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Influence of substituting B₂O₃ with Li₂O on the viscosity, structure and crystalline phase of low-reactivity mold flux

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Abstract: The low-reactivity mold flux with low SiO₂ content is considered suitable for the continuous casting of high-aluminum steel since it can significantly reduce the reaction between Al in steel and SiO₂ in mold flux. However, the traditional low-reactivity mold flux still presents some problems such as high viscosity and strong crystallization tendency. In this study, the co-addition of Li₂O and B₂O₃ in CaO–Al₂O₃–10wt%SiO₂ based low-reactivity mold flux was proposed to improve properties of mold flux for high-aluminum steel, and the effect of Li₂O replacing B₂O₃ on properties of mold flux was investigated. The viscosity of the mold flux with 2wt% Li₂O and 6wt% B₂O₃ reached a minimum value of 0.07 Pa·s. The break temperature and melting point showed a similar trend with the viscosity. Besides, the melt structure and precipitation of the crystalline phase were studied using Raman and X-ray diffraction spectra to better understand the evolution of viscosity. It demonstrated that with increasing Li₂O content in the mold flux from 0 to 6wt%, the degree of polymerization of aluminate and the aluminosilicate network structure increased because of increasing Li⁺ released by Li₂O, indicating the added Li₂O was preferentially associated with Al³⁺ as a charge compensator. The precipitation of LiAlO₂ crystalline phase gradually increased with the replacement of B₂O₃ by Li₂O. Therefore, Li₂O content should be controlled below 2wt% to avoid LiAlO₂ precipitation, which was harmful to the continuous casting of high-aluminum steels.

Keywords: low-reactivity mold flux; viscosity; structure; crystalline phase

1. Introduction

High-aluminum steel contains 0.5wt%–2.5wt% dissolved aluminum [1], which is widely used in automotive, shipping, and other fields because of its lightweight, high strength, and good plasticity. However, the continuous casting process of high-aluminum steel is restricted by the steel–slag interface reaction [2–3]. The reactive CaO–SiO₂-based mold flux brings difficulty in avoiding the strong reaction at the steel–slag interface between Al and SiO₂ [4–8]. As a result, the viscosity of mold flux increases, the surface quality of the slab reduces, and the smooth continuous casting process harms [9–10]. Street *et al.* [11] proposed a nonreactive CaO–Al₂O₃-based mold flux without SiO₂ to prevent the interface reaction. However, it greatly lowered glass properties and increased the crystallization tendency of the mold flux. Therefore, for a long time, reactive and nonreactive mold fluxes were barely used to cast high-aluminum steel continuously. Afterwards, the low-reactivity mold flux with a certain amount of SiO₂ was proposed, which helped weaken the steel–slag interface reaction and maintained glass properties of the mold flux.

Fig. 1 summarizes the reduction of SiO₂ content and the

required time for reaction equilibrium during the continuous casting of high-aluminum steel for different compositions of mold flux. When the initial SiO₂ content of the mold flux was approximately 35wt%, 18wt%, and 10wt%, more than 57%, approximately 55%, and less than 40% SiO₂ was decreased, respectively, after the equilibrium reaction between steel and mold flux. It means that the CaO–Al₂O₃–10wt%SiO₂ low-reactivity mold flux can substantially alleviate the steel–slag interface reaction.

However, the low-reactivity mold flux also presented some problems, such as high viscosity and strong crystallization tendency. Thus, most researchers tried to improve its properties by optimizing the composition of the mold flux, such as addition B₂O₃ or Li₂O. Table 1 presents the variation trend of properties for some low-reactivity mold flux with increasing B₂O₃ or Li₂O content [7, 15–16, 18–31]. It was well-known that the addition of B₂O₃ effectively improve properties of mold flux [18–23], but the excessive addition of B₂O₃ to the mold flux significantly promoted the interface reaction between Al and B₂O₃, leading to the fluctuation in mold flux properties [15–16]. Besides, a moderate amount of Li₂O in the mold flux was more obviously beneficial to lower the melting point, reduce the viscosity, and weaken the crystal-

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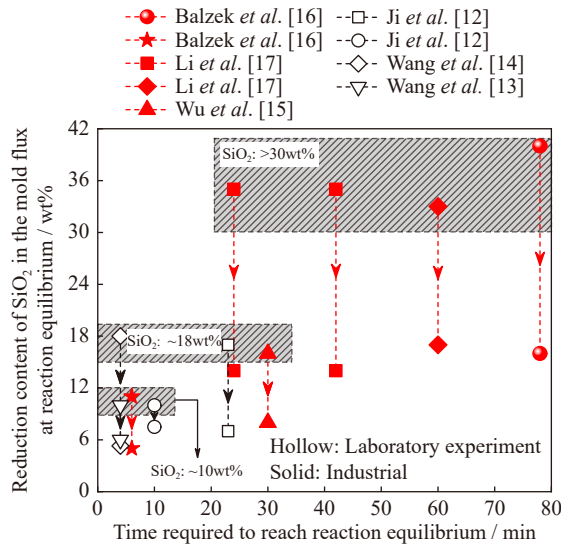


