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COMBING ROLE OF MgO AND Al_2O_3 ON VISCOSITY AND ITS CORRELATION TO STRUCTURE OF FLUORINE-FREE MOLD FLUXES

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Abstract

By using FactSage calculations, Fourier transform infrared spectroscopy (FTIR), rotational viscometers, and X-ray diffraction (XRD), the combined effect of MgO and Al_2O_3 on fluorine-free mold flux was confirmed. The viscosity of the slag at 1300 °C decreased with 2-10 wt% MgO, and higher Al_2O_3 increased the overall viscosity. The trend of the experimental results was consistent with the models of Riboud and Iida, while the FactSage calculation values were relatively higher. The viscosity of the slag was more influenced by the Si-O network than by the Al(B)-O structure and the MgO has a dual effect on the slag structure. The viscosity-temperature curves changed from alkaline to acidic slag characteristics when Al_2O_3 increased from 8 wt% to 12 wt%, and the trend was not uniform with the addition of 2-10 wt% MgO. Both FactSage calculation and XRD patterns showed that increasing MgO content gradually promoted the growth of $Ca_3MgSi_2O_8$ and $Ca_{11}Si_4B_2O_{22}$ crystals, while the addition of Al_2O_3 inhibited crystal precipitation.

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

1. Introduction

The role of mold fluxes was indispensable in continuous casting of steel [1-3]. Therefore, fluorides can promote the precipitation of cuspidine ($Ca_3Si_2O_7F_2$) in mold fluxes, thus controlling heat transfer [4-7]. It was also noted that fluorides volatilize at high temperatures to form compounds as HF and SiF_4, which enter the atmosphere and cause adverse effects on the environment. They are also dangerous to human health if inhalation of these gases beyond excess amount occurs. Therefore, substitutes need to be added in mold fluxes which would minimize the negative effects of fluorine. Many oxides such as Na_2O, K_2O, Li_2O, TiO_2, B_2O_3, have been implied to reimburse the adverse influences produced by the absence of fluorides. Hence, the development of fluorine-free mold fluxes with highly efficient and environment friendly is the indispensable way to maintain the principle of sustainable development.

The presence of MgO in the mold fluxes would result in properties adjustment, and then effect the continuous casting process substantially. Zhang et al [8] certified that the MgO component performed as the basic oxide in the $CaO-SiO_2-TiO_2-8$ wt% MgO−14 wt% Al_2O_3 system, and it had a noteworthy consequence on depolymerizing the slag networks. Another study exposed the outcome of MgO on crystallization and heat transfer of fluorine-free mold fluxes, and their results proposed that the crystallization tendency of mold fluxes was progressed, whereas its heat transfer ability was reduced with MgO enhancement [9]. Feng et al. [10] found that the viscosity of $CaO-SiO_2-MgO-Al_2O_3$-based fluorine-free mold fluxes reduced when the MgO content changed from 10 wt% to 14 wt%.

A number of studies have focused on the effects of Al_2O_3 concentration on the structure properties of the mold fluxes. For high aluminum steel, Zhao et al. [11] studied a kind of mold flux with high Al_2O_3 content and low SiO_2 content, which was helpful to inhibit the steel-slag reaction during casting. However, the influence of crystallization performance and morphology of mold flux on heat transfer and lubrication has not been studied in detail. The effect of Al_2O_3 content on viscosity of mold flux has been widely studied [12-15] and the results showed that the increase of Al_2O_3 content would significantly increase the viscosity, while there have been relatively few studies on its effects on the crystallization of mold fluxes.

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In current study, the combined role of MgO and Al_2O_3 contents on viscosity and its correlation to structure of fluorine-free mold fluxes is investigated through FactSage thermodynamic calculation, spectral experiment, rotary viscometer, and X-ray diffraction test, to give guidance for the development of fluorine-free mold fluxes for casting medium carbon steels.

