between the unmolten layer and the molten layer, the molten layer and the molten steel was determined in this paper. A simple and feasible method (electrode method) for measuring the molten layer thickness was designed. The traditional method (manual measurement method) was used to verify the relevant results of conductivity method, which provided a new idea for the measurement of the molten layer thickness of mold flux.

2. Conductive mechanism

According to ion theory, melted slag is composed of charged particles (atoms or atom groups), i.e. ions. Some scholars had conducted experiments to prove the presence of ions in the melted slag. The X-ray diffraction structure analysis indicated that the basic constituent units of oxides and other compounds that make up the slag were ions, i.e., charged atoms or atom groups. In addition, powering on the interface between the molten metal and the melted slag, the interfacial tension also changed, which proved that there were ions and electrons been transferred at the interface between the two phases. The melted slag is ionically conductive, which conductivity is lower than that of liquid metal, but higher than that of molecular substances \[10\]. Molten mold flux is a type of melted slag, which is a good ion conductor \[9\]. The physical nature of the conductive phenomenon of mold flux is its ions migrating to the two poles with the action of an external electric field.

Zhang G H et al. \[11\] considered that if the mold flux is regarded as an oxides slag system, the characteristics of the conductivity change in the liquid phase conform to Arrhenius’s law, as in equation (1).

\[
\kappa = Ae^{\frac{B}{RT}} \text{ or } \ln\kappa = \ln A - \frac{B}{RT}
\]

Where: \(\kappa\) is mold flux conductivity, \(\Omega^{-1} \cdot \text{cm}^{-1}\); \(A\) is the experimental constant, \(\Omega^{-1} \cdot \text{cm}^{-1}\); \(R\) is the gas constant, 8.314 J · K\(^{-1}\) · mol\(^{-1}\); \(T\) is the temperature, K; \(B\) is the conductance activation energy, J · mol\(^{-1}\).

In the above formula, the value of conductance activation energy \(B\) is related to the slag composition, which empirical formula is as follows \[11\].

When \(X_{Ca0} > X_{Al2O3}\),

\[
B = m \cdot \frac{1.0(X_{Ca0}-X_{Al2O3})+0.78X_{Mg0}+0.6\times3X_{Al2O3}+0.48\times2X_{SiO2}}{(X_{Ca0}-X_{Al2O3})+X_{Mg0}+3X_{Al2O3}+2X_{SiO2}} + n
\]

When \(X_{Ca0} < X_{Al2O3}\) and \(X_{Ca0} + X_{Mg0} > X_{Al2O3}\),

\[
B = m \cdot \frac{0.78(X_{Ca0}+X_{Mg0}-X_{Al2O3})+0.6\times3X_{Al2O3}+0.48\times2X_{SiO2}}{(X_{Ca0}+X_{Mg0}-X_{Al2O3})+3X_{Al2O3}+2X_{SiO2}} + n
\]

Where \(X_i\) is the molar fraction of component \(i\); \(m\) and \(n\) are both constants, which are -276.838 J · mol\(^{-1}\) and 323.789 J · mol\(^{-1}\), respectively.

From Equation (1) to Equation (3), we can conclude that the Arrhenius law neglects the change of the liquid slag structure with temperature, and considers the conductivity been influenced by the composition and temperature. When the composition of the liquid slag is constant, conductance activation energy \(B\) is a constant value. At this time, the ln \(\kappa\) is linear with 1/T, which slope is -B/R.

3. Experimental method

A certain amount of mold flux sample (two type of slag samples were adopted in this experiment, whose compositions and performances are shown in Table 1) were firstly decarburized and placed in a corundum crucible. And then the corundum crucible was placed in a Si-Mo resistance furnace.
Secondly, two conductivity electrodes were fixed and inserted vertically into the mold flux sample to a position about 10 mm from the bottom of the crucible. The furnace was sealed and a peephole was left. Thirdly, the circuit was connected according to Figure 1, the resistance furnace heating program was booted. Finally, through the digital-to-analog conversion device and the external processor, the relationship between the voltage \( U \) of the two electrodes and the temperature \( T \) was obtained.

