DOI: https://doi.org/10.24425/amm.2025.152501

TING WU[1,2], HAI-XIANG ZHUANG[2], SHAMA SADAF[2], YI-LONG JI[1], HAI-CHUAN WANG[1,2*]

EFFECT OF ALKALI OXIDES ON THE STRUCTURE AND PROPERTY OF FLUORINE-FREE MOLD FLUXES

To confirm the impact of Li_2O and Na_2O on the structure and property of CaO-SiO_2-B_2O_3 based fluorine-free mold fluxes, devices including rotary viscometer, X-ray diffraction, combined with Fourier transform infrared (FTIR) spectroscopy were applied in the present study. From FTIR results, it was noted that with the addition of Li_2O (0-3 wt%) and Na_2O (4-12 wt%), there would be simpler Si-O and B-O structural units formed. However, all the structure units were intensified when the content of Li_2O (4 wt%) was added in slag. By the accumulation of Li_2O and Na_2O in mold fluxes with various BaO content, the viscosity at 1300°C decreased generally, showing that viscosity was influenced by the combination of structure and superheat, and superheat gradually played a dominant role as Li_2O reached 4 wt%. Depending on the viscosity-temperature curve, all samples showed acidic slag characteristics and the decrement activation energy of slag came as the increment of Li_2O and Na_2O at the basicity 1.15 in overall, which were beneficial for the play of slag lubrication function. The effect of Li_2O on crystallization of fluorine-free mold fluxes with 5 wt% of BaO were analyzed that all the diffraction peaks displayed in the XRD patterns corresponded to the standard peaks of Ca_2SiO_4 and $Ca_{11}Si_4B_2O_{22}$. Li_2O has an imperative role in all samples that enhanced the crystallization performance of the mold fluxes in the low-temperature zone.

Keywords: Mold fluxes; Fluorine-free; Structure; Viscosity; Crystallization

1. Introduction

Continuous casting technology produces more than 95% of the crude steel output for modern steel industry [1]. Mold flux can not only isolate oxygen, inhibits molten steel oxidation, but also provides heat insulation. Moreover, an essential role of mold fluxes is coordination control of heat transfer and lubrication between cooper mold and strand shell [2-5]. The presence of fluorides in the slag can reduce the viscosity and melting temperature of mold flux [6-7], promote crystallization of solid film, and contribute to precipitation of a vital phase-cuspidine ($Ca_4Si_2O_7F_2$), thus effectively controlling the horizontal heat transfer [8-10]. However, the utilization of fluorine-containing flux is bound to be accompanied by HF, SiF_4, NaF and other toxic gases emissions, which causes equipment corrosion, environmental pollution, health hazards and other adverse consequences [11-12]. Many oxides such as Na_2O, K_2O, Li_2O, TiO_2, and B_2O_3, have been suggested to compensate the negative effects caused by the absence of fluorides. Hence, the principle of sustainable development requires us to focus on fluorine-free slag preferably rather than fluorine-containing slag.

The addition of alkali oxide provides free oxygen, which further diffuses the silicate network [9] and increases the crystallization rate [13]. It is normally reported as Li_2O decreases melting temperature and viscosity [14], while increases crystallization [13,15-18] that with adding Li_2O of high content, the crystallization rate was promoted, and the heat transfer was weakened [13]. However, Li_2O may inhibit the precipitation ability of cuspidine, although theoretically as a role of alkaline oxide, it should reduce the activation energy [15]. A hypothesis of this counter-effect is that high affinity between SiO_2 and Li cations [17] reduces the activity of SiO_2, which is the main component of cuspidine, while this explanation needs to be verified by structural analysis of mold fluxes to reveal the effect of Li_2O addition. As a whole, previous studies about the effects of Li_2O on properties of mold fluxes were generally limited to the fluorine containing system.

As for Na_2O, existing research [19-20] on the development of low F mold fluxes for casting medium carbon steels indicated Na_2O is beneficial to control the crystallization extent. Further studies about Na_2O showed that it has been regarded as a network modifier to promote the crystallization of mold fluxes [21].

[1] ANHUI UNIVERSITY OF TECHNOLOGY, KEY LABORATORY OF METALLURGICAL EMISSION REDUCTION & RESOURCE RECYCLING (MINISTRY OF EDUCATION), ANHUI, MA'ANSHAN, 243002, CHINA
[2] ANHUI UNIVERSITY OF TECHNOLOGY, SCHOOL OF METALLURGICAL ENGINEERING, ANHUI, MA'ANSHAN, 243032, CHINA

* Corresponding author: which@ahut.edu.cn

Lu et al. [22] have studied the effects of Na_2CO_3 on the properties include melting temperature, viscosity, and surface tension of mold fluxes, and suggested that partial fluorine could be replaced by Na_2CO_3, but its content should be lower than 9 wt%. Mills et al. [2] summarized the effect of individual components in mold flux and indicated that higher amounts of Na_2O or K_2O can decrease the viscosity. Gao et al. [23] reported that the critical cooling rate and crystallinity of $CaO-Al_2O_3$-based mold fluxes containing 14 wt% SiO_2 initially decreased and then increased with Na_2O addition, while an effect of Na_2O on the incubation time was minor. Lu's work also showed that Na_2O concentration exceeding a critical value greatly accelerated the low temperature flux crystallization as a result of the formation of a new $Na_xAl_ySi_zO_4$ crystal phase [24]. As a whole, the Na_2O effect may be used for the development of low/free fluorine mold flux for casting medium carbon steels.

In the present study, the role of Li_2O and Na_2O contents on the structure and property of fluorine-free mold fluxes are investigated by combing rotary viscometer, FTIR and X-ray diffraction test. The relationship between composition, structure and properties are discussed to give guidance for development of fluorine-free mold fluxes.

