Abstract: It is an effective way to decrease power consumption, pollution emission, to increase productivity and improve ingot quality by using lower CaF2 content even CaF2 free slag during the electro-slag remelting (ESR) process. In this study, a conventional slag, namely ANF-8 with composition of 60 mass%CaF2-20 mass%CaO-20 mass%Al2O3 was chosen as a reference slag. A new quaternary slag system of CaF2-CaO-Al2O3-SiO2 with four lower CaF2 content levels in mass fraction, 59%, 55%, 50%, 45% were prepared and labeled as S1, S2, S3 and S4 respectively. The effects of CaF2 content and temperature on the physicochemical properties of the slag were investigated. The results showed that the melting points and the conductivity of the samples S1–S4 were all lower than those of the sample ANF-8. The melting point and the conductivity (1600°C) of Sample S4 achieved 1372°C and 1.936Ω-1·cm-1, respectively. The conductivities of Sample S4 at 1550–1650°C reached 1.741–2.131Ω-1·cm-1, and were lower than those of ANF-8 and S1–S3. Considering the physicochemical properties of the four new slags in the CaF2-CaO-Al2O3-SiO2 quaternary system and low CaF2 in the slag to decrease the power consumption and pollution emission, the slag S4 was the most suitable for the ESR process.

Keywords: Melting point, viscosity, conductivity, calcium fluoride, electro-slag remelting

1. Introduction

Electro-slag remelting (ESR) is an advanced technology, which has been widely used in the production of high performance alloy steels, high speed steels, dies steels, creep resistant steels and super alloys [1]. Reducing power consumption and pollution, increasing productivity and improving ingot quality is an important development trend of ESR technology. Hence, the development of new slag and their application to the ESR process have been attracted much attention [2–4]. Many researchers of ESR have focused on the study of the physicochemical properties of slag, such as melting point, viscosity and conductivity, etc [5–10]. So far, there are few reports on the effects of CaF2 content and temperature on the physicochemical properties of the quaternary slag in CaF2-CaO-Al2O3-SiO2 system.

ANF-6 slag (70%CaF2-30%Al2O3, mass fraction) has been widely used in ESR process. However, high CaF2 content can increase the power consumption and severe fluorine pollution during the ESR process, which is not suitable for the green metallurgy and safe production. In the present work, the new quaternary slag in the CaF2-CaO-Al2O3-SiO2 system containing low CaF2 was prepared, and the effects of CaF2 content and temperature on the physicochemical properties of the slag were investigated.

2. Experimental procedures

2.1 Design and preparation of the new quaternary slag system
According to the CaF₂-CaO-Al₂O₃ ternary phase diagram as shown in Fig. 1 [11], the basic components of slag with reasonable melting point were determined firstly. Then the high power consumption and severe fluorine pollution were eliminated by adding CaO and SiO₂ and reducing the amount of CaF₂ in the ANF-6 slag. Finally, four kinds of slag in the CaF₂-CaO-Al₂O₃-SiO₂ quaternary system with different CaF₂ content were designed (see Table 1). In order to study on the effects of CaF₂ content and temperature on the physicochemical properties of slag, a conventional slag, namely ANF-8 (60 mass%CaF₂-20 mass%CaO-20 mass%Al₂O₃), was chosen as a reference slag system.

**Fluorite (mass fraction of CaF₂ > 95%), alumina powder (mass fraction of Al₂O₃ > 97%), silica (mass fraction of SiO₂ > 97%) and calcium oxide reagent (AR) were chosen as the raw materials. The raw materials were heated at 850°C for 10h in air to remove the moisture and some volatile impurities, such as CO₂. The raw materials were weighed in terms of the compositions of the slag (see Table 1), and mixed fully. Then the slag samples S₀–S₄ were prepared.**

### 2.2 Measurements of the physicochemical properties

The melting point and the viscosity of the slag samples S₀–S₄ were measured by hemispherical method and the rotating cylinder method, respectively. The conductivity at 1550–1650°C was calculated using the following empirical formula [12].

$$
\sigma = \exp(1.911 - 1.38x - 5.69x^2) + 0.0039(t - 1700)
$$

(1)
\[ x = x_{\text{Al}_2\text{O}_3} + 0.75x_{\text{SiO}_2} + 0.5(x_{\text{TiO}_2} + x_{\text{ZrO}_2}) + 0.2x_{\text{CaO}} \]  

(2)

where \( \sigma \) is the conductivity of the molten slag, \( \text{\Omega}^{-1}\text{cm}^{-1} \), \( t \) is the temperature, \( ^\circ\text{C} \), \( t = 1550–1780^\circ\text{C} \), \( x \) is the molar fraction, \( x_{\text{Al}_2\text{O}_3} = 0–0.38 \), \( x_{\text{SiO}_2} = 0–0.17 \), \( x_{\text{TiO}_2} = 0–0.18 \), \( x_{\text{ZrO}_2} = 0–0.15 \), and \( x_{\text{CaO}} = 0–0.65 \).