2. Materials and Methods

2.1. Thermodynamic calculation

For composition design, the isothermal section diagram at 1300 ℃ of CaO-SiO_2-MgO-Al_2O_3-9 wt%Na_2O-6 wt%B_2O_3 system with various Al_2O_3 of 8 wt% or 12 wt% was calculated by thermodynamic software FactSage 7.2. As revealed in Figure 1, the MgO content in the range of 2-10 wt% at basicity (CaO/SiO_2) of 1.15 is within the liquidus phase, so that the composition of mold fluxes was set in Table 1 to ensure the completely molten state at 1300 ℃. Then the viscosity at 1300 ℃ and crystallization phase of fluorine-free mold fluxes were also studied by FactSage 7.2 to assist in analyzing the combing influence mechanism of MgO and Al_2O_3 on properties of fluorine-free mold fluxes. Due to the lack of Li_2O database in FactSage7.2, the content of Li_2O were converted to Na_2O as an approximate treatment.

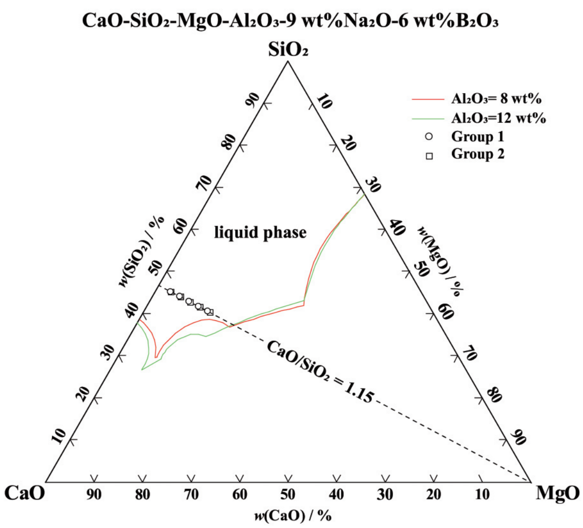

Figure 1. Isothermal section diagram at 1300℃ of CaO-SiO_2-MgO-Al_2O_3-9 wt%Na_2O-6 wt%B_2O_3 system with various Al_2O_3 of 8 wt% or 12 wt%

Table 1. Composition content of fluorine-free mold fluxes (wt%)

Composition	R	Al_2O_3	Na_2O	B_2O_3	MgO	Li_2O
Group 1	1.15	8	8	6	2, 4, 6, 8, 10	1
Group 2	1.15	12	8	6	2, 4, 6, 8, 10	1

2.2. Viscosity measurement

Viscosity is a key parameter of performance evaluation of mold fluxes. Slag samples without fluorine, shown in Table 1, were prepared with pure chemical reagents $CaCO_3$, SiO_2, B_2O_3, Al_2O_3, MgO, Na_2CO_3 and Li_2CO_3. As described in previous studies [16-18], the viscosity at 1300 °C and viscosity-temperature curve were measured by the rotational viscometer method with the Brookfield DV2T (Brookfield Inc. USA). The instrumental constant *k* value refers to the proportional relationship between the viscosity measured by the viscometer and the actual viscosity at a certain temperature. Since the instrumental constant *k* value is one of the important parameters of viscometer and directly affects the measuring precision and accuracy of viscometer, it was calibrated with a standard liquid with known viscosity before test. The mixed sample was placed in a graphite crucible, which was heated to 1300 °C (1573 K) and held for 20 min to obtain a homogeneous melt. Then the 15 mm diameter cylinder was immersed into the liquid slag bath and then rotated at a fixed shear rate with 0.565 m/min [19-21]. After the indicative of viscosity stability, it was cooled at a rate of 6 ℃/min, and the test was stopped immediately when the viscosity value exceeded the 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.

2.3. FTIR spectroscopy

The melt structure at high temperature has a great influence on its performance. Therefore, under the condition of limited experimental conditions and equipment, in order to obtain an approximate microstructure of molten state, the high-temperature slag was quickly placed in liquid nitrogen to rapidly cool it to a glassy state, and the quenched sample was studied by FTIR (Nicolet 6700). When testing, it was necessary to dry, crush and grind the quenched sample to below 200 mesh. Then, 1 mg of each sample was mixed with an appropriate amount of KBr and pressed into uniform transparent sheets [22-24]. The measurements were researched in the range of 400-4000 cm^{-1} and a resolution of 2 cm^{-1}.