2. Materials and methods

2.1. Viscosity measurement

In the current study, a high temperature viscometer (DV-II+, Brookfield Inc., USA) was utilized to measure viscosity of the designed $CaO-SiO_2-B_2O_3$-based mold fluxes. TABLE 1 showed the composition content of fluorine-free mold fluxes, and the slag samples were prepared with pure chemical reagents $CaCO_3$, SiO_2, B_2O_3, Al_2O_3, MgO, $BaCO_3$, Na_2CO_3 and Li_2CO_3.

TABLE 1

Composition content of fluorine-free mold fluxes (wt%)

Composition	R = CaO/SiO_2	BaO	Al_2O_3	Na_2O	B_2O_3	MgO	Li_2O
Li_2O samples	1.15	5, 10	4	8	6	2	0-4
Na_2O samples	1.15	5, 10	4	4-12	6	2	1

The viscosity was measure by rotating cylinder method. The temperature was measured through a thermal couple contacted with the outside bottom of the crucible in the $MoSi_2$ furnace, and it was calibrated before testing. The instrument constant k was also calibrated by standard liquid with known viscosity. The homogeneous mixed sample was placed in a graphite crucible (internal diameter = 50 mm; height = 80 mm; wall thickness = 10 mm; bottom thickness = 20 mm), and then the crucible was heated to 1300°C (1573 K). After 20 mins of homogenization, a graphite probe (diameter = 15 mm; height = 18 mm) was slowly inserted to 10 mm from the crucible bottom and rotate at a fixed speed of 12 r/min [14,25-26]. After the indicative of viscosity stability, it was cooled at a rate of 6°C/min, and the test was stopped immediately when the viscosity value exceeded an upper limit. Viscosity-temperature curve was recorded every 5 seconds during the cooling process with 99.99% Ar gas protection at a flow rate of 200 mL/min.

2.2. FTIR spectroscopy

The melting state of the slag at 1300°C was the basis for studying its microstructure, which was in consistent with viscosity test temperature. In order to approximately obtain the melt microstructure, the 1300°C molten slag shown in TABLE 1 was quickly quenched in liquid nitrogen to rapidly cool it to glassy and the quenched samples were studied by FTIR. The glassy state slag was dried, crushed and ground to below 200 mesh. Then 1 mg of each sample was mixed with an appropriate amount of KBr and pressed into a uniform transparent sheet. The measurements were performed using a Nicolet 6700 FTIR spectrometer in the range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1} [27-29].

2.3. XRD experiment

The crystallinities of air-cooled sample were analyzed via XRD (Bruker D8 Advance, Cu target K_α radiation with $\lambda = 0.54056$ Å). The radiant tube voltage was 40 kV, the scanning rate was 2°/min, and the scanning angle was from 10° to 80°.

3. Results and discussion

3.1. Relationship between structure and viscosity at 1300°C of fluorine-free mold fluxes

3.1.1. Effect of Li_2O and Na_2O on the structure of fluorine-free mold fluxes

As shown in Fig. 1, the spectra of all fluorine-free fluxes exhibit four broad transmittance bands in the range of 400-4000 cm^{-1}. The bending vibration of Si-O-Si bond and B-O-B bond [29-30], the stretching vibration of the $[SiO_4]^{4-}$ and $[BO_4]^{5-}$ tetrahedrons [31-32], and the B-O vibration in the $[BO_3]^{3-}$ triangle [33] are located in the 400-600 cm^{-1}, 650-800 cm^{-1}, 800-1200 cm^{-1}, and 1200-1500 cm^{-1} regions, respectively.

With the addition of Li_2O (0-4 wt%), the results were corresponded as follows, when the Li_2O contents were 0 wt% to 3 wt%, the vibration bands at wavelengths of 400-1600 cm^{-1} became less pronounced, which indicated that the structures of B-O and Si-O network were simplified, while all the vibration bands turned to noticeable by the addition of 4 wt% Li_2O, it means that, first simple structure of slag was found then changed to a complex structure. When Li_2O 0-3 wt% contents were added, the released

