Influences of Li_2O on the Properties of Ultrahigh-Basicity Mold Fluxes for Continuous Casting of Peritectic Steel

Min Li, Yuan bing Wu, Sheng ping He, Qiang qiang Wang and Qian Wang

Abstract The ultrahigh-basicity $(R = 1.75)$ mold flux has been proved to be effective in coordinating heat transfer and lubrication during continuous casting of peritectic steel in industry, Properties of the mold flux may be further improved through the adjustment of the Li_2O content in the flux. The effects of Li_2O content on the properties of ultrahigh-basicity mold flux were systematically investigated. With the increase of the Li_2O content from 0.8 to 2.4%, the viscosity of the ultra-high basicity mold flux at the temperature of 1573 K increased and then decreased, and the maximum viscosity was 0.148 Pa·s at the Li_2O content of 2.0%. With the increase of the Li_2O content from 0.8 to 2.4%, the break temperature was reduced from 1484 to 1435 K, the initial crystallization temperature, which was measured by an in-house apparatus, could decline by approximately 100 K with 2.4% Li_2O addition while the crystallization rate represented an increasing trend except for the case with 2.0% Li_2O. This study enhances the understanding of specified mold flux for peritectic steel.

Keywords Ultrahigh-basicity mold flux · Li_2o · Viscosity · Crystallization properties

Introduction

Mold fluxes have been indispensable metallurgical material in the continuous casting process since they appeared in the 1960s. They are critical to ensure continuous casting and improve the surface quality of slab. The most important function of mold fluxes is to control the heat transfer as well as lubricate solidified shells [1–4]. The realization of these functions is highly related to the viscosity, the melting temperature and the crystallization properties of the slag [2, 5]. Longitudinal cracks

M. Li · Y. Wu · S. He (✉) · Q. Wang · Q. Wang
College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China
e-mail: heshp@cqu.edu.cn

Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and New Materials, Chongqing 400044, China

often occurred on the slab surface of peritectic steel with the carbon content of 0.08–0.16% of continuous casting, resulting from the peritectic reaction with 4.7% volume contraction [6, 7]. The ultra-high basicity mold flux (R = 1.75) with low break temperature and rapid crystallization rate has been developed to reduce the occurrence of longitudinal cracks [8, 9]. The improvement of the heat transfer and lubrication of the ultra-high basicity mold flux was related to the Li_2O addition into the flux. In general, Li_2O was a kind of alkaline metal oxide which could significantly reduce the melting temperature and the viscosity [9, 10]. Besides, it also deeply affected the crystallization behavior of mold flux. However, to date, only a few studies concentrate on Li_2O, especially with respect to its crystallization. In a study employing the double hot thermocouple technique (DHTT), Lu [11] found that the Li_2O can suppress crystallization via decreasing the initial crystallization temperature in the $CaO-Al_2O_3$ mold fluxes for the casting of high-Al steels. On the contrary, Yang [12] determined that the Li_2O can enhance the crystallization capability by improving the crystallization fraction in a $CaO-SiO_2-Al_2O_3$ mold flux with 8% Na_2O through differential scanning calorimetry (DSC) measurements. MYUNG-DUK SEO [13] reported that the initial crystallization temperature decreased with Li_2O addition in $CaO-SiO_2-Al_2O_3-Na_2O-CaF_2-Li_2O$ mold fluxes. It was demonstrated that the influences of Li_2O were complex in various mold fluxes. Therefore, it is necessary to systematically investigate the influence of Li_2O on the properties of ultrahigh-basicity mold fluxes.

Experimental Apparatus and Procedures

Materials

Five mold fluxes with different Li_2O content were investigated. All the fluxes were prepared by melting pure chemical reagents ($CaCO_3$, SiO_2, CaF_2, Na_2O, Li_2CO_3 MgO, Al_2O_3, Fe_2O_3). The basicity of mold fluxes were approximately 1.75, and the Li_2O content was within 0–2.4%. In order to resemble the condition in steel plant, some Fe_2O_3 was added into the five mold fluxes, whose specific compositions were shown in Table 1.