2.4. XRD experiment

The crystal phases of typical fluorine-free mold fluxes were analyzed via X-ray diffractometer (XRD, Bruker D8 Advance, Cu target K_α radiation with λ=0.54056 Å). The radiation tube voltage was 40 kV, the scanning rate was 2°/min, and the scanning angle from 10^o to 80^o.

3. Results and discussion

3.1. Effect of MgO and Al_2O_3 on high temperature viscosity and its correlation to structure of fluorine-free mold fluxes

3.1.1. High temperature viscosity

The slag viscosities at 1300 °C were tested by rotational viscometer, which were compared with the Riboud [25] and Iida [26] models, and thermodynamic software FactSage calculation. As revealed from Figure 2, the viscosity at 1300 °C of fluorine-free mold fluxes reduced in the range of MgO = 2-10wt% with various Al_2O_3, while higher Al_2O_3 increased the viscosity as a whole. This tendency was matched well with the effects of MgO/Al_2O_3 ratio on viscous behaviors and structures of $MgO-Al_2O_3-TiO_2-CaO-SiO_2$ slag systems with high TiO_2 content and low CaO/SiO_2 ratio as reported by Feng [27]. Meanwhile, the trend of experiment results was also consistent with Riboud and Iida models, which verified the accuracy of viscosity test. However, the FactSage calculation values were relatively higher, which may be due to the approximate treatment of Li_2O converted to Na_2O with the absence data in the software, whereas the effects of Li_2O and Na_2O on the viscosity of slag may be different from the perspective of cation size, anion force and charge compensation.

3.1.2. High temperature structure

To explore the essential cause of viscosity change, the FTIR transmission of mold fluxes presents in the range of 400-4000 cm^{-1} were depicted in Figure 3. The characteristic trough for T-O-T (where T denotes Al or Si) bending vibration of mold fluxes appeared in transmission bond within 400–600 cm^{-1} [28, 29], and the bands in the region of 600-750 cm^{-1} were due to bending vibrations of B-O-B bonds and asymmetrical stretching of $[AlO_6]^{9-}$ octahedron [28, 30]. Equally, the $[AlO_4]^{5-}$ and $[BO_4]^{5-}$ tetrahedra located at the band of 750–900 cm^{-1}, and the $[SiO_4]^{4-}$ tetrahedra at 900–1150 cm^{-1} [31], while the 1150–1600 cm^{-1} range represented an asymmetric tensile pattern of $[BO_3]^{3-}$ trihedron [20].

It was revealed in Figure 3 that the 600–750 and 1150–1600 cm^{-1} vibration peaks became less pronounced, while the wavenumber of 750–900 cm^{-1} vibration bands moved forward with increasing MgO contents. This trend was contributed to the addition of MgO promoted the polymerization of $[AlO_6]^{9-}$ octahedron and $[BO_3]^{3-}$trihedron forming $[AlO_4]^{5-}$ and $[BO_4]^{5-}$ tetrahedra. However, as for the wavelengths of 400–600 and 900–1150 cm^{-1}, the vibration peak became less noticeable with increasing MgO contents. This trend indicated that, with an increase in the MgO contents, the networks of the $[SiO_4]^{4-}$ tetrahedron structures were destroyed, and the complex Si-O groups evolved into simple structures, resulting in slag depolymerization. It suggested that MgO had a dual effect on the structure of mold fluxes. On the one hand, as a typical alkaline oxide, it provided O^{2-} to break the Si-O-Si bond and depolymerized the silicate network. On the other hand, it also provided Mg^{2+}, which merged into the network structure and compensated for the charges excess in the $[AlO_4]^{5-}$ and $[BO_4]^{5-}$ tetrahedra.