### Table 1. Main compositions and performances of mold flux sample for experiments.

| No. | \( \text{Al}_2\text{O}_3\)/% | \( \text{MgO}\)/% | \( \text{Na}_2\text{O}\)/% | \( \text{CaF}_2\)/% | C/\% | \( \text{CaO/\text{SiO}}_2 \) | Melting temp./°C | Melting speed/s | Viscosity/pa•s (1300°C) |
|-----|-----------------|-----------------|-----------------|-----------------|-----|-----------------|-----------------|-----------------|-------------------|
| 1   | 3.20            | 0.60            | 9.70            | 10.20           | 4.40| 1.51            | 965             | 24              | 0.09              |
| 2   | 1.45            | 1.40            | 7.58            | 7.13            | 5.99| 1.07            | 1198            | 39              | 0.95              |

For better data acquisition and data analysis, a DC power supply with a voltage \( U_0 \) of 8V was used in this experiment; an external protection resistor \( R_0 \) in the circuit was 10Ω; and the electrode was a MoSi\(_2\) electrode, whose resistance was \( R \), Ω; diameter \( d \) was 4mm, length \( L \) was 500mm, and the resistivity \( \rho \) was 21.50×10\(^{-6}\)Ω·cm; the electrode insertion depth was \( h \) (the distance from the bottom of the electrode to the surface of the mold flux), mm; the horizontal distance between the two electrodes was \( l \), mm; the resistance of the mold flux was \( R_{\text{slag}} \), Ω.

The circuit in Figure 1 can be equivalently described by the electrotechnical principle as shown in Figure 2. According to Ohm's law,

\[
\frac{U}{R+R_{\text{lag}}} = \frac{U_0}{R+R_{\text{lag}}+R_0}
\]

Formula (5) can be derived,

\[
R_{\text{lag}} = \frac{U_0R_0}{U_0-U} - R = \frac{R_0}{\frac{U_0}{U}-1} - R
\]

The resistance \( R \) of the electrode in formula (5) can be calculated by the solid resistance calculation method,

\[
R = \rho \frac{L}{S} = \frac{L}{\pi d^2}
\]
According to the resistance law,

\[ R_{\text{slag}} = \frac{l}{\kappa_3} = \frac{l}{\kappa h_d} \]  

(7)

The value of the conductivity \( \kappa \) of the mold flux can be calculated and derived from Equation (7).

\[ \kappa = \frac{l}{h_d R_{\text{slag}}} \]  

(8)

In summary, through the above derivation formula, the curve of the voltage \( U \) between the conductivity electrodes with the temperature \( T \) was converted into the curve of \( \ln \kappa \) and \( 1/T \), and the change law of the slope \(-B/R\) was found in this paper. The mold flux is a non-uniform slag system [12-13]. Its longitudinal structure, from top to bottom, include the particle layer, the sintered layer and the molten layer. There is no ionized ion in the particle layer, and also the gap between the particles is large, the little content carbon is also blocked, so it is almost non-conductive in this layer. The liquid phase starts to form in the sintered layer, ionizing out some ions and having a certain conductivity. As the liquid phase increases, more and more ions ionize and the conductivity increases. When the melting temperature of the mold flux reaches the hemispherical point (i.e. the melting point), the mold flux mainly exists in the ionic state, and its electrical conductivity rapidly increases [5,14-15]. Therefore, the measurement point \( K_1 \) where the slope \(-B/R\) was changed for the first time was regarded as the junction point of the particle layer and the sintered layer, and the measurement point \( K_2 \) where the slope \(-B/R\) was changed for the second time was regarded as the junction point of the sintered layer and the molten layer.

4. Results and discussion

4.1. Boundary criterion of the conductivity of slag layer

The experiment results of mold flux samples were shown in Figure 3. The graph showed the variation of the voltage between two electrodes with temperature during the temperature rising process of two samples. It could be seen from the figure that the voltage between two electrodes decreased as the temperature increased and eventually approached zero, which was consistent with the theory. Wu’s research [14] showed that as the mold flux temperature was close to the melting point, the sintering phase gradually melted into small liquid beads, which might contact each other to form large liquid beads. The ionic was increased, and the conductivity was also increased. As a result, the voltage between the mold flux layers would be decreased.