3. Results and discussion

The measured melting points of slag are listed in Table 2. The melting points of the slag samples \( S_1–S_4 \) containing 45%–59% CaF\(_2\) were 1361–1386\(^\circ\text{C} \), and all lower than that of ANF-8 (1396\(^\circ\text{C}\)). Meanwhile, the melting points of the new slag samples were lower than those of the metal or alloys by the ESR process about 100–200\(^\circ\text{C}\), which was preferable for forming slag pool early. Basing on the melting point of slag, the designed new slag samples all could meet the metallurgical requirement for the ESR process. The slag \( S_4 \) was more suitable for the ESR process due to lower melting point of slag and CaF\(_2\) content.

<table>
<thead>
<tr>
<th>Slag samples</th>
<th>ANF-8(S(_0))</th>
<th>( S_1 )</th>
<th>( S_2 )</th>
<th>( S_3 )</th>
<th>( S_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemispheric temperature(Melting point) /°C</td>
<td>1396</td>
<td>1361</td>
<td>1379</td>
<td>1386</td>
<td>1372</td>
</tr>
</tbody>
</table>

Fig. 2 shows the variation of viscosity of the new slag with CaF\(_2\) content and temperature. It can be seen that CaF\(_2\) content and temperature had a great impact on the viscosity. The viscosities of the samples \( S_1–S_4 \) at 1350–1375\(^\circ\text{C} \) increased obviously with decreasing the amount of CaF\(_2\) (Fig. 2a). For the slag \( S_4 \) containing 59% CaF\(_2\), the viscosity at 1350\(^\circ\text{C} \) reached 0.114Pa·s. When the CaF\(_2\) content was decreased to 45%, the viscosity at 1350\(^\circ\text{C} \) increased up to 0.274Pa·s sharply. At 1400–1500\(^\circ\text{C} \), CaF\(_2\) content had a slight influence on the viscosities of the samples \( S_1–S_4 \), and they were stable. In Fig. 2(b) among the samples \( S_1–S_4 \), the viscosity of the slag \( S_1 \) changed most slightly followed by the samples \( S_2, S_3 \) and \( S_4 \). It is well known that the solidification temperature of most steels and alloys were often higher than 1375\(^\circ\text{C} \). In Fig. 2(b) the viscosities with different CaF\(_2\) content had changed slightly with the temperature variation from 1400 to 1500\(^\circ\text{C} \). In this case, it could benefit for improving the surface quality of ESR ingot. Considering the viscosity stability of slag at 1375–1500\(^\circ\text{C} \), the new slag samples \( S_1–S_4 \) were all suitable for the ESR process.
Fig. 2 Variation of viscosity of the new slag with CaF$_2$ content and temperature

Fig. 3 shows the calculated conductivities of the slag with different CaF$_2$ content and temperature. CaF$_2$ content had a great impact on the conductivities of slag. With decreasing the CaF$_2$ content, the conductivities at 1550–1650°C decreased gradually. For the slag S$_0$ containing 60% CaF$_2$, the conductivity at 1600°C was $3.661 \Omega^{-1} \text{cm}^{-1}$. When the mass fraction of CaF$_2$ decreased to 59%, the conductivity at 1600°C was decreased to $3.002 \Omega^{-1} \text{cm}^{-1}$ sharply. While further decreasing the amounts of CaF$_2$ to 55%, 50% and 45%, the conductivities at 1600°C were decreased to 2.637, 2.273, and 1.936 $\Omega^{-1} \text{cm}^{-1}$, respectively. When the mass fraction of CaF$_2$ remained constant, the conductivity was increased with increasing the temperature. Moreover, the conductivities of the samples S$_1$–S$_4$ were all lower than those of ANF-8. The conductivities of S$_4$ at 1550–1650°C reached 1.741–2.131 $\Omega^{-1} \text{cm}^{-1}$, and were lower than those of S$_1$–S$_3$. So it was good for reducing the power consumption and the production cost.

4. Conclusions

A new quaternary slag system of CaF$_2$-CaO-Al$_2$O$_3$-SiO$_2$ with four lower CaF$_2$ content levels of mass fraction, 59%, 55%, 50%, 45% were prepared and denoted as slag, S$_1$, S$_2$, S$_3$ and S$_4$ respectively. The melting temperature and high-temperature viscosity and electrical conductivity were measure and compared with those of
60%CaF2-20%CaO-20%Al2O3 slag (S0). The conclusions attained are listed below.

1. The melting points of the samples S1–S4 were all lower than that of the conventional slag ANF-8. The melting points of the samples S4 reached 1361°C and 1372°C, respectively.

2. With decreasing the amount of CaF2, the viscosities of the samples S1–S4 at 1350–1375°C increased obviously. At 1400–1500°C, CaF2 content and temperature had a slight influence on the viscosity of the slag. Considering the viscosity stability of the slag at 1375–1500°C, the new slag samples S1–S4 were all proper for the ESR process.

3. With decreasing the CaF2 content and temperature, the conductivities at 1550–1650°C decreased gradually. The conductivities of the sample S4 at 1550–1650°C reached 1.741–2.131Ω⁻¹·cm⁻¹, and were lower than those of S1–S3.

4. Considering the physicochemical properties of the new quaternary slag in the CaF2-CaO-Al2O3-SiO2 system and low CaF2 in the slag to decrease the power consumption and the pollution emission, the slag S4 was the most suitable for the ESR process.

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References