Table 1 Chemical composition of mold fluxes (wt%)

Mold flux	CaO	SiO_2	Na_2O	Li_2O	F^-	Al_2O_3	MgO	Fe_2O_3
CSF 1	34.54	28.61	6	0	10.5	4	3	1.5
CSF 2	34.03	28.32	6	0.8	10.5	4	3	1.5
CSF 3	33.52	28.03	6	1.6	10.5	4	3	1.5
CSF 4	33.78	28.17	6	2.0	10.5	4	3	1.5
CSF 5	34.29	28.46	6	2.4	10.5	4	3	1.5

Experimental Methods

(1) In the current study, the viscosity, the break temperature, and the melting temperature of the ultra-high basicity mold flux were measured through the rotating cylinder method [8], and hemisphere point method [8], respectively.

(2) The crystallization properties of ultrahigh-basicity mold fluxes were investigated by digital optical microscopy with an isolated observation system in an infrared furnace (IR-MOP). As shown in Fig. 1, a halogen lamp was applied to heat the sample. The crystallization process was recorded by digital microscopy with a wide field of view. The equipment can effectively avoid the volatilization of fluorides with a quartz glass over the platinum crucible. Besides, the ToupView software can adjust the color, contrast, and brightness of the images in a suit to avoid the high temperature irradiation interference.

In every experiment, a 6–80 mg mold powder from the mold flux CSF 1–CSF 5 was heated through the IR-MOP apparatus to 1300 °C at the heating rate of 10 °C/s and held for 60 s to eliminate bubbles and homogenize the chemical composition. Then, the sample was cooled to room temperature at the rate of 1, 2, 3, 4 °C/s. The phase transformation from molten to the crystalline state was observed and recorded via the CCD camera. The temperature of sample was monitored and recorded using the temperature acquisition system. The image processing software Photoshop was used to measure the crystallinity of the flux. Afterwards, based on the relationships among the temperature, time, and phase fraction a CCT diagram was constructed. At the 5% degree of crystallinity, the corresponding temperature was defined as the initial crystallization temperature. When the degree of crystallinity reached 85%, the corresponding temperature was defined as the end of crystallization temperature.
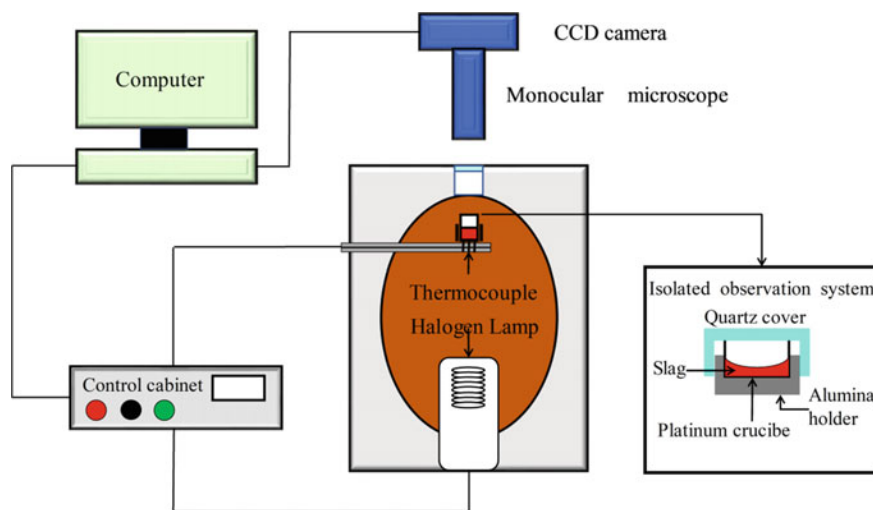

Fig. 1 Schematic of experimental devices

Results and Discussion

In Figure 2, the viscosity-temperature curves of ultra-high basicity mold fluxes with different Li_2O contents was shown. The viscosity at 1300 °C, the break temperature and the melting temperature were recorded in Table 2, with the increase of Li_2O content in the mold fluxes from 0 to 2.4%, the viscosity at 1300 °C increased from 0.034 to 0.148 Pa s and then decreased to 0.109 Pa s. The break and the melting temperatures decreased from 1232 °C to 1162 °C and 1192 °C to 1068 °C, respectively.

