Lubrication and heat transfer control are two significant functions of mold fluxes. In order to coordinate the contradiction between lubrication and heat transfer, the effects of BaO and Li₂O on basic characteristics of CaO-SiO₂ based mold fluxes were studied by hemispherical melting temperature instrument, rotating cylinder method, X-ray diffractometer (XRD) in present study. The results show that the melting temperature and viscosity at 1300°C all represent a downward trend with BaO and Li₂O enhancement at different basicity, and the break temperature decrease with BaO addition while decrease and then increase with Li₂O addition, which illustrates that Li₂O content should be no more than 0.8 wt% for the purpose of lubrication. Meanwhile, to ensure a sufficient thickness of the liquid slag film and avoid discontinuity of the liquid slag film, the BaO content is better to be 10 wt% with low melting temperature and viscosity. The main crystalline phase in the mold fluxes is cuspidine (3CaO·2SiO₂·CaF₂), and the crystallization ratio rises sharply when basicity increased to 1.65. For better deal with the contradiction of lubrication and heat transfer, the mold fluxes composition w(BaO) = 10 wt%, w(Li₂O) = 0.8 wt%, R ≥1.65 is reasonable, which has a profound impact on high crystallization and lubricity mold fluxes.

Keywords: mold fluxes; lubrication; heat transfer

1. Introduction

At the end of 1980s, in order to enhance the production efficiency of continuous casting, the development and research of high-speed continuous casting process demonstrated by thin slab continuous casting and rolling technology started in the world [1-3]. Compact Strip Production (CSP) has received extensive attention due to its highly compact design, low cost, and low energy consumption [4]. As a key functional material and important technology in thin slab continuous casting, mold fluxes can prevent molten steel from oxidation, absorb inclusions, insulate heat, lubricate slab, and control heat transfer [5]. The mold fluxes will flow into the gap between the slab and the copper wall after melting, forming a solid slag film and a liquid slag layer. The solid slag film is formed near the mold wall to control the transverse heat transfer [6-7], and the liquid slag film is formed near the strand shell, of which the thickness impacts the lubrication effect. Therefore, the heat transfer and lubrication behavior of mold fluxes directly affect the smooth running of continuous casting and product quality [8-9].

With the development of CSP thin slab continuous casting and the increase of casting speed, the contradiction between lubrication and heat transfer of traditional mold flux for crack-sensitive steel is more and more difficult to reconcile. A lot of research have been carried out that one of the commonly used methods is to upgrade the crystallization characteristics of mold fluxes, which weaken the heat flux density from solidified shell to the mold wall, so as to alleviate longitudinal crack on the slab surface [10-11]. P. Tang et al. [12] illustrated that the chemical composition and cooling rate of mold fluxes have important effects on the heat flux through the mold fluxes film, and the basicity of mold fluxes for crack sensitive steel should be designed above 1.4 with lowest heat flux, and the F⁻ content influences the heat transfer and lubrication of slag film by affecting the crystallization characteristics. Tylor et al. [13] showed that increasing the crystallization rate of solid slag film can reduce the heat flow and thermal gradient, which is beneficial to reduce the longitudinal crack of slab. Overall, the traditional design idea of mold fluxes avoiding crack is to increase the basicity (CaO/SiO₂ = 1.20~1.40) and the F⁻ content, reduce the
content of Al₂O₃ or MgO [14], and increase the precipitation of cuspidine. However, when increases basicity of mold fluxes to enhance its crystallization ability, the break temperature of mold fluxes also increases, so that the lubrication of liquid slag film deteriorates, which is easy to cause sticking breakout in actual production.

It was found that with the increase of Li₂O content below 1.5 wt%, the critical cooling rate of mold fluxes is decreased, which inhibits crystallization and improve the lubrication characteristics of mold fluxes [15]. However, H. Liu et al. [16] studied the crystallization performance of CaO-SiO₂-based mold fluxes containing Li₂O, and found that the crystallization speed increase with the Li₂O addition. M.D. Seo et al. [17] showed that with Li₂O addition, the crystallization temperature of mold flux decrease. Z. Piao et al. [18] stated that with the increase of BaO content, both the viscosity and break temperature show a decreasing trend. G.R. Li et al. [19] found that BaO can reduce the viscosity and melting temperature of mold fluxes. J. Weng [20] put forward the technological route of mold fluxes with high crystallization and lubricity, which has achieved industrial production with good effect, in the high-speed continuous casting of hypoperitectic steel and thin slab of medium carbon steel. B.Y. Zhai et al. [21] suggested that mold fluxes with \( \eta_{1300°C} \leq 0.086 \text{ Pa·s} \) could be applied for high casting speed (3.5 m/min) of medium carbon steel, while to avoid slab defects caused by excessive heat transfer caused by high casting speed, it is necessary to adopt mold fluxes with more uniform and stronger heat control ability.