Fig. 1. Reduction content of SiO₂ and the required time for reaction equilibrium during the continuous casting of high-aluminum steel using the low-reactivity mold flux [12–17].

lization tendency [24–26], but excessive addition in the Li₂O content of the mold flux promoted the precipitation of high melting point crystalline phase LiAlO₂, which would deteriorate properties of mold flux [27–29]. It was noted that the Li₂O in the mold flux does not participate in the steel–slag reaction [7,15,30], so maybe replacing B₂O₃ with moderate Li₂O in the mold flux not only improved properties of the mold flux, but also alleviated the interface reaction between Al and B₂O₃. A few studies on substituting Li₂O for B₂O₃ in the mold flux have been reported [13,15] and a suitable content of Li₂O in the low-reactivity mold flux for LiAlO₂ formation need further research especially with different B₂O₃ contents.

In this study, the effect of substituting B₂O₃ with different Li₂O content on the viscosity, structure, and crystalline phase of a CaO–Al₂O₃–10wt%SiO₂ low-reactivity mold flux was researched systemically to obtained the best ratio of B₂O₃ and Li₂O. Besides, the crystallization behavior of Li₂O in the B₂O₃-containing CaO–Al₂O₃–10wt%SiO₂ mold flux was investigated.

2. Experimental

The mold flux was prepared using the reagent-grade powders of CaO, SiO₂, Al₂O₃, BaCO₃, CaF₂, Li₂CO₃, and B₂O₃. CaO powder was calcined at 1000°C for 5 h in a muffle furnace to decompose carbonate and hydroxide. The powders of SiO₂, Al₂O₃, BaCO₃, CaF₂, Li₂CO₃, and B₂O₃ were heated at 500°C for 2 h. Mixed powders were melted at 1400°C for 0.5 h in a graphite crucible to homogenize the chemical composition and eliminate bubbles. Ar gas with a purity of 99.999% was blown at a flow rate of 0.5 L/min. Samples were quenched in water and grounded into powders with a diameter smaller than 75 μm. The mold flux compositions were analyzed using X-ray fluoroscopy and inductively coupled plasma atomic emission spectrometry. The composition of the mold flux before and after pre-melting was almost identical, as listed in Table 2.

Rotational viscometry was used to investigate mold flux viscosity. The details of the experimental apparatus were presented in a previous study [19]. After the calibration measurement of the viscometer, a 250-g pre-melted sample was added to a graphite crucible at 1200°C in a MoSi₂ heating furnace. Samples were heated at 1300°C for 20 min to obtain a homogeneous melt under an Ar atmosphere at a flow rate of 0.5 L/min. The cylinder was slowly submerged into

Table 1. Effect of B₂O₃ and Li₂O on CaO–Al₂O₃-based mold flux properties [7,15–16,18–31]

Authors	Additive	Additive amount / wt%	Slag	Melting point	Viscosity	Crystallization	Reaction	Year
Wang et al. [18]	B ₂ O ₃	0–4	CaO–8wt%SiO ₂ –Al ₂ O ₃	↓	↓			2011
Li et al. [19]	B ₂ O ₃	8–12	CaO–Al ₂ O ₃	↓	↓	↓		2017
Yan et al. [20]	B ₂ O ₃	10–20	CaO–5wt%SiO ₂ –Al ₂ O ₃		↓			2017
Yan et al. [21]	B ₂ O ₃	10–20	CaO–5wt%SiO ₂ –Al ₂ O ₃			↓		2016
Yu et al. [22]	B ₂ O ₃	4–10	CaO–6wt%SiO ₂ –Al ₂ O ₃	↓	↓	↓		2011
Huang et al. [23]	B ₂ O ₃	0–9	CaO–6wt%SiO ₂ –Al ₂ O ₃		↓			2013
Blazek et al. [16]	B ₂ O ₃	10–16	CaO–SiO ₂ –Al ₂ O ₃				React	2011
Wu et al. [15]	B ₂ O ₃	18	CaO–SiO ₂ –Al ₂ O ₃				React	2016
Kim et al. [24]	Li ₂ O	0–4	CaO–Al ₂ O ₃		↓			2012
Wu et al. [25]	Li ₂ O	5–8	CaO–Al ₂ O ₃	↓↑	↓↑			2012
Li et al. [26]	Li ₂ O	0–8	CaO–Al ₂ O ₃			↓		2018
Qi et al. [27]	Li ₂ O	10–18	CaO–Al ₂ O ₃		↓			2017
Zhou et al. [28]	Li ₂ O	0–6	CaO–9wt%SiO ₂ –Al ₂ O ₃	↓		↓↑		2018
Lu et al. [29]	Li ₂ O	2–7	CaO–11wt%SiO ₂ –Al ₂ O ₃			↓*		2014
Qi et al. [30]	Li ₂ O	10–18	CaO–2wt%SiO ₂ –Al ₂ O ₃		↓↑	↑		2016
Wu et al. [15]	Li ₂ O	~2	CaO–5wt%SiO ₂ –Al ₂ O ₃				Non-react	2016
Yang et al. [7,31]	Li ₂ O	~2	CaO–7wt%SiO ₂ –Al ₂ O ₃				Non-react	2019