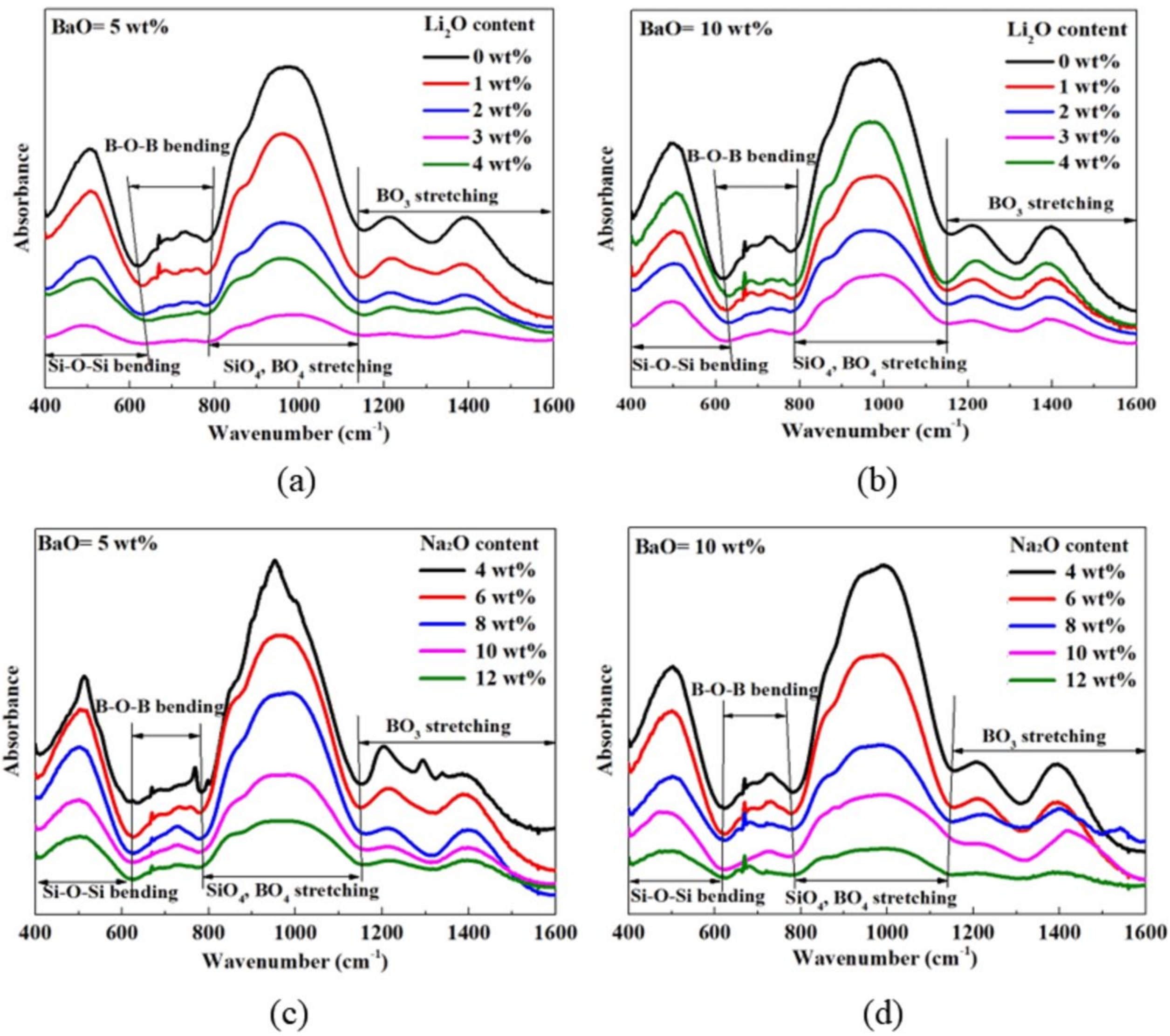

Fig. 1. Effect of Li_2O (a), (b) and Na_2O (c), (d) on the structure of fluorine-free mold fluxes

free oxygen ions (O^{2-}) from Li_2O would interact with the bridged oxygen (O_b) (which was formed between the $[BO_3]^{3-}$ trihedral and the $[BO_4]^{5-}$ tetrahedral structural units), resulted in depolymerize the diborate structural units, which helps the boroxol rings dissociation by the symmetric / asymmetric stretching vibration of B-O bonds. Moreover, once $[BO_3]^{3-}$ trihedral was introduced into three-dimensional complex structure, it diminished the symmetry of structure, and the linkage of borate structure with near Si atoms was occurred, which could decrease the uniformity of networks [34]. However, the structures of B-O and Si-O were intensified by the addition of Li_2O (4 wt%) in slag, resulted in the complexity of the structures of borate and silicate, which in turn may enhance the viscosity of mold fluxes.

With the addition of Na_2O (4-12 wt%), there would be simpler borate and silicate structural units formed, as suggested all the bands corresponding to B-O and Si-O structure in the wavenumber range of 400-1600 cm^{-1} becomes less pronounced. Thus, the strength of the whole structure was weakened; consequently, the viscosity would decrease by the addition of Na_2O (4-12 wt%) in mold fluxes.

3.1.2. Effect of Li_2O and Na_2O on the viscosity at 1300°C of fluorine-free mold fluxes

The addition of Li_2O (0-4 wt%) and Na_2O (4-12 wt%) in mold fluxes with various BaO content (5 and 10 wt%) was shown in Fig. 2. It can be seen that the viscosity at 1300°C reduced generally with Li_2O or Na_2O addition, while increased with BaO changed from 5 wt% to 10 wt%. The depolymerization was explained as follows, the dissociated O^{2-} from Li_2O and Na_2O lead to simplified the stable structural units of $[SiO_4]^{4-}$ tetrahedral, $[BO_3]^{3-}$ trihedral and $[BO_4]^{5-}$ tetrahedral. However, when the Li_2O content is 4 wt%, though the network structure was intensified as shown from FTIR results, the continuous decrease of viscosity was because of Li_2O prevents the formation of high melting temperature substances. It was revealed in Fig. 3 that with the increase of Li_2O content, the melting point of fluorine-free mold fluxes decreased gradually. The results exposed that the viscosity was affected by the sequence of structure and superheat, the superior role of the superheat was checked gradually, as the content of Li_2O increased. As for