In recent years, some studies have shown [15] that ultra-high basicity mold fluxes, which have strong crystallization ability, and the break temperatures were not too high to assure lubrication, can better overcome the contradiction between lubrication and heat transfer. Therefore, the effects of BaO and Li₂O on the properties of mold fluxes were studied, and the composition ranges of mold fluxes with high crystallization and lubricity were obtained, which has significance for optimization of CSP continuous casting production technology.

2. Materials and methods

2.1. Experimental materials

The designed compositions of samples are listed in Table 1. The experimental samples were prepared with chemical reagents of CaCO₃, SiO₂, Al₂O₃, CaF₂, Na₂CO₃, Li₂CO₃, Fe₂O₃ and BaCO₃. Each sample with 250 g were fully mixed and put into a graphite crucible in the induction furnace for pre-melting.

2.2. Viscosity measurement

In this study, the viscosity was measured by rotating cylinder method with MTLQ-ND-6 sensor high-temperature viscosity measurement system and Brookfield DV-II (Brookfield Inc., USA) viscometer. The equipment shown in Fig. 1 consists of a resistance furnace with MoSi₂ heating elements, high-purity alumina tubes, two thermocouples, and so on. The error range of temperature is within ±5°C. Before the measurements, the standard castor oil was used to calibrate the viscometer owing to its known viscosity values at different temperature. The prepared sample (250 g) was poured into a graphite crucible, heated to 1300°C at 10°C/min, and kept isothermally for a while to ensure the temperature stability and chemical homogenization of the sample. Then the viscosity-temperature curve was measured by cooling down at 6°C/min (rotating speed 12 r/min).

2.3. Hemisphere melting point test

Measurement of hemispherical melting temperature is as the industry standard of mold flux. 50 g of pre-melted slag was taken and ground to less than 0.074 mm. Then, mixing the slag powder with absolute ethanol and pressing it into a 3 × 3 mm cylinder for shape. After dried on a corundum spacer, the sample was measured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO/SiO₂</th>
<th>BaO</th>
<th>Li₂O</th>
<th>Na₂O</th>
<th>F⁻</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>1.25–1.85</td>
<td>5–15</td>
<td>0.8–1.2</td>
<td>6</td>
<td>10.5</td>
<td>4</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Step</td>
<td>0.1</td>
<td>5</td>
<td>0.4</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>
was sent into the furnace for testing (heating rate 15°C/min). The sample was measured multiple times and the hemisphere melting temperature was averaged to eliminate errors.

### 2.4. XRD measurement

In order to identify the precipitated crystallizes in the mold fluxes, the air-cooled slag was ground to below 0.074 mm, and tested by an X-ray diffractometer (Bruker Advance D8) with Cu Kα radiation (1.54184 Å). The XRD data were collected in a range of 2θ = 10 to 90 deg with a rate of 2 deg/s.

### 2.5. Crystallization ratio measurement

The mold fluxes were heated to 1300°C, kept for 5 minutes, and then quickly poured into a stainless-steel tank for air cooling. After the condensed slag sample was taken out, the fracture morphology was observed.

Using a ruler to measure the thickness of crystals and glass, the crystal ratio $R_p$ is:

$$R_p = \frac{\sum_{i=1}^{n} \frac{d_i}{d_i} \times 100\%}{n}$$

where $R_p$ is the crystallization ratio (%); $d_i$ is the crystal thickness measured at position $i$ (mm); $d_i$ is the total thickness of the slag sample measured at position $i$ (mm); $n$ is the total number of measurement positions for each thickness, $n = 1, 2, 3, \cdots, 10$.