Note: ↓—decrease; ↑—increase; ↓↑—initial decrease and then increase; *—in the high temperature zone; blank indicates there are no relevant results shown in the reference; reaction means the reaction between steel and B₂O₃ or Li₂O in mold flux.

Table 2. Compositions of different mold flux

wt%

Sample	Before pre-melting							After pre-melting						
	CaO	SiO ₂	Al ₂ O ₃	BaO	CaF ₂	Li ₂ O	B ₂ O ₃	CaO	SiO ₂	Al ₂ O ₃	BaO	CaF ₂	Li ₂ O	B ₂ O ₃
S-LB-1	26.00	10.00	26.00	10.00	20.00	0	8.00	27.72	9.52	26.57	9.92	18.85	0	7.42
S-LB-2	26.00	10.00	26.00	10.00	20.00	2.00	6.00	27.50	9.69	26.45	9.79	19.08	1.92	5.55
S-LB-3	26.00	10.00	26.00	10.00	20.00	4.00	4.00	27.27	9.59	26.66	9.70	19.19	4.00	3.60
S-LB-4	26.00	10.00	26.00	10.00	20.00	6.00	2.00	27.27	9.75	26.58	10.01	18.80	5.95	1.64

the mold flux at a rotational rate of 12 r/min for the viscosity measurement. The melt was cooled at a rate of 6°C/min until the recorded viscosity approached 3 Pa·s.

The melting point was determined using the hemisphere melting point method. Alcohol was used to cement a 2-g sample of pre-melting powder into a cylinder with an inner radius of 3 mm and a height of 3 mm. The cylinder was placed in a furnace at 800°C and heated on a corundum plate at a rate of 25°C/min. The hemispherical temperature was recorded automatically when the cylinder height decreased to half of the original height. Precipitated crystalline phases in mold fluxes quenched at 950°C and 1150°C were identified using X-ray diffraction (XRD) (Rigaku-TTR III, Rigaku Corporation, Japan). The XRD data were collected in a range of 10°–80° at a rate of 2°/s.

To identify the high-temperature melt structure at 1300°C, flux samples were quenched on a water-cooled copper plate for Raman spectrum (LabRAM HR800, Horiba Jobin Yvon, France) measurements. The quenched sample was taken from the crucible before the viscosity test. XRD results confirmed the glassy structure of quenched fluxes, as shown in Fig. 2. The Raman spectra were observed between 400 and 1600 cm⁻¹ through a 514-nm excitation source laser. The spectrum data were background subtracted and deconvoluted with the Gaussian function.

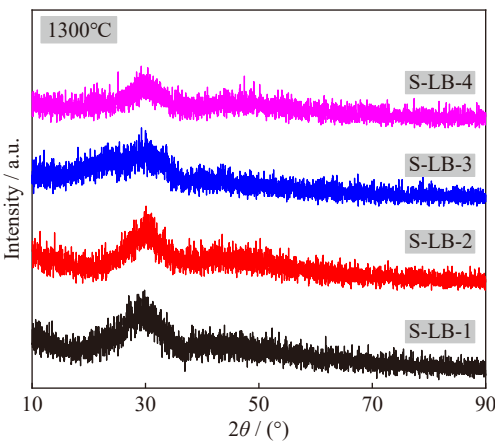


Fig. 2. XRD results of the as-quenched slag at 1300°C.

3. Results and discussion

3.1. Effect of substituting Li₂O for B₂O₃ on the viscosity and melting point of the mold flux

The viscosity of the mold flux with the substitution of Li₂O for B₂O₃ at different temperatures is shown in Fig. 3.