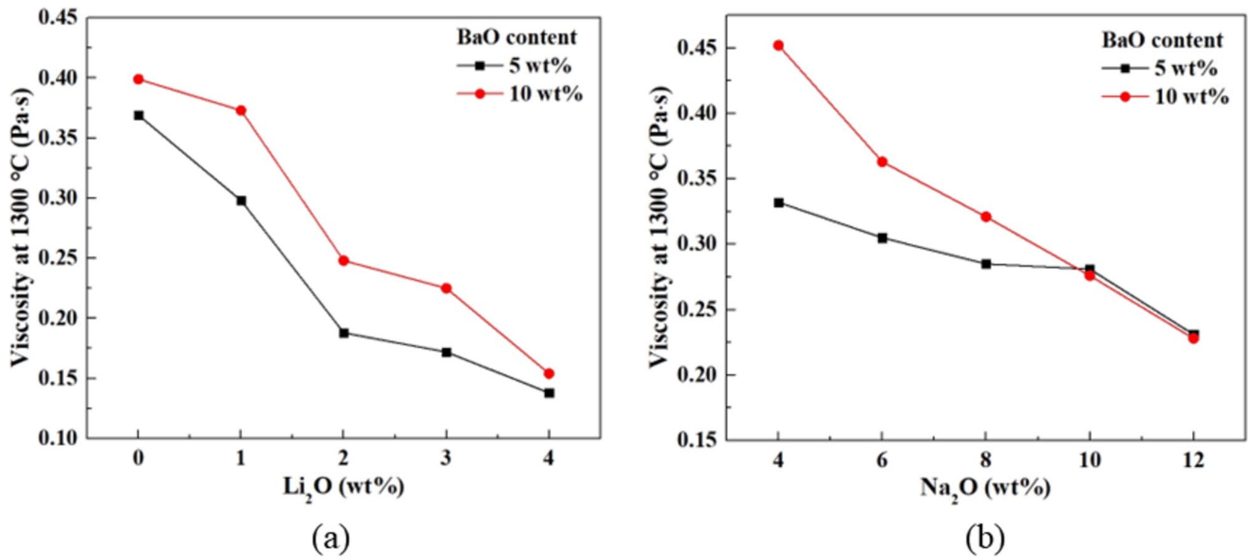

Fig. 2. Effect of Li_2O (a) and Na_2O (b) on the viscosity at 1300°C of fluorine-free mold fluxes

Na_2O addition, the viscosity showed a trend of decline; however, when Na_2O increased to 10 wt%, the viscosity of slags with 5 wt% and 10 wt% BaO content trended to accord. This is a comprehensive result of superheat and structure that the melting point of slag with more than 6-8 wt% Na_2O presented a turning rise as shown in Fig. 3, while the structure was simplified continuously. It was also concluded that the structure had a greater influence on the viscosity at high temperature in slags with Na_2O addition.

Besides, CaO and BaO belong to alkaline earth metal oxides. In the CaO-SiO_2 based mold fluxes with traditional $[SiO_4]^{4-}$ tetrahedral network framework, the partial substitution of BaO for CaO can reduce the viscosity of slag to a certain extent [39]. This is because the Ba^{2+} radius (1.45A) is larger than the Ca^{2+} radius (1.06A), and the electrostatic potential of Ba^{2+} is smaller than that of Ca^{2+}, that is, BaO is easier to dissociate O^{2-}, and has a better depolymerization effect on the Si-O network structure, thus reducing the slag viscosity. However, within the composition range of fluorine-free slag in this study, the 1300°C viscosity increases with the increase of BaO content, which mainly depends on the competitive mechanism of BaO and B_2O_3 on the structural complexity. Due to the high content of B_2O_3 in the fluorine-free mold fluxes, BaO replaces CaO to enhance the alkalinity of the slag, thus offering more cations to balance the negative charge of $[BO_4]^{5-}$ tetrahedron, making $[BO_3]^{3-}$ trihedron polymerization to form $[BO_4]^{5-}$ tetrahedron, thus making the melt structure complex [36]. Macroscopically, it is reflected in the increase of viscosity.

3.2. The relationship between the fluid behavior and crystallization of F-free mold fluxes

3.2.1. Effect of Li_2O and Na_2O on the viscosity-temperature curve of fluorine-free mold fluxes

The viscosity-temperature curves in Fig. 4 showed acidic slag characteristics and were beneficial for the play of slag

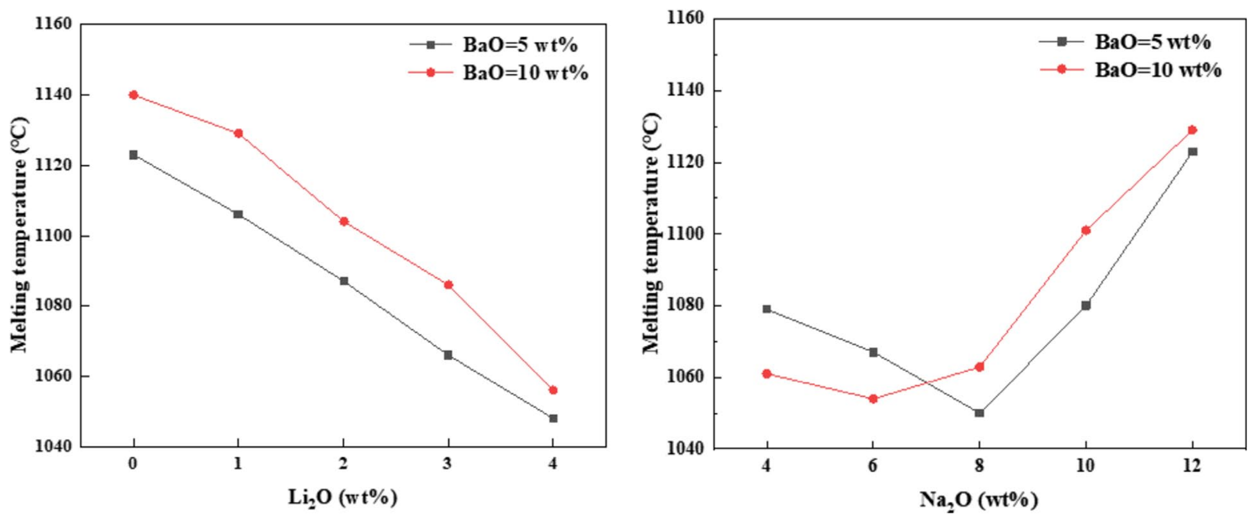

Fig. 3. Effect of Li_2O (a) and Na_2O (b) on the melting point of fluorine-free mold fluxes

