



Article Effects of CeO₂ on Viscosity, Structure, and Crystallization of Mold Fluxes for Casting Rare Earths Alloyed Steels

Zeyun Cai[®], Bo Song *, Longfei Li, Zhen Liu and Xiaokang Cui

School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China; zexiaoyun@126.com (Z.C.); aifei_0105@126.com (L.L.); liuzhen_ustb@163.com (Z.L.); cuixiaokang126@126.com (X.C.)

* Correspondence: songbo@metall.ustb.edu.cn; Tel.: +86-010-6233-2208

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Abstract: The CaO-Al₂O₃-based mold fluxes are proposed for the Ce-bearing heavy rail steel continuous casting because of the low reactivity. Effects of CeO₂ on the melting temperature, the viscous property, and the crystallization behavior of the CaO-Al₂O₃-Li₂O-B₂O₃ mold fluxes were studied using hemisphere melting point method, rotating cylinder method, and X-ray diffraction (XRD) in the present work. The microstructure of the mold fluxes was analyzed by Fourier-transform infrared spectroscopy (FTIR). The results revealed that the addition of CeO₂ would increase the melting temperature, but decrease the viscosity at each temperature due to its influence on increasing the depolymerization of the mold fluxes at high temperature. The precipitation of CaO was restrained and CaCeAlO₄ generated with increasing CeO₂ content since the crystal phases were affected by the microstructure of the melts. The change of the crystalline phases in mold fluxes influences the break temperature and the viscosity of the mold fluxes below the break temperature. These results obtained can provide guidelines for designing new mold fluxes for casting rare earth alloy heavy rail steels.

Keywords: CeO₂; melting temperature; viscosity; structure; crystallization; CaO-Al₂O₃-based mold fluxes

1. Introduction

Rare earth is widely used for the production of rare earth treated steels and rare earth alloyed steels as an effective additive [1–3]. Nowadays, rare earth was usually added into the heavy rail steel to improve its fatigue resistance, low-temperature impact toughness, and heat resistance [4]. The adding amount of rare earth in the continuous casting process of heavy rail steel is ~0.02%. However, amounts of rare earth oxides will generate since rare earth is easy to react with partial oxides in common mold fluxes and oxidize at a high temperature. The increase of the generated rare earth oxides has effects on melting temperature, viscous property, and crystallization behavior of the mold fluxes according to the previous studies [5–7].

In order to restrain the slag-metal interface reaction in the continuous casting of the rare earth alloy heavy rail steels, the concept of the mold fluxes with low reactivity was proposed. The low-reactive or nonreactive mold fluxes will be obtained by reducing the contents of SiO₂, Na₂O, and other components with strong oxidizability. For example, the CaO-Al₂O₃-based mold fluxes were investigated in previous literature, which reported that the slag-metal interface reaction was reduced by 75%. CaF₂ was usually used in mold fluxes to control the melting temperature, viscosity, and crystallization [8,9], but its fluoride compounds pollute the environment [10]. Thus in this paper, B₂O₃ has been taken into consideration for being introduced into the mold fluxes instead of CaF₂. Besides, some researchers studied the influences of CaO/Al₂O₃ ratio and the contents of Li₂O and B₂O₃ on the viscosity and crystallization of the CaO-Al₂O₃-based mold fluxes for casting heat resistant steel [11–13]. The results revealed that the proportion of CaO/Al₂O₃ ratio of 1.5 in mold fluxes is the most appropriate for the viscosity. In their studies, the fluxing agents—Li₂O and B₂O₃—are added to ensure the stability of the mold fluxes. Thus, in this paper, the ratio of CaO/Al₂O₃ in the experimental mold fluxes was set at 1.5, and the contents of Li₂O and B₂O₃ were approximately 9% and 10%, respectively.

The viscous property and crystallization behavior have direct effects on the lubrication and heat transfer between the mold and the solidified shell. However, the slag properties are influenced by its microstructure. The microstructure of the quenched mold fluxes is similar to that of the melts since the glassy state is a supercooled liquid from the thermodynamic viewpoint. FTIR spectroscopy can be used to analyze the microstructure of the melts.

In the present work, the effects of different CeO_2 contents on the melting temperature, viscosity property, microstructure, and crystallization behavior of the CaO-Al₂O₃-based mold fluxes were investigated, and the relationship between the viscosity and microstructure of the mold fluxes is discussed. The results and conclusions provide a theoretical foundation for developing the mold fluxes for casting the rare earth alloy heavy rail steels and facilitate further improvement by providing data for melting temperature, viscosity, microstructure, and crystallization of the mold fluxes.