Fig. 4 presents the viscosity–temperature curves of the mold flux, which reflect the crystallization trend of the mold flux during cooling. With increasing Li₂O content in the mold flux, the viscosity first decreased and then obviously increased, particularly in the low-temperature zone. When it contained 2wt% Li₂O and 6wt% B₂O₃, the mold flux had a minimum viscosity of 0.07 Pa·s at 1300°C. When the mold flux contained 8wt% B₂O₃ (without Li₂O) or 6wt% Li₂O (i.e., 2wt% B₂O₃), the mold flux viscosity was 0.19 Pa·s or 0.34 Pa·s, respectively. Wang [13] found that 1.8wt% Li₂O and 7.2wt% B₂O₃ contained in the mold flux reduced the viscosity of the mold flux, consistent with the current results. Therefore, a combined addition of Li₂O and B₂O₃ to mold flux was beneficial to effectively reduce the mold flux viscosity.

Seetharaman *et al.* [32] proposed a mathematical method

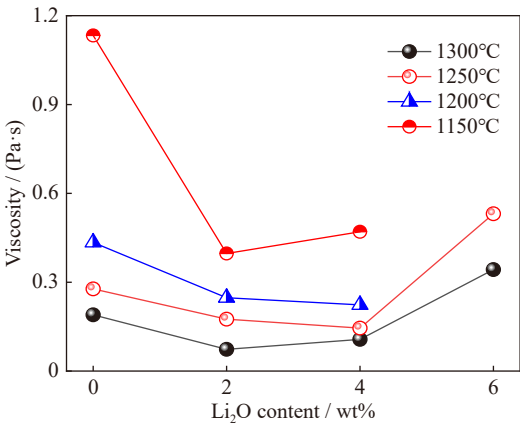


Fig. 3. Effect of Li₂O substituting for B₂O₃ on the mold flux viscosity.

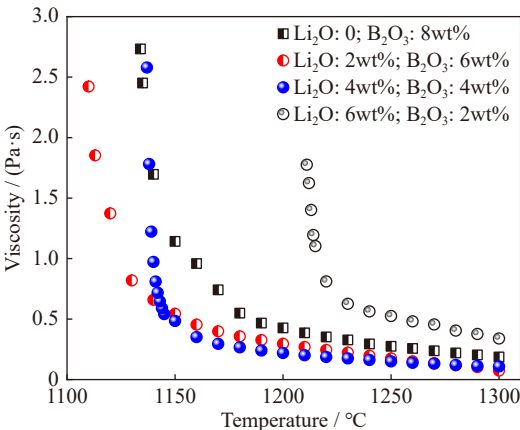


Fig. 4. Viscosity–temperature curves of the mold flux with various Li₂O and B₂O₃ contents.

for estimating the break temperature of mold flux using the viscosity–temperature relationship. Eq. (1) is the Arrhenius equation, and Eq. (2) is obtained from Eq. (1) by taking the derivative of the reciprocal of the temperature. Eqs. (3) and (4) are derived from the first and second partial derivatives of the activation energy with respect to the temperature, respectively. When the second partial derivative equals 0, the temperature is defined as the break temperature [32].

$$\ln \eta = \ln A + \frac{E_a}{RT} \quad (1)$$

$$\frac{E_a}{R} = \frac{\partial \ln \eta}{\partial (1/T)} \quad (2)$$

$$\frac{1}{R} \frac{\partial E_a}{\partial T} = \frac{\partial \left(\frac{\partial \ln \eta}{\partial (1/T)} \right)}{\partial T} \quad (3)$$

$$\frac{1}{R} \frac{\partial^2 E_a}{\partial T^2} = \frac{\partial^2 \left(\frac{\partial \ln \eta}{\partial (1/T)} \right)}{\partial T^2} \quad (4)$$

where T is the temperature, °C; η is the viscosity of the mold flux at T , Pa·s; E_a is the activation energy of viscous flow, kJ/mol; A is the apparent exponential prefactor; R is the universal gas constant.

The break temperature calculation process is shown in Fig. 5. The melting point was measured using the hemispheric point method. Fig. 6 shows the variation in the melting point and break temperature of the mold flux. With increasing Li₂O content in the mold flux, the melting point and break temperature first decreased and then increased, consistent with the evolution tendency of the viscosity. The combined addition of B₂O₃ and Li₂O to the mold flux reduced the viscosity, melting point, and break temperature of the mold flux.