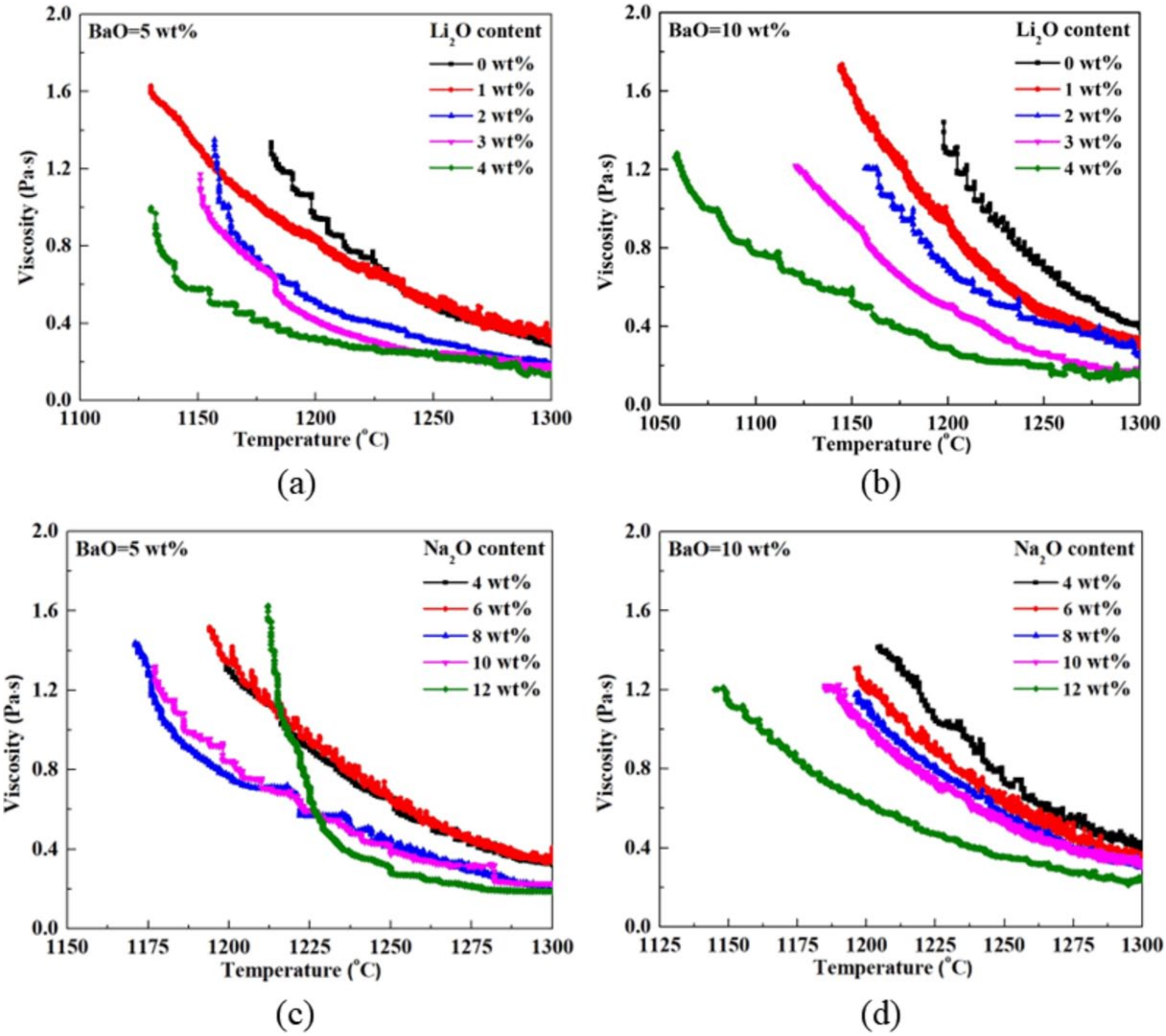

Fig. 4. Effect of Li_2O (a), (b) and Na_2O (c), (d) on the viscosity-temperature curve of fluorine-free mold fluxes

lubrication function. The glass properties were gradually intensified with Li_2O and Na_2O addition at the basicity of 1.15 in the fluorine-free mold fluxes, with BaO 5-10 wt%. Since the Li_2O and Na_2O addition tends to prevent the formation of high melting temperature crystals and lower the system melting temperature zone, the fluidity of mold fluxes during the cooling process would be improved. However, when Na_2O further increases to 12 wt% in mold fluxes with 5 wt% BaO, the viscosity-temperature curve shows basic characteristic to some extent, because the alkaline of slag was enhanced with high content of Na_2O.

3.2.2. Effect of Li_2O and Na_2O on the activation energy of fluorine-free mold fluxes

Depending on the viscosity-temperature curves, the activation energy values of samples at high-temperature region were obtained in TABLE 2.

It can be seen from TABLE 2 that when BaO content was 5-10 wt%, the activation energy of slag was decreased with the addition of Li_2O and Na_2O at the basicity 1.15 overall. With the decrease of activation energy, the unapparent trend of its polymerization into complex structures was checked while

TABLE 2

Effect of Li_2O and Na_2O on the activation energy of fluorine-free mold fluxes with different BaO contents

	BaO = 5 wt%					**BaO = 10 wt%**				
Li_2O content, wt%	0	1	2	3	4	0	1	2	3	4
Ea, KJ/mol	228	197	195	180	166	238	162	200	140	156
Na_2O content, wt%	4	6	8	10	12	4	6	8	10	12
Ea, KJ/mol	268	258	273	252	219	254	239	243	216	198

the temperature was decreased. From the macroscopical view, it exhibited that the viscosity augmented slowly as the temperature decreased, which is beneficial to lubrication performance of molten slag during the high-temperature region.