The CCT diagrams from the relationship among the temperature, time and crystallization fraction of CSF1–CSF5 was shown in Fig. 3. With the increase of the Li_2O content from 0 to 2.4%, at the cooling rate of 1 °C/s, the initial crystallization temperatures were 1225 °C, 1173 °C, 1155 °C, 1145 °C, and 1116 °C, respectively. At the higher cooling rate, namely 4 °C/s, the initial crystallization temperatures were 1194 °C 1161 °C, 1143 °C, 1114 °C, and 1060 °C, respectively. With the gradual increase of Li_2O by 0.8%, the initial crystallization temperature decreased on average by 42 °C. Additionally, with the increase of the cooling rate, the decrease of the initial crystallization temperature was also observed. This observation was related to the high viscosity and iron migration resistance in mold fluxes as a function of

Fig. 2 Viscosity-temperature cures of ultra-high basicity mold fluxes with different Li_2O contents
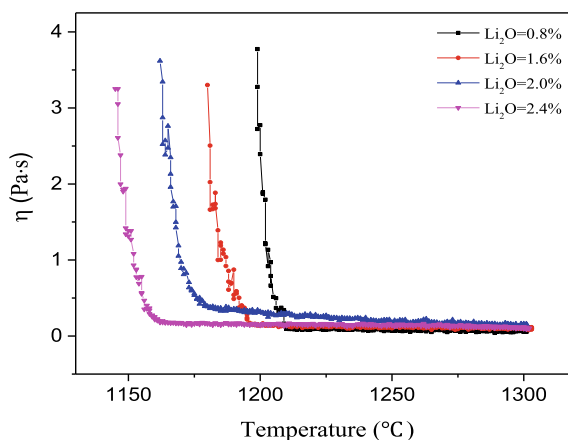
Table 2 Viscosity (1300 °C) and break temperature of ultra-high basicity mold fluxes

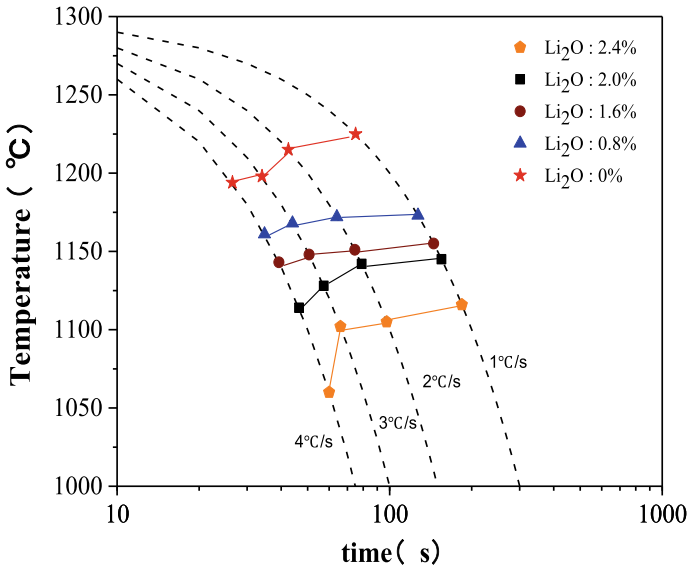| Mold flux	Viscosity/(Pa·s)	Break temperature/°C	Melting temperature/°C
CSF 1	0.034	1232	1192
CSF 2	0.062	1211	1134
CSF 3	0.104	1196	1098
CSF 4	0.148	1180	1072
CSF 5	0.109	1162	1068

Fig. 3 CCT diagrams of Ultra-high basicity mold fluxes with different Li$_2$O contents

decreased temperature. Therefore, the formation of crystals required a large degree of undercooling.

The crystallization process is related to both nucleation and crystal growth rate, relationships of temperature, and the degree of undercooling. Therefore, the detailed kinetics analysis is discussed below in the next chapter.

