The physical properties of CaF_2-CaO-Al_2O_3-SiO_2 slag system for ESR of 12Cr

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Abstract: It is an effective way to decrease power consumption, pollution emission, to increase productivity and improve ingot quality by using lower CaF_2 content even CaF_2 free slag during the electro-slag remelting (ESR) process. In this study, a conventional slag, namely ANF-8 with composition of 60 mass%CaF_2-20 mass%CaO-20 mass %Al_2O_3 was chosen as a reference slag. A new quaternary slag system of CaF_2-CaO-Al_2O_3-SiO_2 with four lower CaF_2 content levels in mass fraction, 59%, 55%, 50%, 45% were prepared and labeled as S_1, S_2, S_3 and S_4 respectively. The effects of CaF_2 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 S_1–S_4 were all lower than those of the sample ANF-8. The melting point and the conductivity (1600°C) of Sample S_4 achieved 1372°C and 1.936$\Omega^{-1}cm^{-1}$, respectively. The conductivities of Sample S_4 at 1550–1650°C reached 1.741–2.131$\Omega^{-1}\cdot cm^{-1}$, and were lower than those of ANF-8 and S_1–S_3. Considering the physicochemical properties of the four new slags in the CaF_2-CaO-Al_2O_3-SiO_2 quaternary system and low CaF_2 in the slag to decrease the power consumption and pollution emission, the slag S_4 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 CaF_2 content and temperature on the physicochemical properties of the quaternary slag in CaF_2-CaO-Al_2O_3-SiO_2 system.

ANF-6 slag (70%CaF_2-30%Al_2O_3, mass fraction) has been widely used in ESR process. However, high CaF_2 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 CaF_2-CaO-Al_2O_3-SiO_2 system containing low CaF_2 was prepared, and the effects of CaF_2 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 CaF_2-CaO-Al_2O_3 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 SiO_2 and reducing the amount of CaF_2 in the ANF-6 slag. Finally, four kinds of slag in the CaF_2-CaO-$A1_2O_3$-SiO_2 quaternary system with different CaF_2 content were designed (see Table 1). In order to study on the effects of CaF_2 content and temperature on the physicochemical properties of slag, a conventional slag, namely ANF-8 (60 mass%CaF_2-20 mass%CaO-20 mass%Al_2O_3), was chosen as a reference slag system.

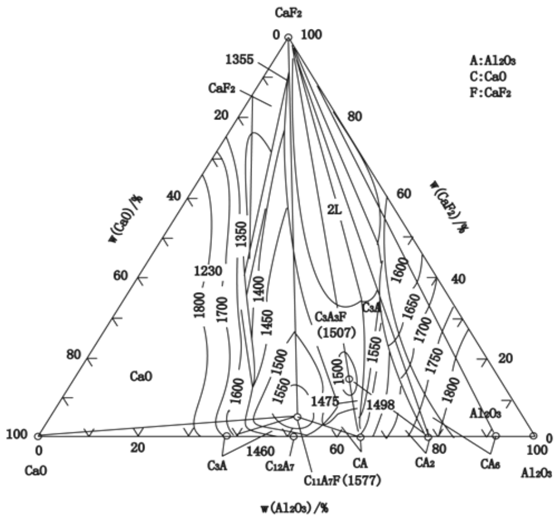

Fig. 1 CaF_2-CaO-Al_2O_3 ternary phase diagram [11]

Table 1 The compositions of the slag samples (mass fraction)/%

Slag samples	CaF_2	CaO	Al_2O_3	SiO_2
ANF-8(S_0)	60	20	20	-
S_1	59	15	18	8
S_2	55	16	20	9
S_3	50	18	22	10
S_4	45	20	24	11

Fluorite (mass fraction of CaF_2 > 95%), alumina powder (mass fraction of $A1_2O_3$ > 97%), silica (mass fraction of SiO_2 > 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 CO_2. The raw materials were weighed in terms of the compositions of the slag (see Table 1), and mixed fully. Then the slag samples S_0–S_4 were prepared.

2.2 Measurements of the physicochemical properties

The melting point and the viscosity of the slag samples S_0–S_4 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].

$$\sigma = \exp(1.911 - 1.38x - 5.69x^2) + 0.0039(t - 1700) \quad (1)$$

$$x = x_{Al_2O_3} + 0.75x_{SiO_2} + 0.5(x_{TiO_2} + x_{ZrO_2}) + 0.2x_{CaO} \tag{2}$$

where σ is the conductivity of the molten slag, $\Omega^{-1}\cdot cm^{-1}$, t is the temperature, °C, t =1550–1780°C, x is the molar fraction, $x_{Al_2O_3} = 0-0.38$, $x_{SiO_2} = 0-0.17$, $x_{TiO_2} = 0-0.18$, $x_{ZrO_2} = 0-0.15$, and $x_{CaO} = 0-0.65$.