2. Materials and Methods

2.1. Sample Preparation

All reagent grade powders of CaO (\geq 98 wt. %), Al₂O₃ (\geq 99 wt. %), Li₂O (\geq 99.8 wt. %), B₂O₃ (\geq 98.5 wt. %), and CeO₂ (\geq 99 wt. %) were dried in a muffle furnace at 500 °C for 12 h to remove the retaining water. The ratio of CaO/Al₂O₃ in the experimental mold fluxes was chosen to be 1.5 according to the previous studies about the CaO-Al₂O₃-based mold fluxes. Li₂O and B₂O₃ were both added into the mold fluxes since the CaO-Al₂O₃-based slags have a relatively high melting temperature. Approximately 0 wt. %, 4 wt. %, 8 wt. %, and 12 wt. % CeO₂ were added into the mold fluxes of experimental samples. All the samples were firstly mixed well and pressed into blocks. Then they were premelted in a graphite crucible by using a silicon molybdenum rod furnace at 1450 °C for 30 min to reach homogenization with Ar gas protection. All the premelted samples were water quenched followed by being dried at 130 °C for 12 h and ground into powders. The composition of four experimental samples was measured and listed in Table 1. The premelted samples were prepared and used for the property measurement.

Sample Number -	Composition (wt. %)					
		CaO	Al_2O_3	Li_2O	B_2O_3	CeO ₂
1	Calculated	48.06	32.04	9.43	10.07	0
	Analyzed	47.94	32.38	9.10	10.58	0
2	Calculated	46.14	30.76	9.05	9.63	4.00
	Analyzed	46.89	30.99	9.58	9.07	3.47
3	Calculated	44.21	29.48	8.68	9.63	8.00
	Analyzed	44.69	29.91	8.59	9.24	7.57
4	Calculated	42.29	28.20	8.30	9.21	12.00
	Analyzed	42.18	28.38	8.45	9.08	11.91

Table 1. The chemical composition of the experimental mold fluxes.

2.2. The Melting Temperature Test

The hemisphere melting point temperature was used to measure the melting temperature using an automatic melting point tester (RDS-04, Shenyang, Liaoning, China). The schematic diagram of the experimental apparatus is shown in Figure 1. Two S-type thermocouples were employed to measure the temperature. The premelting mold fluxes were placed, uniformly mixed, and made into cylindrical samples of φ 3 mm × 3 mm using a sample preparation device. All prepared samples were naturally

dried for 24 h and then heated at a rate of 5 to 10 $^{\circ}$ C/min during the measurement. The height of the sample decreased gradually with increasing temperature. The melting temperature was recorded automatically when the height became half of the original height. The measurement was repeated three times and the melting temperature was determined.



Figure 1. The schematic diagram of the experimental apparatus for measuring melting temperature.

2.3. The Viscosity Test

The schematic diagram of the rotating cylinder viscometer (AMETEK Brookfield, Middleboro, MA, USA) is shown in Figure 2. In this experimental setup, a $MoSi_2$ electric resistance furnace (SHIMADEN FP21, Tokyo, Japan) was used to heat the slags, which can move up and down with the sliding rails. A molybdenum crucible and a molybdenum spindle also shown in Figure 2 with Pt-30Rh thermocouples were arranged to the rotating system. The standard deviation of the measured viscosity values from the mean value is within 2%. Before the measurement, the spindle multiplier constant needs to be determined using the equation as follows

$$\eta = TK \times SMC \times \frac{10}{RPM} \times Torque \tag{1}$$

where η is viscosity in Pa·s; TK is the torque constant of 0.09373 for viscosimeter DV2T; SMC is the spindle multiplier constant of 41.75; *RPM* is the rotating speed of the spindle in revolutions per minute; and *Torque* is the percentage of the measured torque value relative to the full scale of the spiral spring. The viscometer was calibrated at room temperature (25 °C) using a standard oil with the viscosity value of 0.495 Pa·s.



Figure 2. The schematic diagram of the inner cylinder rotating viscometer.

The experimental mold fluxes were heated at a rate of 10 $^{\circ}$ C/min from 25 $^{\circ}$ C to 1400 $^{\circ}$ C and held at 1400 $^{\circ}$ C for half an hour to homogenize the melt with Ar gas. Then the spindle was slowly immersed into the melts and the distance between the bottom of the molybdenum crucible and the tip of the bob was controlled about to 10 mm. Viscosity values were measured and obtained during the cooling

process from 1400 °C. A Mo spindle was used to stir the melts for ~15 min before each measurement. Three different rotating speeds were adopted to measure the viscosity and the rotating time at each speed was more than 5 min. The averaging values were determined to be the final viscosity value.