3.2.3. Effect of Li_2O and Na_2O on the crystallization of fluorine-free mold fluxes

Since the glass properties were gradually intensified by Li_2O addition in mold fluxes with 10 wt% BaO and Na_2O addition in mold fluxes with 5 wt% and 10 wt% BaO, only the effect of Li_2O on XRD patterns of fluorine-free mold fluxes with 5 wt% of BaO were studied in Fig. 5. All the diffraction peaks displayed in the XRD patterns corresponded to the standard peaks of Ca_2SiO_4 and $Ca_{11}Si_4B_2O_{22}$ (JCPDS 48-0953), which indicated the successful formation of crystals. Besides, almost no other peaks from residues or contaminants were noticed, indicating the high purity of Ca_2SiO_4 and $Ca_{11}Si_4B_2O_{22}$. On the other hand, the intensity of XRD diffraction peaks of Ca_2SiO_4 and $Ca_{11}Si_4B_2O_{22}$ increased when the contents of Li_2O were increased, which disclosed that Li_2O has an imperative role in all samples that enhanced the crystallization ability of the slag in low-temperature zone.

4. Conclusion

In order to examine the effect of Li_2O and Na_2O on the structure and property of fluorine-free mold fluxes, the results were confirmed by devices such as rotary viscometer, XRD and FTIR spectroscopy. The conclusions were concise as follows:

(1) From FTIR results it was concluded that, with the addition of Li_2O (0-3 wt%) and Na_2O (4-12 wt%), there would be simpler Si-O and B-O structural units formed. However, all the bands were intensified when the content of Li_2O (4 wt%) was added in slag, it means the structures of borate and silicate were more complex.

(2) The viscosity at 1300°C reduced generally with Li_2O or Na_2O addition, while increased with BaO changed from 5 wt% to 10 wt%. Combing the network structure was intensified when Li_2O was 4 wt%, the continuous decrease of viscosity was because Li_2O prevents the formation of high melting temperature substances, thereby reducing the melting temperature of the system. The results exposed that the viscosity was affected by the sequence of structure and superheat, the superior role of the superheat was checked gradually, as the content of Li_2O increased. As for Na_2O addition, with the turning rise of melting point at 6~8 wt% Na_2O but continuous simplify of structure, it was concluded the effect of structure on 1300 °C viscosity is greater than that of superheat.

(3) Depending on the viscosity-temperature curve, most of the samples showed acidic slag characteristics and the activation energy of slag was decreased, which were beneficial for the play of slag lubrication function during high-temperature region. The glass properties were gradually intensified with Li_2O (0-4 wt%) and Na_2O (4-10 wt%) addition at the basicity of 1.15 in the fluorine-free mold fluxes, with BaO 5-10 wt%. However, when the content of Na_2O was 12 wt%, the mold flux with 5 wt% BaO was alkaline slag with high break temperature, which was not conducive to slab lubrication.

(4) The effect of Li_2O on the crystallization of fluorine-free mold fluxes with 5 wt% of BaO was analyzed that all the diffraction peaks displayed in the XRD patterns corresponded to the standard peaks of Ca_2SiO_4 and $Ca_{11}Si_4B_2O_{22}$. Besides, the intensity of XRD diffraction peaks of Ca_2SiO_4 and $Ca_{11}Si_4B_2O_{22}$ increased when the contents of Li_2O were

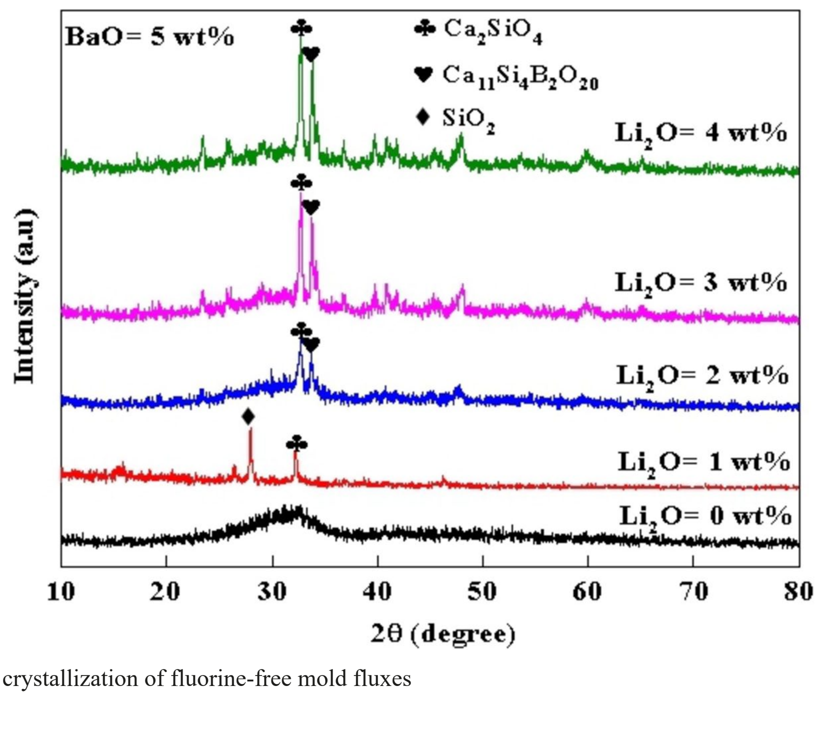

Fig. 5. Effect of Li_2O on the crystallization of fluorine-free mold fluxes

increased, which disclosed that Li_2O has an imperative role in all samples that enhanced the crystallization ability of the mold fluxes in low-temperature zone.