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°C, and all lower than that of ANF-8 (1396°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°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 2 The experimental measured melting points of slag samples S_0–S_4

Slag samples	ANF-8(S_0)	S_1	S_2	S_3	S_4
Hemispheric temperature(Melting point) /°C	1396	1361	1379	1386	1372

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°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°C reached 0.114Pa·s. When the CaF_2 content was decreased to 45%, the viscosity at 1350°C increased up to 0.274Pa·s sharply. At 1400–1500°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°C. In Fig. 2(b) the viscosities with different CaF_2 content had changed slightly with the temperature variation from 1400 to 1500°C. In this case, it could benefit for improving the surface quality of ESR ingot. Considering the viscosity stability of slag at 1375–1500°C, the new slag samples S_1–S_4 were all suitable for the ESR process.

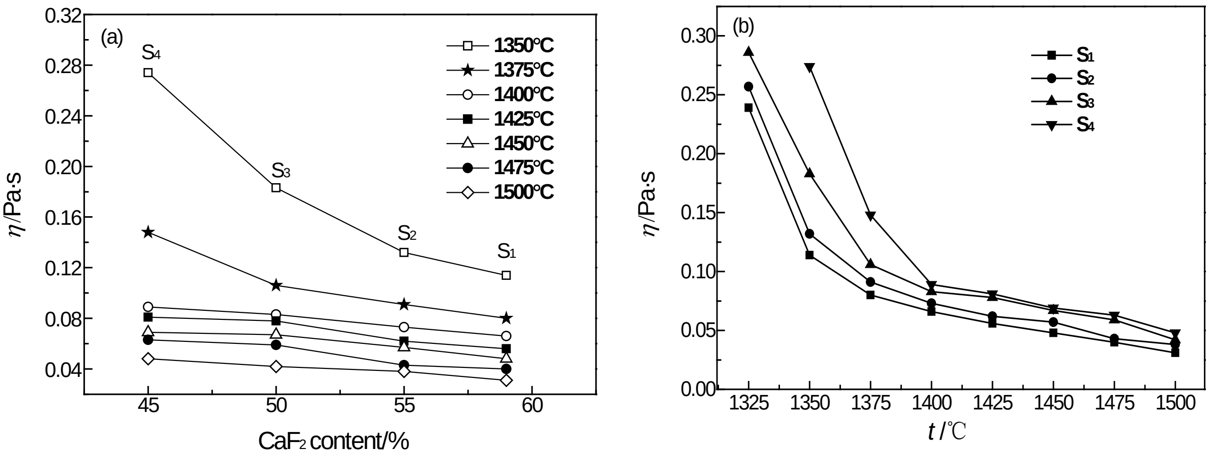

Fig. 2 Variation of viscosity of the new slag with CaF_2 content and temperature

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$\Omega^{-1}\cdot cm^{-1}$. When the mass fraction of CaF_2 decreased to 59%, the conductivity at 1600°C was decreased to 3.002$\Omega^{-1}\cdot cm^{-1}$ 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 $\Omega^{-1}\cdot cm^{-1}$, 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$\Omega^{-1}\cdot cm^{-1}$, and were lower than those of S_1–S_3. So it was good for reducing the power consumption and the production cost.

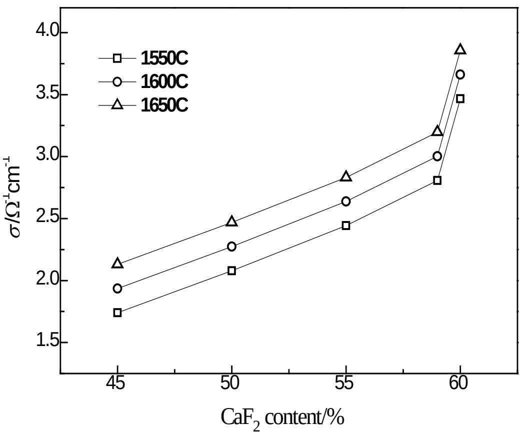

Fig. 3 Effects of CaF_2 content and temperature on the conductivities of the slag samples S_0–S_4

4. Conclusions

A new quaternary slag system of CaF_2-CaO-Al_2O_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%CaF_2-20%CaO-20%Al_2O_3 slag (S_0). The conclusions attained are listed bellow.

(1) The melting points of the samples S_1–S_4 were all lower than that of the conventional slag ANF-8. The melting points of the samples S_1 and S_4 reached 1361°C and 1372°C, respectively.

(2) With decreasing the amount of CaF_2, the viscosities of the samples S_1–S_4 at 1350–1375°C increased obviously. At 1400–1500°C, CaF_2 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 S_1–S_4 were all proper for the ESR process.

(3) With decreasing the CaF_2 content and temperature, the conductivities at 1550–1650°C decreased gradually. The conductivities of the sample S_4 at 1550–1650°C reached 1.741–2.131$\Omega^{-1}\cdot cm^{-1}$, and were lower than those of S_1–S_3.

(4) Considering the physicochemical properties of the new quaternary slag in the CaF_2-CaO-Al_2O_3-SiO_2 system and low CaF_2 in the slag to decrease the power consumption and the pollution emission, the slag S_4 was the most suitable for the ESR process.

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