3.2. Effect of substituting Li₂O for B₂O₃ on the structure of the mold flux

Aluminate and silicate network structures exist in the low-reactivity mold flux. The theory of silicate network structure is relatively mature [33–39]. The aluminate network struc-

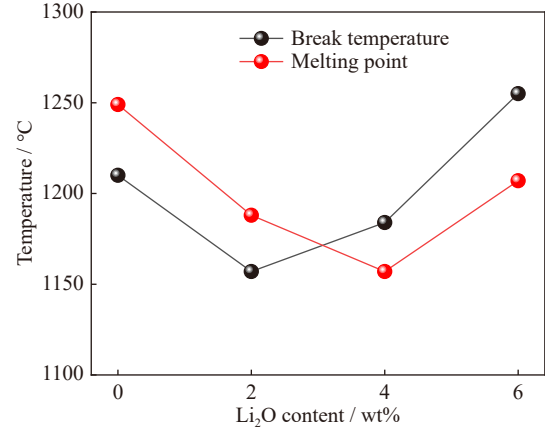


Fig. 6. Melting point and break temperature of the mold flux with various Li₂O and B₂O₃ contents.

ture is more complex than the silicate network structure. Aluminum has three coordination numbers of 4, 5, and 6, which form the network former ([AlO₄] structural unit) and network modifier ([AlO₅] and [AlO₆] structural units), respectively. Scholars [40–42] used high-resolution solid-state NMR spectroscopy (²⁷Al NMR) and molecular dynamics simulations to study the structural unit of the CaO–Al₂O₃ binary system and obtained consistent results. With the CaO/Al₂O₃ molar ratio greater than 1, the possibility of [AlO₄] structural units being present in the highly peralkaline composition is higher. Two coordination environments enable the boron atom to form [BO₄] and [BO₃] structural units. The major structure in the borate structure is the two-dimensional boroxol ring, which is linked by the [BO₃] triangular structure [24,43–44]. The three-dimensional borate structure is formed by the interconnection of the triangular [BO₃] and tetrahedral [BO₄] structural units [9,24,43–45]. With the addition of the above 30mol% network modifiers (including alkali metals and alkaline earth metals) to the mold flux, the [BO₃] structural unit is dominant [46]. Because the content of network modifiers in the low-reactivity mold flux in the current study is higher than 60mol% [46], the borate network structure is mainly composed of [BO₃] structural units.

Assignments of the deconvoluted Raman bands are summarized in Table 3 [9,46–65]. The original and deconvoluted Raman spectra of mold fluxes with various Li₂O and B₂O₃ contents are shown in Figs. 7 and 8. The related fractions of structural units are shown in Figs. 9 and 10. As Li₂O replaced B₂O₃ in the mold flux, the fraction of Al_{IV}–O–B_{III} structural units composed of [BO₃] gradually decreased, and the total fraction of the borate structure decreased from approximately 18wt% to 10wt%. The borate structure decreased because of a reduction in B₂O₃ content in the mold flux. The fraction of the Al–F linkage decreased slightly with the substitution of Li₂O for B₂O₃ in the mold flux. With the Li₂O content of the mold flux increasing from 0 to 6wt%, the fraction of the Al–O–Al linkage increased from 6wt% to 12wt%, and the fraction of Al–O[–] decreased, indicating that the fraction of the bridging oxygen in the aluminate structure increased. The higher content of free oxygen ions (O^{2–}) generated by Li₂O led to the breakage of the Si–O–Si linkage to

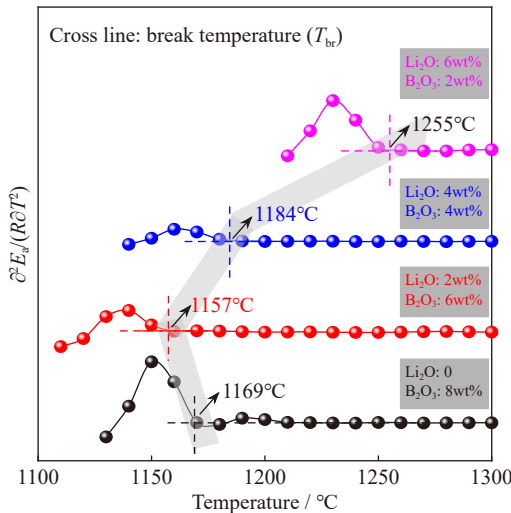


Fig. 5. Calculation process of the break temperature.

Table 3. Assignments of deconvoluted Raman bands [9,46–65]

Raman shift / cm^{-1}	Assignment	References
~ 530	Al–F stretching vibration ($[\text{AlF}_6]$ octahedral structure)	[47–49]
540–560	Al–O–Al bending vibrations	[47,49–55]
630–650	$\text{Al}_{\text{IV}}\text{–O–B}_{\text{III}}$ bending vibration	[56–57]
750–780	Al–O^- stretching vibration in AlO_4 units with 1 or 2 non-bridge oxygens	[47,50–51]
830–850	Al–O–Si linkage	[49]
850–880	Q_{Si}^0	[58–61]
900–920	Q_{Si}^1	[58–61]
950–1000	Q_{Si}^2	[58–61]
1200–1300	B–O $^-$ linkage in pyroborate units ($[\text{B}_2\text{O}_5]^{4-}$)	[62–64]
1320–1340	B–O $^-$ linkage in chain and ring metaborate units	[9,46,64–65]

form the Si–O $^-$ linkage, reducing the degree of polymerization (DOP) of the silicate network structure in the CaO–SiO $_2$ –based mold flux [66–67]. However, for the CaO–Al $_2$ O $_3$ –10wt%SiO $_2$ –based low-reactivity mold flux, Li $_2$ O played a more important role as a charge compensator. With the Li $_2$ O in the mold flux increased, the Al–O $^-$ linkage-transformed Al–O–Al linkage was promoted. Meanwhile, the charge compensation of Li $^+$ between Al $^{3+}$ and Si $^{4+}$ could link the