### 2.6. Break temperature confirmation

Take a sample as an example. According to the Arrhenius equation [22],

$$H = A \exp\left(\frac{E}{RT}\right)$$

where $A$ is the Arrhenius constant, $E$ is the activation energy for viscous flow, $R$ is the gas constant, and $T$ is the absolute temperature. Taking the natural logarithm of both sides of Eq. (1) to determine the abrupt change in viscosity [23],

$$\ln \eta = \ln A + \frac{E}{RT}$$

Then, by plotting $10^4/T$ versus $\ln \eta$. As shown in Fig. 2, in a given temperature range, the slope $E/R$ is constant and the intercept is $\ln A$. The temperature corresponding to the sudden change in viscosity is the break temperature.

### 3. Results and discussion

#### 3.1. Effects of BaO and Li$_2$O on viscosity at 1300°C of mold fluxes

It can be seen from Fig. 3 that the viscosity at 1300°C shows a downward trend with BaO or Li$_2$O addition at different basicity. The reason is that both BaO and Li$_2$O are alkaline metal oxides, which are extremely alkaline and can dissociate Ba$^{2+}$ ions, Li$^+$ ions and O$^{2-}$ ions. The electrostatic potential of Ba$^{2+}$ ions is smaller than that of Ca$^{2+}$ ions, and the radius of Li$^+$ ions is smaller, both of them have weak binding ability to O$^{2-}$ ions, which can dissociate O$^{2-}$ ions and can depolymerize slag structure [24]. In addition, Li$^+$ has a strong effect on oxygen ion polarization and deformation of Si-O bond, and it is easy to form defects and asymmetric centers in the slag network structure, leading to a decrease in the viscosity of mold fluxes. Since too little viscosity will affect the continuity of liquid slag film, the suitable content of BaO and Li$_2$O should not be too much.

#### 3.2. Effects of BaO and Li$_2$O on hemispherical melting point of mold fluxes

Fig. 4 shows the effect of BaO and Li$_2$O on the melting point of mold fluxes. The melting point, which ranges from 1003 to 1157°C, decreases obviously with BaO and Li$_2$O addition at different basicity. As stated before, BaO and Li$_2$O are network modifiers, and the M-O bond strength is small (M = Ba, Li),
Fig. 3. Effects of BaO and Li$_2$O on viscosity at 1300°C of mold fluxes

Fig. 4. Effects of BaO and Li$_2$O on melting point of mold fluxes
which can provide non-bridging oxygen ions in the slag, destroy the silicate network chain structure, and reduce the melting point of the mold slag [25]. To ensure adequate liquid slag layer, it is better for the melting temperature of mold fluxes to be lower. Considering the cost together, it is more appropriate when \( w(\text{BaO}) = 10 \text{ wt\%} \) and \( w(\text{Li}_2\text{O}) = 0.8 \text{ wt\%} \).

### 3.3. Effects of \( \text{BaO} \) and \( \text{Li}_2\text{O} \) on break temperature of mold fluxes

The break temperature is an important property parameter of mold fluxes, which corresponding to the temperature at which the viscosity of the system increases sharply at a certain cooling rate [26]. This occurs because the crystal phases precipitate in large quantities at this temperature, and the molten slag exhibits non-Newtonian flow behaviors when the temperature is below break temperature, according to Sridhar et al. [11] It can be observed form Fig. 5 that the break temperatures of slags are in the range of 1109~1239°C. The viscosity-temperature curves with varied basicity are given in Fig. 6. The slag system shows strong alkaline that the viscosity keeps unchanged with temperature drop before the break temperature and rises sharply after arriving at the break temperature.

At different basicity, it can be seen from Fig. 5(a)(b) that when the \( \text{Li}_2\text{O} \) content is constant, the break temperature decreases with \( \text{BaO} \) enhancement. From Fig. 5(c)(d), it can be concluded that with the increase of \( \text{Li}_2\text{O} \) content, the break temperature decreases first and then increases. Probably because when the \( \text{Li}_2\text{O} \) content increases from 0.8 wt% to 1.2 wt%, the structure of the mold fluxes becomes more complicated, resulting in the break temperature rises.

![Fig. 5. Effect of \( \text{BaO} \) and \( \text{Li}_2\text{O} \) on break temperature of mold fluxes](image1)

![Fig. 6. Viscosity-temperature curves for testing](image2)
As shown in Fig. 7, when the basicity is 1.35, the crystalline phase is cuspidine, while when the basicity is 1.75, the crystalline phase is transformed (3CaO·2SiO2·CaF2 → Ca2SiO4), so that the composition of mold fluxes has deviated from the crystallizing area of the cuspidine, resulting in a decrease in the break temperature [15]. On the whole, the break temperature in this paper is generally within a suitable range. To ensure sufficient thickness of the liquid slag layer and provide support for the coordination of lubrication and heat transfer, the break temperature of samples with 0.8 wt% Li2O is more appropriate.