Analysis Through Avrami Equation

Avrami equation [14] has been widely used in the study of crystallization kinetics of mold fluxes. The theory is based on the assumption that the non-isothermal crystallization process which has a constant cooling rate can be approximated as an isothermal crystallization process. The specific equation is:

$$\ln[-\ln(1 - X(t))] = \ln Z_t + N_A \ln t \tag{1}$$

where $X(t)$ represents the relative crystallinity at a given time, Z_t is the compound crystallization rate constant, and N_A is the Avrami exponent. The relative crystallinity and the compound crystallization rate are related to the temperature, the rate of nucleation, and crystal growth. The value of N_A was the slope from the plots of $\ln[-\ln(1-X(t))]$ versus $\ln t$.

Plots of $\ln[-\ln(1-X(t))]$ and $\ln t$ with different Li$_2$O contents in ultra-high basicity mold fluxes are demonstrated in Fig. 4. It should be mentioned that, the plots based on
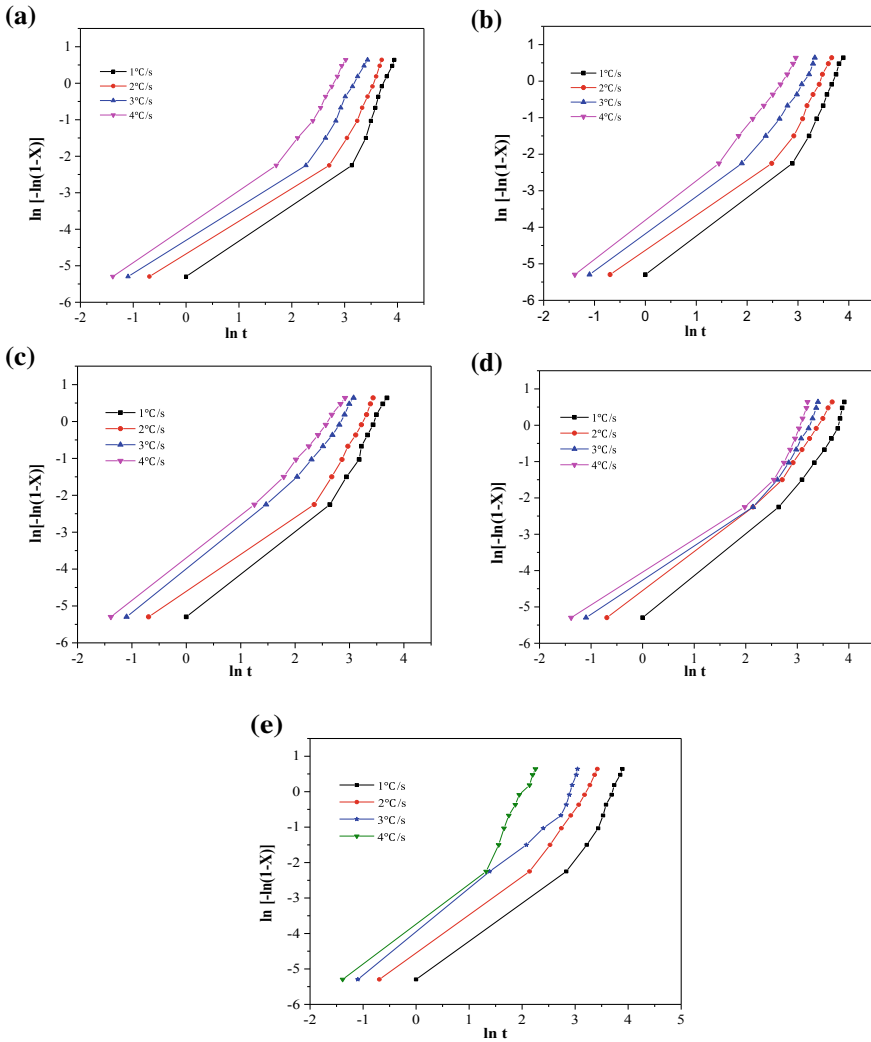
Fig. 4 Plots between ln[-ln(1-$X(t)$)] and ln$t$ with different Li$_2$O content of **a** 0%, **b** 0.8%, **c** 1.6%, **d** 2.0% and **e** 2.4% under different cooling rates