Acknowledgements

The authors would like to deeply appreciate the fund support from the Anhui Province Key Laboratory of Metallurgical Engineering & Resources Recycling (SKF22-08) and the Key Projects of National Natural Science Foundation of China (U1760202).

Conflict of interest statement

A conflict of interest exists whenever an author has a financial or personal relationship with a third party whose interests could be positively or negatively influenced by the article's content. On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

[1] B. Brussels, Steel Statistical Yearbook. World Steel Association 3 (2017).

[2] K.C. Mills, A.B Fox, Z. Li, R.P Thackray, Performance and properties of mould fluxes. Ironmak Steelmak **32** (1), 26-34 (2005). DOI: http://dx.doi.org/10.1179/174328105X15788

[3] G. Kim, I. Sohn, Influence of Li_2O on the viscous behavior of $CaO–Al_2O_3$–12 mass% Na_2O–12 mass% CaF_2 based slags. ISIJ Int. **52** (1), 68-73 (2012). DOI: http://dx.doi.org/10.2355/isijinternational.52.68

[4] J.Y. Park, G.H. Kim, J.B. Kim, S. Park, I. Sohn, Thermo-physical properties of B_2O_3–containing mold flux for high carbon steels in thin slab continuous casters: structure, viscosity, crystallization, and wettability. Metall. Mater. Trans. B. **47** (4), 2582-2594 (2016). DOI: https://doi.org/10.1007/s11663-016-0720-z

[5] J.Y. Park, E.Y. Ko, J. Choi, I. Sohn, Characteristics of medium carbon steel solidification and mold flux crystallization using the multi-mold simulator. Met. Mater. Int. **20** (6), 1103-1114 (2014). DOI: https://doi.org/10.1007/s12540-014-6013-7

[6] H.Y. Chang, T.F. Lee, T. EJIMA, Effect of alkali-metal oxide and fluoride on mold flux viscosity. Transactions of the Iron and Steel Institute of Japan **27** (10), 797-804 (1987). DOI: https://doi.org/10.2355/isijinternational1966.27.797

[7] Z. Wang, Q. Shu, K. Chou, Viscosity of fluoride-free mold fluxes containing B_2O_3 and TiO_2. Steel Research International **84** (8), 766-776 (2013). DOI: https://doi.org/10.2355/isijinternational.ISIJINT-2018-232

[8] P. Grieveson, S. Bagha, N. Machingawuta, Physical properties of casting powders. II. mineralogical constitution of slags formed by powders. Ironmaking Steelmaking **15** (4), 181-186 (1988).

[9] T. Watanabe, H. Hashimoto, M. Hayashi, Nagata K, Effect of alkali oxides on crystallization in $CaO–SiO_2–CaF_2$ glasses. ISIJ Int. **48** (7), 925-933 (2008).

[10] M. Hanao, M. Kawamoto, T. Watanabe, Influence of Na_2O on phase relation between mold flux composition and cuspidine. ISIJ Int. **44** (5), 827-835 (2004). DOI: http://dx.doi.org/10.2355/isijinternational.44.827

[11] L. Zhou, W. Wang, J. Wei, B. Lu, Effect of Na_2O and B_2O_3 on heat transfer behavior of low fluorine mold flux for casting medium carbon steels. ISIJ Int. **53** (4), 665-672 (2013). DOI: http://dx.doi.org/10.2355/isijinternational.53.665

[12] Z.T. Zhang, G.H. Wen, Y.Y. Zhang, Crystallization behavior of F-free mold fluxes. Int. J. Min, Met. Mater. **18**, 150 (2011). DOI: https://doi.org/10.1007/s12613-011-0415-z

[13] H. Liu, G.H. Wen, P. Tang, Crystallization behaviors of mold fluxes containing Li_2O using single hot thermocouple technique. ISIJ Int. **49**, 843-850 (2009). DOI: https://doi.org/10.2355/isijinternational.49.843

[14] T. Wu, Q. Wang, S. He, Study on Properties of alumina-based mould fluxes for high-Al steel slab casting. Steel Research International **83** (12), 1194-1202 (2012). DOI: http://dx.doi.org/10.1002/srin.201200092

[15] M.D. Seo, C.B. Shi, J.W. Cho, S.H. Kim, Crystallization behaviors of $CaO–SiO_2–Al_2O_3–Na_2O–CaF_2–(Li_2O-B_2O_3)$ mold fluxes. Metall. Mater. Trans. B. **45** (5), 1874-188 (2014). DOI: https://doi.org/10.1007/s11663-014-0091-2

[16] B.X. Lu, K. Chen, W.L. Wang, B.B. Jiang, Effects of Li_2O and Na_2O on the crystallization behavior of lime-alumina-based mold flux for casting high-Al steels. Metall. Mater. Trans. B. **45**, 1496-1509 (2014). DOI: https://doi.org/10.1007/s11663-014-0063-6

[17] V.D. Eisenhüttenleute, M. Allibert, Slag Atlas [M]. Verlag Stahleisen. (1995).