The SiO_2 and B_2O_3 in the slag obviously exhibited the characteristics of acidic oxides, forming complex $[SiO_4]^{4-}$ and $[BO_4]^{5-}$ tetrahedral structure [32, 33], while Al^{3+} dissociated from Al_2O_3 in slag could form $[AlO_6]^{9-}$ octahedron structure and $[AlO_4]^{5-}$ tetrahedron structure, and incorporate with $[SiO_4]^{4-}$ tetrahedron structure, performing as a network former [34]. In present study, although $[AlO_6]^{9-}$ octahedral and $[BO_3]^{3-}$ trihedral polymerized into $[AlO_4]^{5-}$ and

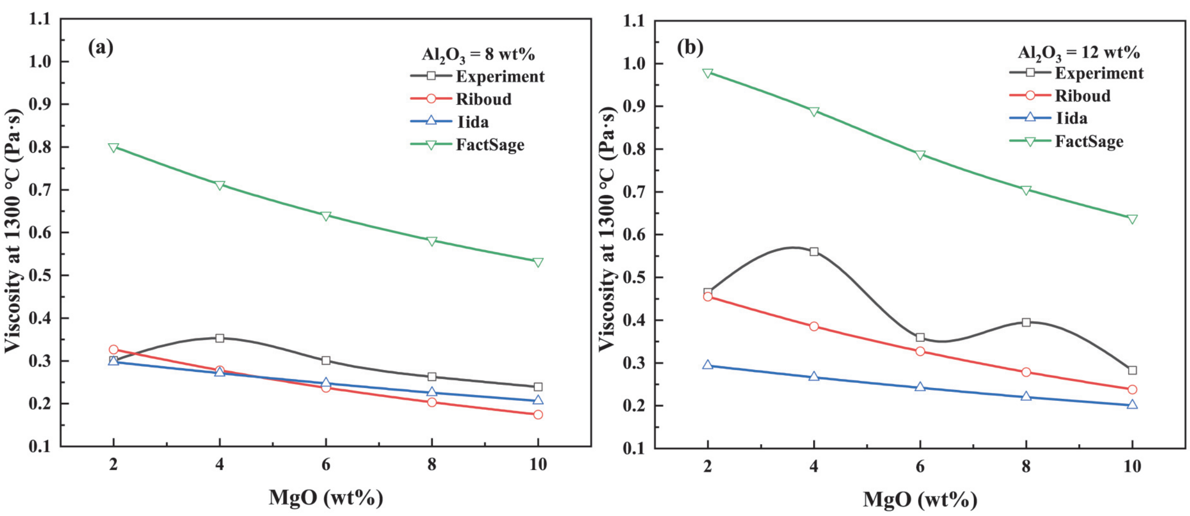

Figure 2. *Viscosity at 1300℃ of fluorine-free mold fluxes for (a) Group 1 and (b) Group 2*

$[BO_4]^{5-}$ tetrahedral as Mg^{2+} acted as charge compensator with MgO addition, the depolymerization of $[SiO_4]^{4-}$ tetrahedral was much more prominent by O^{2-} dissociated from MgO, thus the network structure was reformed, and the viscosity was decreased. The results exposed that the viscosity was more affected by the Si-O network than Al(B)-O structure.

3.2. Effect of MgO and Al_2O_3 on cooling process viscosity and its correlation to structure of fluorine-free mold fluxes

3.2.1. Viscosity-temperature curve

As revealed in Figure 4, the viscosity-temperature curves represented alkaline slag characteristics at 8 wt% Al_2O_3 with various MgO contents while showed acidic slag characteristics when Al_2O_3 increased to 12 wt%. However, since the tendency of viscosity-temperature curve was not regular with the addition of MgO 2-10 wt% under various Al_2O_3 contents, it indicated that the effect of MgO on the fluid behavior was not constrained by specific principle. Since it contained large amounts of Al_2O_3 with amphoteric property in current system, MgO may act as silicate network modifier when Al_2O_3 presented alkaline characteristics which decreased slag viscosity, whereas Mg^{2+} may perform as charge compensator for $[AlO_4]^{5-}$ tetrahedra when Al_2O_3 showed acid characteristics and then the slag viscosity may be increased. It demonstrated that fluorine-free mold fluxes with lower Al_2O_3 content was beneficial for the play of slag heat control function while higher content of Al_2O_3 was in favor of slag lubrication function.