the Avrami equation are not linear, which verified the inappropriateness of Avrami equation in describing the non-isothermal crystallization process of mold fluxes. However, it does not affect the calculation that Avrami exponent. Actually, N_A is a function of crystallinity, temperature, and the cooling rate in the non-crystallization process. Therefore, compared with the isothermal crystallization, it does not have physical meaning. However, it can be employed to obtain the non-isothermal crystallization kinetics parameter No, associated with the m value in the Mo equation [14]. Besides, there is a positive correlation between No and the crystallization rate, the

higher the No, the faster the crystallization speed and the stronger the crystallization ability.

Analysis Through Mo Equation

The Mo equation [14] is also commonly employed in non-isothermal analysis of mold flux.

$$\ln \Phi \;=\; \ln F(T) - m \ln t \tag{2}$$

where Φ is the cooling rate, and $F(T)$ is the crystallization rate constant. The crystallization rate constant is related to both the crystallinity and the cooling rate and has a negative correlation with the crystallization rate, which means the higher the *No*, the slower the crystallization speed and the weaker the crystallization ability. The *No* mentioned above can be obtained by m = N_A/N_O. The relationships between lnΦ and ln$t$ of CSF1–CSF5 were presented in Fig. 5. All plots show a good linear relationship between lnΦ and ln$t$, which verifies the applicability of the Mo equations in describing the non-isothermal crystallization process of ultrahigh basicity mold fluxes.

Relationships between crystallization fraction and ln$F(T)$ as well as, crystallization fraction and *No* from Mo equation are shown in Figs. 6 and 7, respectively. Figure 6 shows that with the increase of Li$_2$O content from 0 to 2.4%, the ln$F(T)$ increased and then decreased, reaching the maximum at the Li$_2$O content of 2.0. It was indicated that the Li$_2$O could suppress the crystallization with the addition of less than 2.0%. The non-isothermal crystallization kinetic parameter *No* firstldecreased with the content of Li$_2$O below 2.0%, and then increased rapidly when the content exceeded 2.0%. Therefore, the opposite trends between ln$F(T)$ and N_O indicated similar results.

Conclusions

Effects of the Li$_2$O content on properties of ultra-high basicity mold fluxes were systematically investigated. The viscosity at 1300 °C, the break and the melting temperatures, as well as, the crystallization properties were measured. Results are summarized as follows:

(1) With the increase of Li$_2$O content in mold fluxes from 0 to 2.4%, the viscosity at 1300 °C increased from 0.034 to 0.148 Pa s and then decreased to 0.109 Pa s. The break temperature decreased from 1232 to 1162 °C, and the melting temperature from 1192 to 1068 °C.
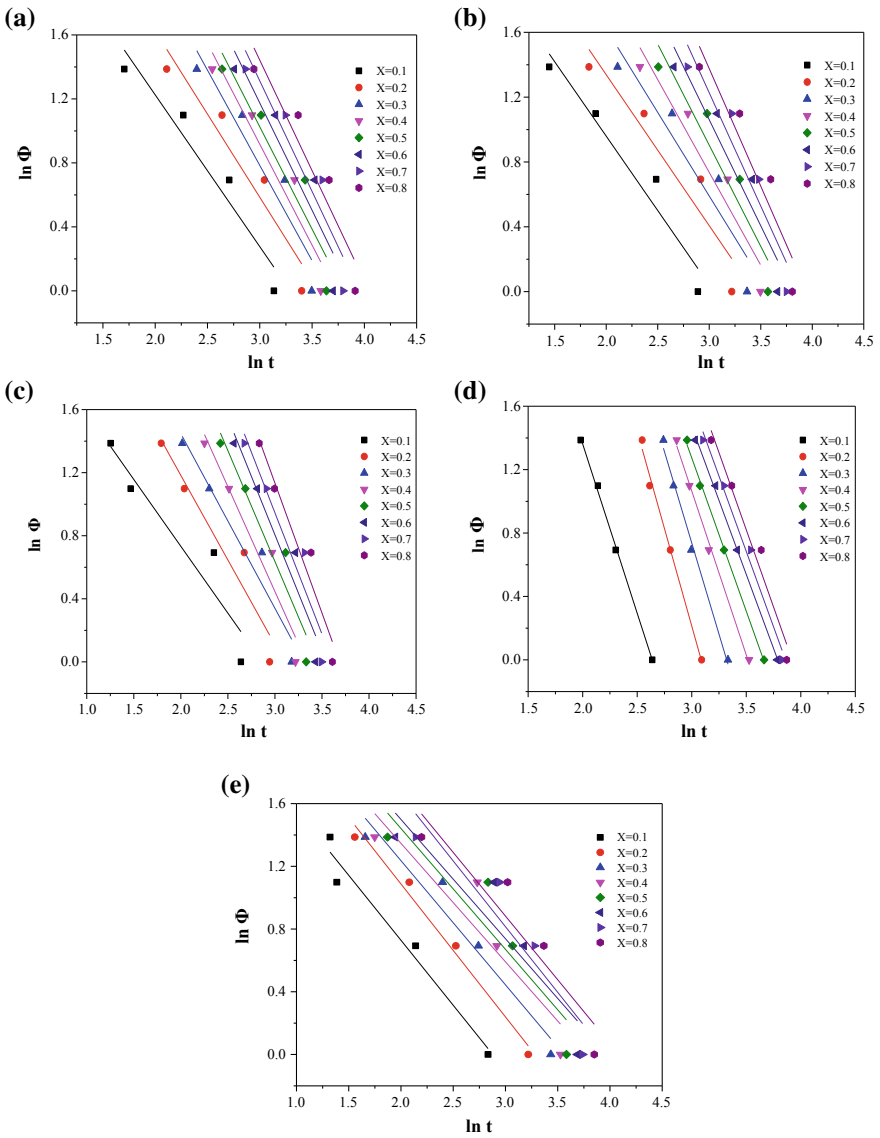
Fig. 5 Relationship between lnΦ and ln*t* for non-isothermal crystallization of different Li₂O contents in ultra-high basicity mold fluxes

(2) With the increase of the Li₂O content from 0 to 2.4%, at the cooling rate of 1 °C/s, the initial crystallization temperatures were 1225 °C, 1173 °C, 1155 °C, 1145 °C, and 1116 °C, respectively. At the cooling rate of 4 °C/s, the initial crystallization temperatures decreased from 1194 to 1060 °C. With the gradual

Fig. 6 Non-isothermal crystallization kinetic parameter ln$F(T)$ based on M$_O$ equation of ultra-high basicity mold fluxes of CSF1–CSF5
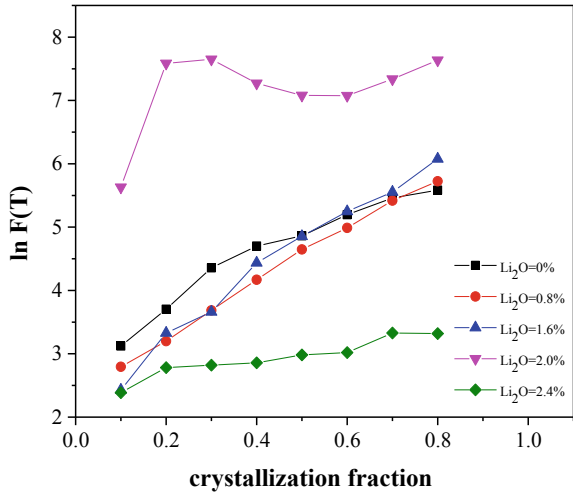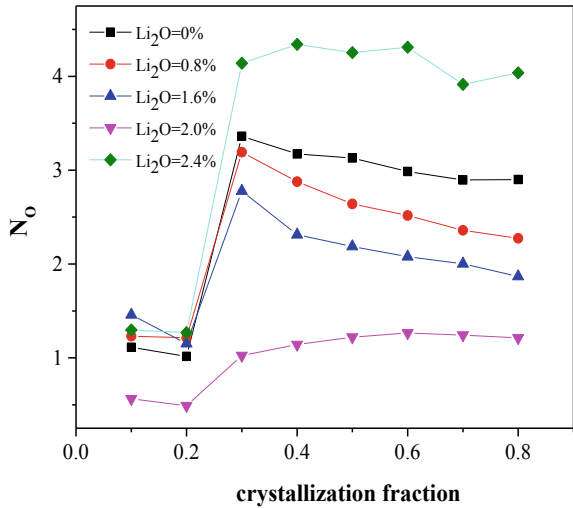