2.4. The Structure Test

Fourier-transform infrared spectroscopy (NEXUS, Nicolet, Middleboro, MA, USA) was employed to analyze the microstructure of water quenched mold fluxes. In this work, the analyzed frequency range was between 400 cm⁻¹ and 4000 cm⁻¹. The FTIR bead is mixed with 2.0 mg of each sample and 200 mg KBr. Then the samples were pressed into pellets with a diameter of 13 mm and analyzed.

2.5. The Crystallization Test

The experimental mold fluxes were heated from room temperature to 1450 °C and held at 1450 °C for 1 h followed by cooling with the furnace to the break temperature of each sample and held at the break temperature about 2 h. Then the samples were water quenched as soon as possible. After this treatment, the samples were dried at 120 °C for 12 h and ground into powders. The phase composition of the samples was determined by X-ray diffraction (SMARTLAB 9 kW, Rigaku, Beijing, China).

3. Results and Discussions

3.1. Effects of CeO₂ Content on Melting Temperature

The melting temperature of experimental mold fluxes with 0 wt. %, 4 wt. %, 8 wt. %, and 12 wt. % CeO₂ are presented in Figure 3. Without adding CeO₂ the melting temperature of the experimental mold fluxes was ~1067 °C. The melting temperature increased continuously with increase in the CeO₂ content. The increase of the melting temperature is ascribed to the addition of CeO₂ with a high melting temperature [14]. When the CeO₂ content was 12 wt. %, the melting temperature was about 1135 °C. It can be concluded that the CaO-Al₂O₃-based mold fluxes within 12 wt. % CeO₂ will show steady melting properties after absorbing CeO₂ in the continuous casting process of rare earth alloy heavy rail steels.



Figure 3. The melting temperature of experimental mold fluxes with different CeO₂ contents.

3.2. Effects of CeO₂ Content on Viscosity

The viscosity results of the experimental mold fluxes with different CeO₂ contents are shown in Figure 4. The viscosity values of all the experimental mold fluxes increased with decreasing temperature as normal. The viscosity at each temperature decreased with the addition of CeO₂ since CeO₂ played the role of the modifier in the network structure of the melts according to the experimental results and analyses of the microstructure below. Besides, the break temperature of the four experimental mold fluxes decreased with the addition of CeO₂ as shown in Figure 5. The break temperature decreased with increasing CeO_2 content, which is related to the precipitation crystalline phases of the CaO-Al₂O₃-based mold fluxes with different CeO₂ contents [15].



Figure 4. Viscosity results of experimental mold fluxes with decreasing temperature.



Figure 5. The break temperature of experimental mold fluxes with different CeO₂ contents.

The apparent viscosity values at 1300 °C of the CaO-Al₂O₃-based mold fluxes with different CeO₂ contents are presented in Figure 6. The viscosity at 1300 °C can represent the viscosity of the mold fluxes at high temperature [16]. The CaO-Al₂O₃-based mold fluxes have a viscosity of ~0.65 Pa·s without CeO₂. When the CeO₂ content increased, the viscosity of the experimental mold fluxes decreased continuously. The main network structure of the CaO-Al₂O₃-based mold fluxes is [AlO₄]-tetrahedral unit, and the chain structure of the melts can be destroyed since CeO₂ behaves as a basic oxide in the melts. The specific explanations will be shown in the following microstructure section.



Figure 6. The viscosity of experimental mold fluxes at 1300 °C with different CeO₂ contents.

3.3. Effects of CeO₂ Content on Microstructure

The viscous properties of mold fluxes are generally influenced by the components and the microstructure of the melts [14–16]. Therefore, the microstructure of the CaO-Al₂O₃-based mold fluxes with different CeO₂ contents was investigated, and the results of FTIR spectra are shown in Figure 7. In the FTIR spectra from 400 cm⁻¹ to 1600 cm⁻¹, five kinds of band groups are observed at 500–600 cm⁻¹, 700–850 cm⁻¹, 850–1000 cm⁻¹, 1150–1250 cm⁻¹, and 1250–1400 cm⁻¹, respectively. Different band units were determined according to the previous literature. In the experimental mold fluxes, the main network structure is Al–O structural units [17–20] and B–O structural units [21–23]. Therefore, the transmittance peak at 500–600 cm⁻¹ corresponds to the [AlO₆]-octahedral structural unit, the transmittance peak at 850–1000 cm⁻¹ corresponds to the [BO₄]-tetrahedral structural unit, the transmittance peak at 1150–1250 cm⁻¹ corresponds to the BO₄]-tetrahedral structural unit, and the transmittance peak at 1250–1400 cm⁻¹ corresponds to the B–O⁻ stretching vibration in [BO₃]-triangular structural unit.



Figure 7. The Fourier-transform infrared spectroscopy (FTIR) spectra of the experimental mold fluxes with different CeO₂ content.