Al–O $^-$ and silicate structural units to form the Al–O–Si linkage with a higher DOP of the melt structure [18–19,21]. Correspondingly, the fraction of Al–O–Si increased, and the structural units of stretching vibrations of Si–O in SiO $_4^{4-}$ (Q_{Si}^2), Si $_2$ O $_7^{6-}$ (Q_{Si}^1), and SiO $_3^{2-}$ (Q_{Si}^0) decreased.

3.3. Effect of substituting Li $_2$ O for B $_2$ O $_3$ on the crystalline phase of the mold flux

Figs. 11 and 12 show the precipitation of crystalline

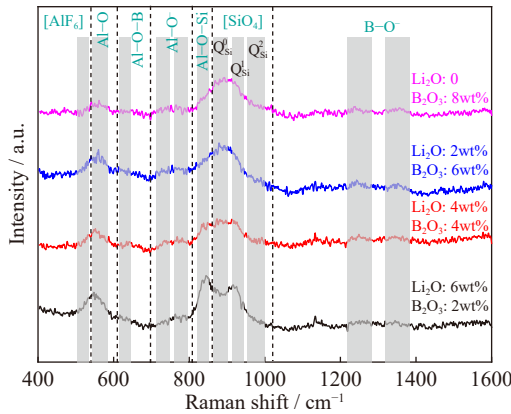


Fig. 7. Original Raman spectra of mold fluxes with different Li $_2$ O and B $_2$ O $_3$ contents.

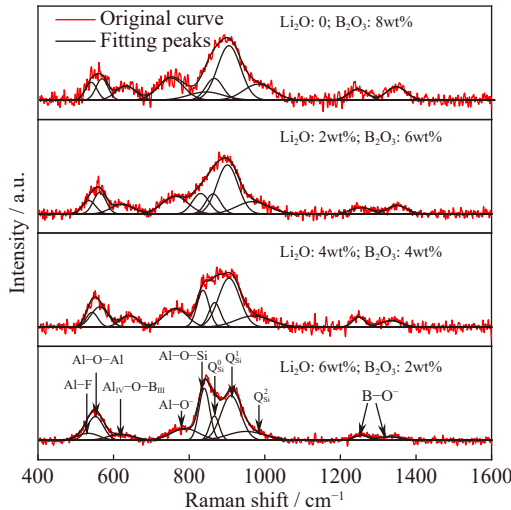


Fig. 8. Deconvoluted Raman spectra of mold fluxes with various Li $_2$ O and B $_2$ O $_3$ contents.

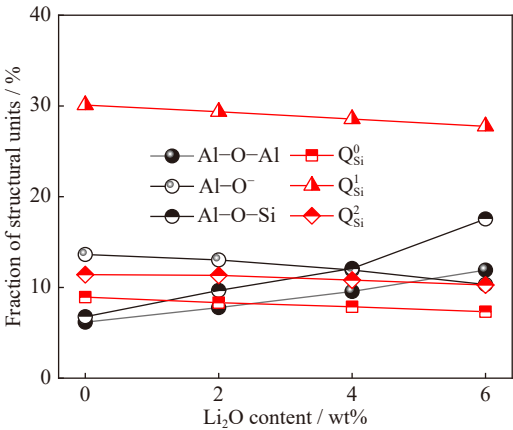


Fig. 9. Fraction of aluminate and silicate structural units of mold fluxes with various Li $_2$ O and B $_2$ O $_3$ contents.

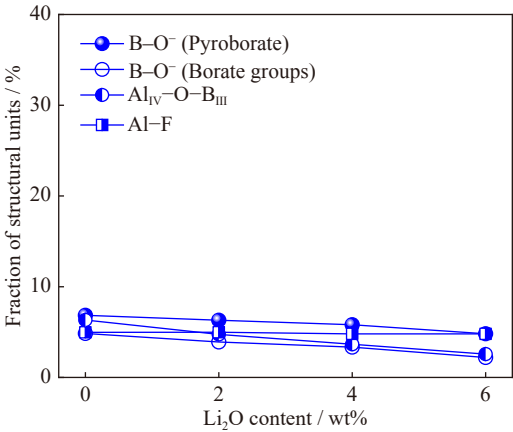


Fig. 10. Fraction of other structural units of mold fluxes with various Li $_2$ O and B $_2$ O $_3$ contents.