Fig. 7 Non-isothermal crystallization kinetic parameter No based on M$_O$ equation of ultra-high basicity mold fluxes of CSF1–CSF5

increase of Li$_2$O by 0.8%, the initial crystallization temperature decreased in average by 42 °C.

(3) The non-isothermal crystallization kinetic parameter ln$F(T)$ and *No* were obtained by Mo equation which is associated with the Avmavi equation. The ln$F(T)$ increased with the Li$_2$O content from 0 to 2.0%. However, the *No* decreased when Li$_2$O content was less than 2.0%. The results *No* and ln$F(T)$ showed that the Li$_2$O can suppress the crystallization when the Li$_2$O content was below 2.0%, On the other hand, the higher Li$_2$O content (>2.0%) has promoted the crystallization.

References

1. Mills KC, Däcker CÅ (2017) The casting powders book. Springer, Berlin
2. Mills KC, Fox AB (2003) The role of mould fluxes in continuous casting so simple yet so complex. ISIJ Int 43(10):1479–1486
3. Mills KC et al (2013) Performance and properties of mould fluxes. Ironmaking Steelmaking 32(1):26–34
4. Nakada H, Nagata K (2006) Crystallization of CaO–SiO$_2$–TiO$_2$ slag as a candidate for fluorine free mold flux. ISIJ Int 46(3):441–449
5. Shaoda Z, Li M, Lilong Z (2019) Effect of substituting Na$_2$O for SiO$_2$ on the non-isothermal crystallization behavior of CaO-BaO-Al$_2$O3 based mold fluxes for casting high Al steels. Ceram Int 45(9):11296–11303
6. Gu S, Wen G, Ding Z (2018) Effect of shear stress on isothermal crystallization behavior of CaO-Al$_2$O$_3$-SiO$_2$-Na$_2$O-CaF$_2$ slags. Materials (Basel) 11(7)
7. Xu J, He S, Wu T (2012) Effect of elements on peritectic reaction in molten steel based on thermodynamic analysis. ISIJ Int 52(10):1856–1861
8. Long X, He SP, Xu JF (2012) Properties of high basicity mold fluxes for peritectic steel slab casting. Ironmaking Steelmaking 19(7):39–45
9. Long X, Wang Q, He S (2017) Structure evolution of slag films of ultrahigh-basicity mold flux during solidification. Metall Mater Trans B 48(4):1938–1942
10. He MY, Wang Q, Hu B (2016) Application of high-basicity mould fluxes for continuous casting of large steel slabs. Ironmaking Steelmaking 43(8):588–593
11. Lu B, Chen K, Wang W (2014) Effects of Li$_2$O and Na$_2$O on the crystallization behavior of lime-alumina-based mold flux for casting high-al steels. In: Minerals, metals materials society and ASM international 2014, vol 45B, pp 1496–1509
12. Yang C, Wen G, Tang P (2015) Effect of Li$_2$O on crystallization of mold fluxes for continuous casting of high aluminum steel. ICS
13. Seo M-D et al (2014) Crystallization behaviors of CaO-SiO$_2$-Al$_2$O$_3$-Na$_2$O-CaF$_2$-(Li$_2$O-B$_2$O$_3$) mold fluxes. Metall Mater Trans B 45(5):1874–1886
14. Shi CB, Seo MD, Wang H (2014) Crystallization kinetics and mechanism of CaO–Al$_2$O$_3$-based mold flux for casting high-aluminum TRIP steels. Metall Mater Trans B 46(1):345–356