Considering the variable viscosity during cooling process, adding MgO though would reduce the high temperature viscosity which is conducive to slag fluid behavior improvement, it seems no obvious effect on the slag solidification characteristics, while appropriate Al_2O_3 is required for effective adjustment

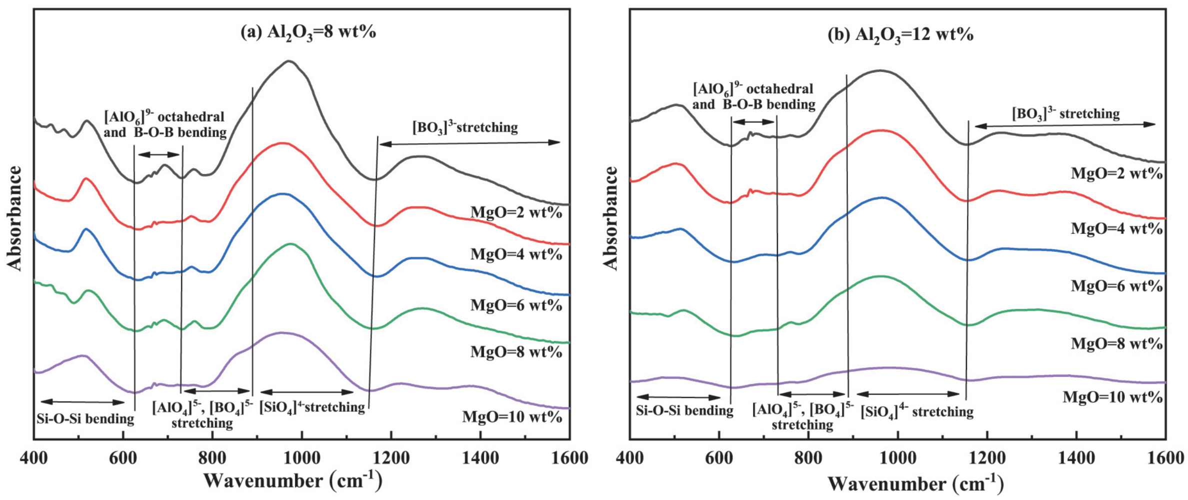

Figure 3. *FTIR spectra of fluorine-free mold fluxes for (a) Group 1 and (b) Group 2*

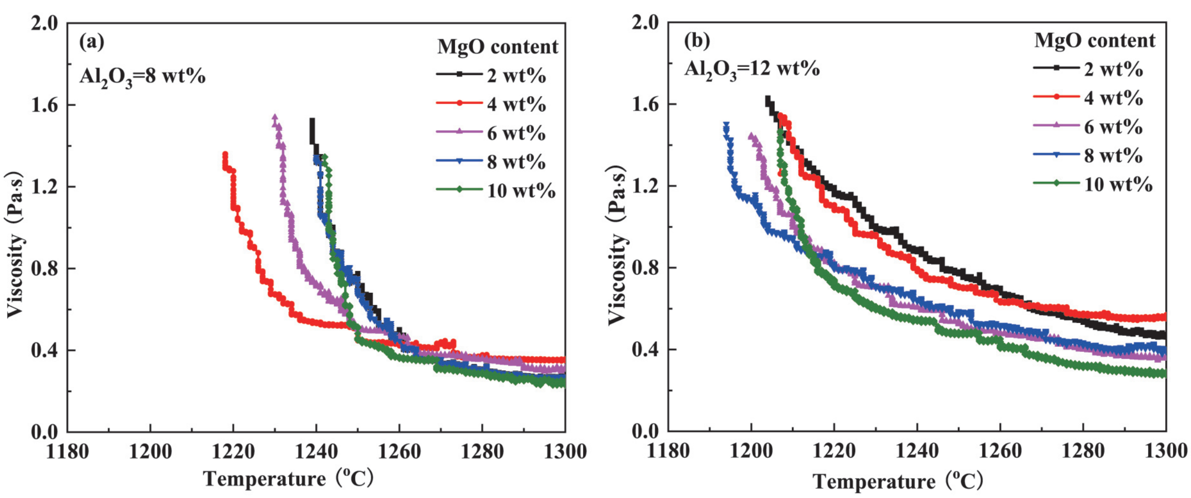

Figure 4. *Viscosity-temperature curve of fluorine-free mold fluxes for (a) Group 1 and (b) Group 2*

of solidification behavior to coordinated control the heat transfer and lubrication.