The microstructure of the experimental mold fluxes can be analyzed from the results of the transmittance-wavenumber curves. The spectra were treated statistically, and the relative area fraction could be obtained to represent the number of the structural units [24,25]. The relative area fractions in the experimental mold fluxes with different CeO₂ contents are presented in Figure 8. When increasing the CeO₂ content from 0 wt. % to 12 wt. %, the [BO₃]-triangular units and the [AlO₆]-octahedral units increase, but the [BO₄]-tetrahedral units and the [AlO₄]-tetrahedral units decrease.



Figure 8. The relative area fraction in the experimental mold fluxes.

For further understanding, the effects of CeO₂ on the different structural units were studied. The area ratios of $[AlO_4]$ to $[AlO_6]$ and $[BO_4]$ to $[BO_3]$, as a function of the CeO₂ content, are presented in Figures 9 and 10, respectively. The area ratio of $[AlO_4]$ to $[AlO_6]$ in the mold fluxes decreases with the addition of CeO₂ as shown in Figure 9, which indicates that CeO₂ increases the depolymerization of Al–O structural units. The possible reason for the depolymerization is the decomposition of CeO₂ into Ce⁴⁺ and O²⁻ in molten slags. The released O²⁻ could react with $[AlO_4]$ -tetrahedral units to form $[AlO_6]$ -octahedral units. Besides, the area ratio of $[BO_4]$ to $[BO_3]$ in the mold fluxes decreases with increasing CeO₂ content simultaneously. It indicates that CeO₂ increases the depolymerization of the B–O structural units since the 2D $[BO_3]$ -triangular unit has a looser structure than the $[BO_4]$ unit. Therefore, CeO₂ played the role of the modifier in the microstructure of the CaO-Al₂O₃-based mold fluxes, leading to a decrease of viscosity at each temperature with increasing CeO₂ content above the break temperature.



Figure 9. The area ratio of [AlO₄] to [AlO₆] in the mold fluxes with different CeO₂ contents.



Figure 10. The area ratio of [BO₄] to [BO₃] in the mold fluxes with different CeO₂ contents.

3.4. Effects of CeO₂ Content on Crystallization

The microstructure of the melts might also affect the crystallization, and the precipitation of crystalline phases of the experimental mold fluxes could influence the break temperature. Thus, the crystal phases of the experimental mold fluxes at the break temperature were investigated under the conditions of increasing the CeO₂ content from 0 wt. % to 12 wt. %. Figure 11 shows the XRD patterns of all the experimental mold fluxes quenched at their break temperatures. The crystal phases were mainly CaO and LiAlO₂ in the mold fluxes without CeO₂. In the present mold fluxes, the network former is [AlO₄]-tetrahedral unit and the [AlO₄] units need to combine with a positive charge for charge compensation since the coordination number in [AlO₄] unit is four. The Li⁺ with the minimum ionic radius is the most likely to compensate the [AlO₄] units to form LiAlO₂ firstly. Then, Ca²⁺ will combine with the free oxygen to form CaO. Therefore, CaO and LiAlO₂ precipitated when the mold

fluxes without CeO₂ were water quenched at the break temperature. However, the crystal phases were mainly LiAlO₂ and CaCeAlO₄ when the content of CeO₂ in the experimental mold fluxes was 4 wt. %, 8 wt. %, and 12 wt. %. The Li⁺ still compensated the [AlO₄] units to form LiAlO₂ firstly. At the same time, the [AlO₆] units which need more positive charges increased with increasing CeO₂ content in the melts. Therefore, Ce⁴⁺ and Ca²⁺ would combine with the [AlO₆] units to form CaCeAlO₄, and the crystalline phases in the mold fluxes quenched at their break temperatures were LiAlO₂ and CaCeAlO₄. Above all, the addition of CeO₂ restrained the precipitation of CaO, but increased the formation of the CaCeAlO₄, resulting in a decrease of the break temperature.



Figure 11. The crystal phases in the experimental mold fluxes quenched at break temperature.

4. Conclusions

Melting temperature, viscosity, and crystallization of mold fluxes with different CeO_2 contents ranging from 0 wt. % to 12 wt. % were studied using hemisphere melting point method, rotating cylinder method, and X-ray diffraction (XRD) in the present work, and the microstructure of the mold fluxes was analyzed by Fourier-transform infrared spectroscopy (FTIR). Three conclusions are summarized as follows.

- 1. The addition of CeO₂ could increase the melting temperature, but decreased the viscosity and the break temperature of the mold fluxes for casting rare earth alloy heavy rail steels.
- 2. CeO₂ could increase the depolymerization of the melts, leading to a decrease in the viscosity of the mold fluxes above the break temperature.
- 3. CeO₂ could restrain the precipitation of CaO, but promoted the precipitation of CaCeAlO₄, which decreases the break temperature.

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