phases in mold fluxes with different Li_2O and B_2O_3 contents at 1150 and 950°C. Crystalline phases in the mold flux substantially increased as the temperature decreased from 1150 and 950°C. The replacement of B_2O_3 by Li_2O in the mold flux promoted the precipitation of CaF_2 , $LiAlO_2$, and

$11CaO \cdot 7Al_2O_3 \cdot CaF_2$ crystals and inhibited the precipitation of $2CaO \cdot Al_2O_3 \cdot SiO_2$ crystals. A higher B_2O_3 content in the mold flux retarded CaF_2 phase precipitation, consistent with previous studies by Yang *et al.* [31] and Xiao *et al.* [68]. With the content of Li_2O more than 2wt%, the high melting point

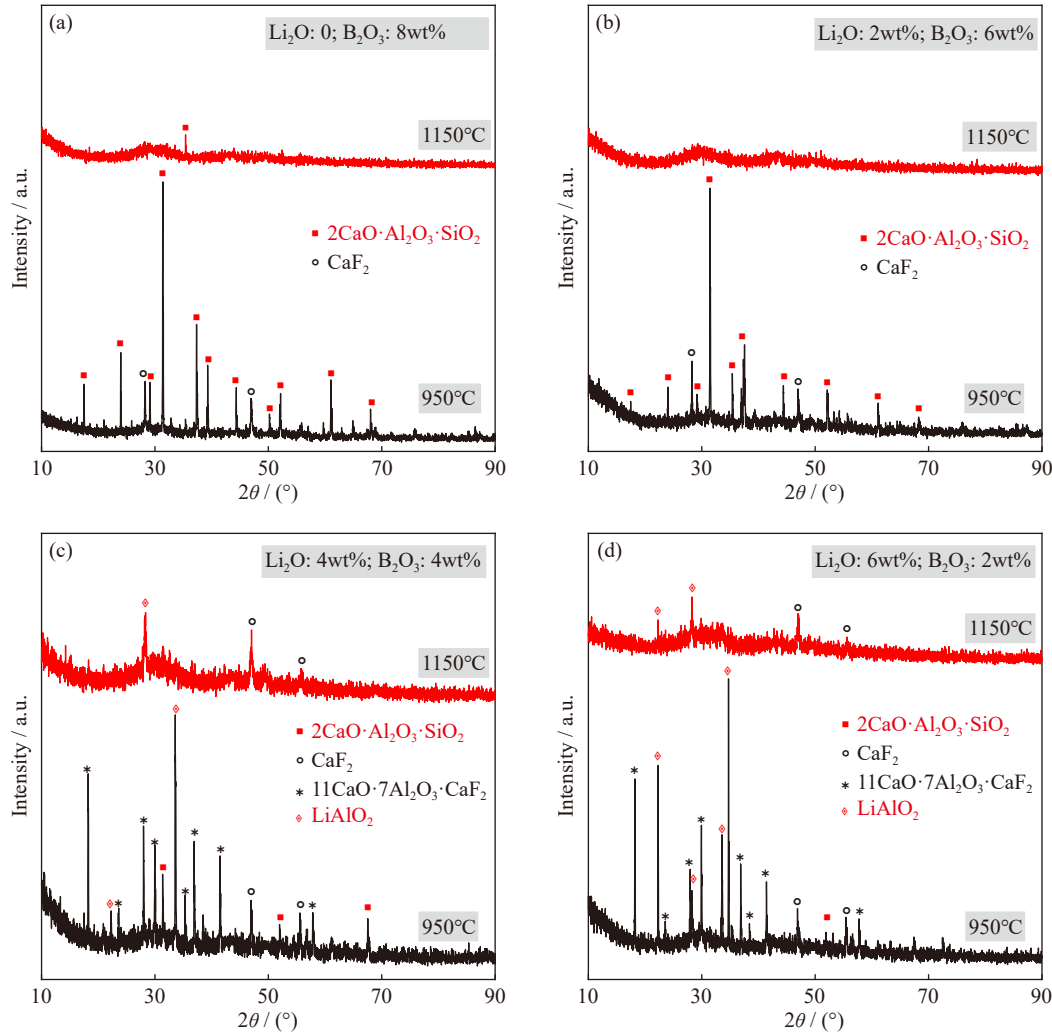


Fig. 11. Effect of various Li_2O and B_2O_3 contents on the crystalline phase of the mold flux. (a) Li_2O : 0, B_2O_3 : 8wt%; (b) Li_2O : 2wt%, B_2O_3 : 6wt%; (c) Li_2O : 4wt%, B_2O_3 : 4wt%; (d) Li_2O : 6wt%, B_2O_3 : 2wt%.