3.2.2. Cooling process structure

Since the thermodynamic analysis based on the Gibbs free energy calculations can provide useful guidance in the flux design and the experimental results interpretation, FactSage calculation of equilibrium phases of fluorine-free mold fluxes were carried out. As revealed in Figure 5 (a), during the cooling process of one mold flux sample as an example, the crystallization solid $Ca_3Si_2O_7$ started to precipitate at 1212 °C, which corresponded to the initial crystallization temperature of this slag theoretically. With further reduce of temperature, relevant crystallization solids $Ca_{11}B_2Si_4O_{22}$, $Ca_3MgSi_2O_8$ and some solid solutions formed successively. As the XRD test results presented the mineral phases below 1300 °C, and it can be seen from Figure 5(a) that the equilibrium of the mineral phase at 1000 °C was more extensive, the temperate 1000 °C was selected as a typical temperature to compare the type and amount of mineral phase precipitation, so as to qualitatively compare with the XRD results. The calculation results were shown in Figure 5(b). It can be seen that, although the equilibrium phases vary with different samples, the main crystallization solids $Ca_{11}B_2Si_4O_{22}$ and $Ca_3MgSi_2O_8$ were present in almost all slag.

Figure 6 showed the XRD patterns of fluorine-free mold fluxes, as the strong and sharp peaks indicated that the sample were well crystallized. All the diffraction peaks displayed in the XRD patterns corresponded to the standard peaks of $Ca_3MgSi_2O_8$, $Ca_{11}Si_4B_2O_{22}$ and $NaAlSiO_4$, which indicated the successful formation of crystals. With the increase of MgO contents in slag, the intensity of the diffraction peaks of $Ca_3MgSi_2O_8$ and $Ca_{11}Si_4B_2O_{22}$ gradually increased, which demonstrated that MgO contents in slag played an imperative role on the growth of crystals. Moreover, the addition Al_2O_3 from 8 wt% to 12 wt% inhibited the crystal precipitation, which was consistent with the characteristic change of viscosity-temperature curve.

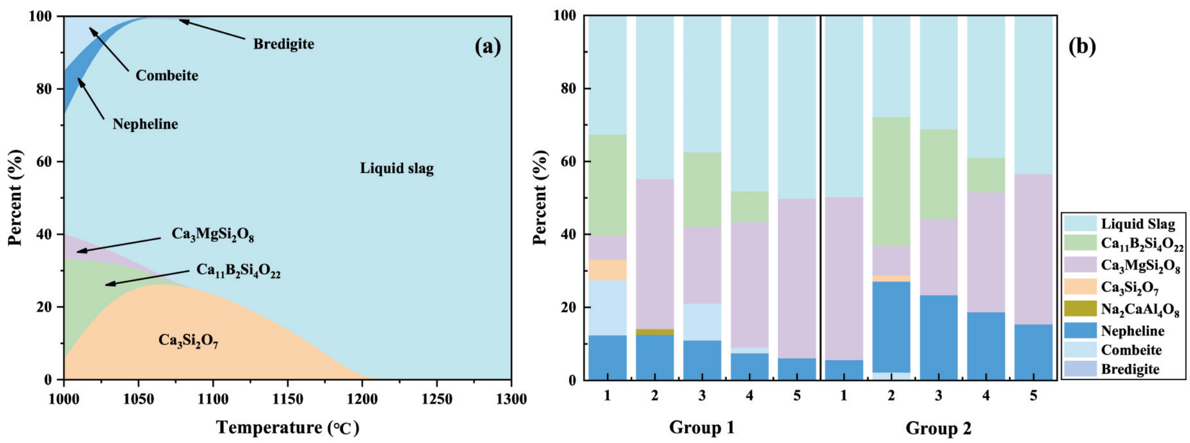

Figure 5. *Equilibrium phases of fluorine-free mold fluxes for (a) sample MgO=4 wt% in Group 1 during cooling process and (b) all samples at 1000 °C*