3.4. Effects of BaO and Li2O on crystallization of mold fluxes

Fig. 7 shows the XRD analysis results of the slag samples. When the basicity is 1.35, the crystalline phase precipitated in mold fluxes is mainly 3CaO·2SiO2·CaF2, and other crystalline phases are precipitated at ultra-high basicity of 1.75, which leads to a sharp increase in the crystallization ratio shown in Fig. 8. From Fig. 8(a)(b), at medium and high basicity in the range of 1.25−1.65, when the Li2O content is constant, the crystallization ratio decreases with BaO addition, while from Fig. 8(c)(d), the crystallization ratio does not change significantly with Li2O enhancement. Overall, at basicity of 1.25−1.65, with the change of BaO and Li2O content, the crystallization ratio is basically stable below 50%, and at ultra-high basicity (R ≥ 1.65), the crystallization ratio rises sharply, which is very effective for mold fluxes to control heat transfer. Combing Fig. 5, Fig. 6 and Fig. 8, it can be concluded that when the basicity is 1.65−1.85, the break temperature is low to ensure lubrication and the crystallization ratio is high to control heat transfer, so that to coordinate lubrication and heat transfer well.

As a whole, to meet the requirements for thin slab continuous casting, the properties of mold fluxes including low melting temperature to ensure slag consumption, relatively low viscosity to avoid discontinuity of liquid slag film, relatively low break temperature to ensure a sufficient thickness of the liquid slag film for lubrication and high crystallization ratio in solid slag film for heat transfer control, the mold fluxes components with 10 wt% BaO, 0.8 wt% Li2O and R ≥ 1.65 are more reasonable, which has a profound impact on high crystallization and lubricity mold fluxes.

4. Conclusion

1) The properties of mold fluxes changes with various BaO and Li2O content at different basicity, including the melting
temperature in the range of 1003~1157°C, the viscosity at 1300°C in the range of 0.01~0.08 Pa·s, the break temperature in the range of 1109~1239°C, and the crystalline mineral phase is mainly 3CaO · 2SiO2 · CaF2.

2) With BaO and Li2O addition, the viscosity at 1300°C and melting temperature show a downward trend at different basicity, and the break temperature decrease with BaO addition while decrease and then increase with Li2O addition.

3) At basicity of 1.25~1.65, with the change of BaO and Li2O content, the crystallization ratio is basically stable below 50%, and at ultra-high basicity (R ≥ 1.65), the crystallization ratio rises sharply.

4) Considering all the properties, the mold fluxes components \( w(\text{BaO}) = 10 \text{ wt\%} \), \( w(\text{Li}_2\text{O}) = 0.8 \text{ wt\%} \), and \( R ≥ 1.65 \) are more suitable for continuous casting of thin slab casting.

Acknowledgements

The authors would like to deeply appreciate the fund support from the Natural Science Foundation of Anhui Provincial Education Department (KJ2021A0358) and the College Students Innovation and Entrepreneurship Training Program in Anhui University of Technology (2021008Y).

REFERENCES


DOI: https://doi.org/10.1179/174328105X15788

DOI: https://doi.org/10.1016/S0040-6031(02)00175-2

DOI: https://doi.org/10.1179/030192302225004133

DOI: https://doi.org/10.1179/030192300677534

DOI: https://doi.org/10.1179/174328112Y.000000006

DOI: https://doi.org/10.1179/030192300677534

DOI: https://doi.org/10.1016/S1006-706X(08)60135-1


DOI: https://doi.org/10.2355/isijinternational.49.843

DOI: https://doi.org/10.1007/s11663-014-0091-2

DOI: https://doi.org/10.1016/j.jnoncrysol.2020.120111

DOI: http://doi.org/10.13228/j.boyuan.issn1006-706x.2003.03.049


DOI: https://doi.org/10.1016/b978-0-08-096986-2.00008-4

DOI: https://doi.org/10.1080/03019233.2018.1552773

DOI: https://doi.org/10.1111/jace.15559


DOI: https://doi.org/10.1007/s11663-011-9512-7