![Figure 3. Variation of the voltage between two electrodes with temperature.](image-url)
Figure 4 was a graph showing the variation of mold flux conductivity (lnκ) with temperature (1/T), as deduced from the above formulas. As could be seen from the figure, mold flux conductivity (lnκ) was linear with the temperature (1/T). As the temperature rose, the slope -B/R of the entire curve did change. The measurement point $K_1$ where the slope -B/R was changed for the first time was regarded as the junction point of the particle layer and the sintered layer, and the measurement point $K_2$ where the slope -B/R was changed for the second time was regarded as the junction point of the sintered layer and the molten layer.

4.2. Molten layer thickness verification

According to the difference of the conductive properties among the slag layers in section 4.1, the molten layer thickness of mold flux samples in Table 1 was measured by the electrode method. The corundum crucible containing mold flux samples was placed in a Si-Mo resistance furnace, heating to 1300°C at a certain rate, and keeping at a constant temperature. A certain amount of pig iron was added into the corundum crucible. In this experiment, pig iron was used instead of steel, because pig iron could be melted into molten iron at around 1300°C, which was convenient for operation. One fixed electrode was placed in the molten iron in the crucible vertically, the other movable electrode was placed vertically on the surface of mold flux samples. The furnace was sealed and a peephole was left. The circuit was connected as shown in Figure 1. The mold flux samples and molten iron were measured by moving down the electrode at a constant rate. Finally, through the digital-to-analog conversion device and the external processor, the results were obtained.

As mentioned before, the unmolten layer (i.e. the particle layer and the sintered layer) is not completely melted, the number of ionized ions is small, the resistance is large, the partial voltage of the unmolten layer between the electrodes is large. While the molten layer is completely melted, and almost ionized completely, the resistance is extremely small, the partial voltage of the molten layer between the electrodes drops sharply. Moreover, the molten iron is generally regarded as the conductor. Therefore, the measurement principle of the molten layer thickness in this experiment was: when the voltage between the electrodes dropped rapidly, the conductivity of the mold flux rapidly increased, indicating that the movable electrode was located between the unmolten layer and the molten layer or the surface of the molten layer. When the voltage between the electrodes dropped rapidly again with the movable electrode been continually moved downwards, the conductivity of the mold flux increased sharply again. At this time, the movable electrode was located in the slag-iron interface. Once the movable electrode was completely inserted into the molten iron, the time interval between two sudden changes in conductivity was automatically obtained by the processor. The molten
layer thickness was the product of the time interval and the electrode's moving speed (i.e. \( \delta = v \cdot \Delta t \), where \( v \) was the electrode moving speed, mm / s, \( \Delta t \) was the time interval, s.). The electrode moving speed in this experiment was 1 mm/s, so that the molten layer thickness could be equivalent to the absolute value of the time interval. In this experiment, the molten layer thickness was measured three times using the electrode method, which average value was taken. Figure 5 showed the result of the molten layer thickness using the electrode method. The molten layer thickness of 1# sample was 5.33 mm, while the molten layer thickness of 2# sample was 6.67 mm.

The traditional method, commonly known as the double wire method, was that a stainless steel wire and a copper wire with the same length were tied together and inserted to the bottom of the crucible; the molten layer thickness was determined by the different length been etched, after keeping the wires in samples for one second. Table 2 showed the comparison of measurement results by different methods. For the two mold flux samples in this experiment, the results of the traditional method were 4.49mm and 7.21mm respectively, which was within 1mm from the results of the electrode method. It meant that measuring the molten layer thickness of mold flux by the electrode method was feasible.

![Figure 5. The result of measuring molten layer thickness by electrode method.](image)

| No. | Traditional method | Electrode method |
|-----|--------------------|------------------|
| 1#  | 4.49               | 5.33             |
| 2#  | 7.21               | 6.67             |

5. Conclusions
The conductive mechanism of the mold flux was theoretically analyzed based on the ion theory in this study. And also, the relationship between the slag conductivity \( \ln \kappa \) and the temperature \( 1/T \) (the slope \( -B/R \)) was found according to the Arrhenius law and electrical engineering principles, results showed that with the increase of temperature, the slope \(-B/R\) would not always stay the same, and the steeply changing measurement point was defined as the point of difference in conductivity between the slag layers.

A simple and feasible method for measuring the thickness of molten layer was designed in this study, and the related results were verified by the double wire method (traditional measurement method). The experiment showed that the electrode method was accurate, which accuracy could be further improved with the improvement of the accuracy of the measurement probe. And the cost was much lower than any other method, which can be used as a measure to study the thickness of the mold flux layer.
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