[18] J. Qi, C.J. Liu, D.P. Yang, C. Zhang. M.F. Jiang, Study of a new mold flux for heat resistant steel containing cerium continuous casting. Steel Research International **87**, 890-898 (2016). DOI: https://doi.org/10.1002/srin.201500259

[19] J. Li, W. Wang, J. Wei, D. Huang, H. Matsuura, A kinetic study of the effect of Na_2O on the crystallization behavior of mold fluxes for casting medium carbon steel. ISIJ Int. **52** (12), 2220-2225. DOI: http://dx.doi.org/10.2355/isijinternational.52.2220

[20] B. Lu, W. Wang, J. Li, H. Zhao, D.Y. Huang, Effects of basicity and B_2O_3 on the crystallization and heat transfer behaviors of low fluorine mold flux for casting medium carbon steels. Metall. Mater. Trans. B. **44B**, 365-377 (2013). DOI: https://doi.org/10.1007/s11663-012-9784-6

[21] J.W. Cho, K. Blazek, M. Frazee, H. Yin, J.H. Park, S.W. Moon, Assessment of CaO-ndash; Al_2O_3 based mold flux system for high aluminum TRIP casting. ISIJ Int. **53** (1), 62-70 (2013). DOI: https://doi.org/10.2355/isijinternational.53.62

[22] Y. Lu, G. Zhang, M. Jiang, H. Liu, T. Li, Effects of Na_2CO_3 on properties of low fluoride content mould flux for thin slab continuous casting. Res. J. Environ. Sci. **23**, S167-S169 (2011). DOI: https://doi.org/10.1016/S1001-0742(11)61104-2

[23] J. Gao, G. Wen, Q. Sun, The influence of Na_2O on the solidification and crystallization behavior of $CaO-SiO_2-Al_2O_3$-based mold flux. Metall. Mater. Trans. B. **46**, 1850-1859 (2015). DOI: https://doi.org/10.1007/s11663-015-0366-2

[24] B. Lu, K. Chen, W. Wang, Effects of Li_2O and Na_2O on the crystallization behavior of lime-alumina-based mold flux for casting high-Al steels. Metall. Mater. Trans. B. **45**, 1496-1509 (2014). DOI: https://doi.org/10.1007/s11663-014-0063-6

[25] E. Gao, W. Wang, L. Zhang, Effect of alkaline earth metal oxides on the viscosity and structure of the CaO-Al_2O_3 based mold flux for casting high-al steels. J. Non-Cryst. Solids. **473**, 79-86 (2017). DOI: https://doi.org/10.1016/j.jnoncrysol.2017.07.029

[26] L. Zhou, W. Wang, Study of the Viscosity of Mold Flux based on the Vogel–Fulcher–Tammann (VFT) Model. Metall. Mater. Trans. B. **48**, 220-226 (2017). DOI: https://doi.org/10.1007/s11663-016-0835-2

[27] J.H. Park, D.J. Min, H.S. Song, FTIR spectroscopic study on structure of CaO-SiO_2 and CaO-SiO_2-CaF_2 slags. ISIJ Int. **42**, 344 (2002). DOI: https://doi:10.2355/isijinternational.42.344

[28] H. Kim, H. Matsuura, F. Tsukihashi, W. Wang, D.J. Min, I. Sohn, Effect of Al_2O_3 and CaO/SiO_2 on the viscosity of calcium-silicate-based slags containing 10 mass pct MgO. Metall. Mater. Trans. B. **44**, 5 (2013). DOI: https://doi.org/10.1007/s11663-012-9759-7

[29] H. Kim. W.H. Kim, I. Sohn, D.J. Min, The effect of MgO on the viscosity of the CaO-SiO_2-20 wt%Al_2O_3-MgO slag system. Steel Research International **81** (4), 261 (2010). DOI: https://doi.org/10.1002/srin.201000019

[30] S. Sadaf, T. Wu, L. Zhong, et al., Effective mechanism of B_2O_3 on the structure and viscosity of CaO–SiO_2–B_2O_3-based melts. Steel Research International **92** (4), 2000531 (2021). DOI: https://doi.org/10.1002/srin.202000531

[31] C.L. Raluca, A. Loan, FTIR and Raman study of silver lead borate-based glasses. J. Non-Cryst. Solids. **353**, 2020-2024 (2007). DOI: http://dx.doi.org/10.1016/j.jnoncrysol.2007.01.066

[32] H. Kim, H. Matsuura, F. Sukihashi, W. Wang, D.J. Min, I. Sohn, Effect of Al_2O_3 and CaO/SiO_2 on the viscosity of calcium-silicate-based slags containing 10 mass pct MgO. Metall. Mater. Trans. B. **44**, 5-12 (2013). DOI: https://doi.org/10.1007/s11663-012-9759-7

[33] L. Zhang, W. Wang, S. Xie, K. Zhang, I. Sohn, Effect of basicity and B_2O_3 on the viscosity and structure of fluorine-free mold flux. J. Non-Cryst. Solids. **460**, 113-118 (2017). DOI: http://dx.doi.org/10.1016/j.jnoncrysol.2017.01.031

[34] Y.Q. Sun, J.L. Liao, K. Zheng, X.D. Wang, Z.T Zhang, Effect of B_2O_3 on the structure and viscous behavior of Ti-bearing blast furnace slags. JOM. **66**, 2168-2175 (2014). DOI: https://doi.org/10.1007/s11837-014-1087-8

[35] Z. Wang, I. Sohn, Effect of substituting CaO with BaO on the viscosity and structure of CaO-BaO-SiO_2-MgO-Al_2O_3 slags. J. Am. Ceram. Soc. **101** (9), 4285-4296 (2018). DOI: https://doi:10.1111/jace.15559

[36] S. Sadaf, J. Lei, H.X. Zhuang, T. Wu, H.C. Wang, Effective mechanism of BaO on the structure and fluid behavior of CaO-SiO_2-B_2O_3-based melts. Metallurgical Research & Technology **119** (2), 208 (2022). DOI: https://doi.org/10.1051/metal/2022020