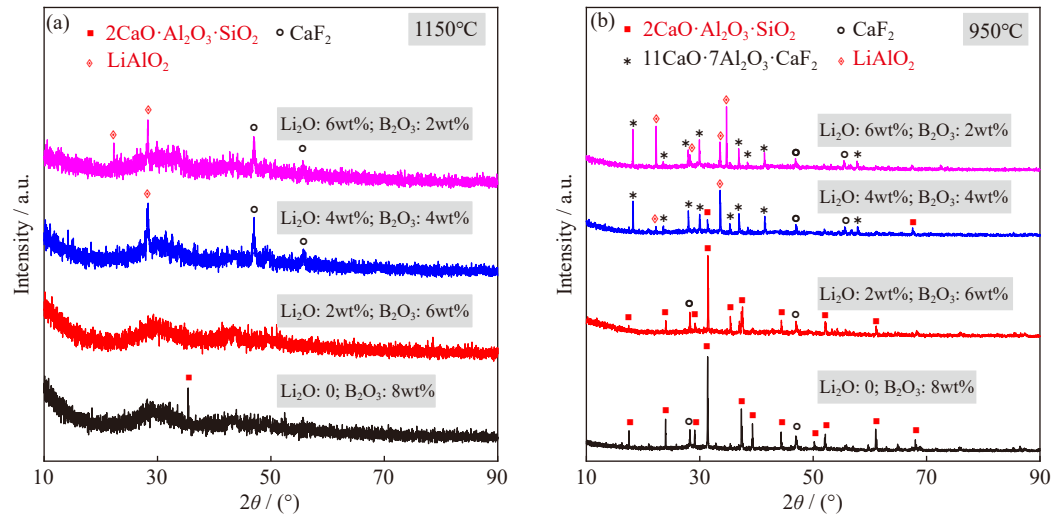


Fig. 12. Effect of Li_2O replacing B_2O_3 on the crystalline phase of the mold flux at different temperatures (a) 1150°C; (b) 950°C.

crystalline phase of LiAlO_2 (1700°C) gradually precipitated. The LiAlO_2 phase easily precipitated in the $\text{CaO-Al}_2\text{O}_3$ slag system because of its structural characteristics [45,69–70]. The precipitated LiAlO_2 increased the viscosity and worsened the crystallization tendency of the mold flux [19–20]. As the Li_2O content in the mold flux increased from 0 to 6wt%, the crystallization tendency of the mold flux first decreased and then increased at 1150°C. Notably, the mold flux with 2wt% Li_2O and 6wt% B_2O_3 was the pure liquid phase at 1150°C.

LiAlO_2 crystal formation required the charge compensation effect of Li^+ on the aluminate structure; thus, with increasing Li_2O content in the mold flux, Li^+ replaced metal cations such as Ca^{2+} in the $[\text{AlO}_4]$ structural unit [21]. As the Li_2O content of the mold flux increased from 0 to 6wt%, Li_2O strengthened the aluminate network structure through Li^+ , while LiAlO_2 crystals gradually precipitated in the mold flux. This result was consistent with the Raman spectroscopy results. In summary, mold flux viscosity first decreased and then increased with the substitution of Li_2O for B_2O_3 in the mold flux. The melt structure and precipitated crystalline phase caused the evolution of viscosity. The precipitation of crystalline phases and the higher DOP increased the viscosity of the mold flux. The addition of 2wt% Li_2O and 6wt% B_2O_3 to the mold flux reduced the reactivity, viscosity, and melting point of the mold flux and lowered the crystallization tendency of the mold flux in the high-temperature zone. The combined addition of Li_2O and B_2O_3 to the mold flux improved the properties of the mold flux of high-aluminum steels.

4. Conclusions

In this study, the evolution of viscosity, melt structure, and crystalline phase of the mold flux with the replacement of B_2O_3 by Li_2O from 0 to 6wt% was investigated. The main results are summarized as follows.

(1) The combined addition of Li_2O and B_2O_3 with appropriate proportion was beneficial to reduced the viscosity, melting point, and break temperature of the low-reactivity mold flux. The viscosity reached a minimum of 0.07 Pa·s with 2wt% Li_2O and 6wt% B_2O_3 in the mold flux.

(2) An increase in Li_2O content in the mold flux from 0 to 6wt% strengthened aluminate and aluminosilicate structures by increasing Li^+ released from Li_2O . Meanwhile, the proportion of silicate structural units decreased.

(3) The replacement of B_2O_3 by Li_2O in the mold flux promoted LiAlO_2 precipitation, and a Li_2O content of no more than 2wt% is suggested to avoid LiAlO_2 phase precipitation.

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Conflict of Interest

The authors declare no conflict of interest.

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