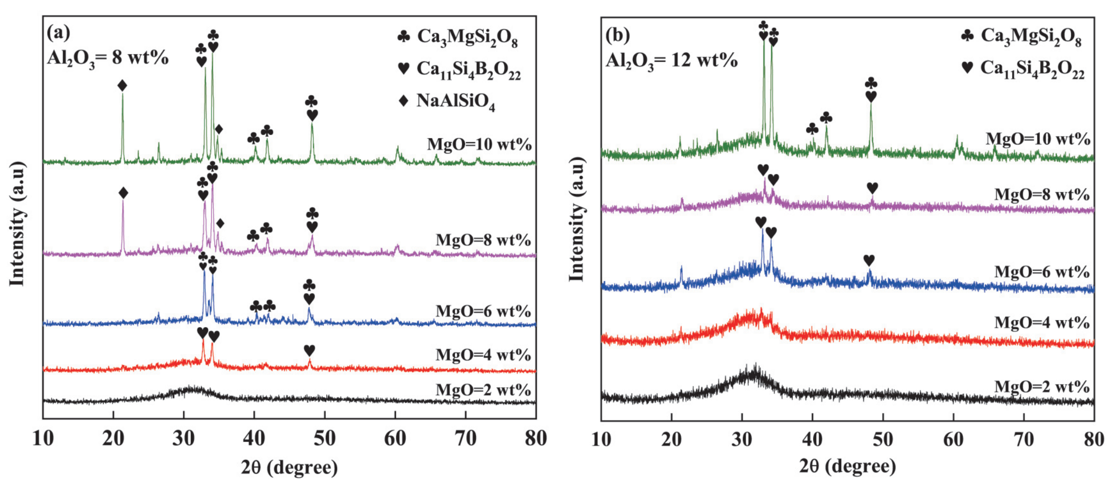

Figure 6. *XRD results of fluorine-free mold fluxes for (a) Group 1 and (b) Group 2*

Since the XRD tested samples were obtained by air cooling from 1300 °C and the cooling rate was not clear consequently, the crystallization of mold fluxes in experiments occurred under non-equilibrium conditions, resulting in some legitimate discrepancy between XRD results and FactSage calculation. However, the XRD results were mostly consistent with the thermodynamic calculation presenting the main crystallization phases of $Ca_3MgSi_2O_8$ and $Ca_{11}Si_4B_2O_{22}$, which verify the accuracy of experiment and calculation results.

4. Conclusion

(1) The viscosity at 1300 °C of fluorine-free mold fluxes reduced in the range of MgO = 2-10 wt%, while higher Al_2O_3 increased the viscosity as a whole. The trend of experiment results was consistent with Riboud and Iida models, while the FactSage calculation values were relatively higher due to lack of Li_2O database.

(2) The FTIR spectrum results exposed that the viscosity was more affected by the Si-O network than Al(B)-O structure. The MgO had a dual effect on the structure of mold flux that it provided O^{2-} to break the Si-O-Si bond, depolymerizing the silicate network, and the dissociated Mg^{2+} merged into the network structure and compensated for the charges difference in the $[AlO_4]^{5-}$ and $[BO_4]^{5-}$ tetrahedron as well.

(3) The viscosity-temperature curves changed from alkaline to acidic slag characteristics with Al_2O_3 increased from 8 wt% to 12 wt%, while the tendency of viscosity-temperature curve was not regular with the addition of MgO 2-10 wt%. Considering the variable viscosity during cooling process, adding MgO was conducive to slag fluid behavior improvement, while appropriate Al_2O_3 was required for coordination control of heat transfer and lubrication.

(4) The XRD patterns of fluorine-free mold fluxes showed that the main crystallization phases $Ca_3MgSi_2O_8$ and $Ca_{11}Si_4B_2O_{22}$ formed. With the increase of MgO contents in slag, the intensity of the diffraction peaks gradually increased, while the addition Al_2O_3 from 8 wt% to 12 wt% inhibited the crystal precipitation. The XRD results were mostly consistent with the thermodynamic calculation presenting the main crystallization phases, which verified the accuracy of experiment and calculation results.

Author's contributions

Ting Wu and Hai-chuan Wang conceived and designed the study. Guang-da Bao, Shama Sadaf, and Si-shuo Mao performed the experiments. Guang-da Bao and Shama Sadaf performed the data analysis. Guang-da Bao wrote the paper. Ting Wu and Hai-chuan Wang reviewed and edited the manuscript. All authors read and approved the manuscript.

Data availability

Data will be made available on request.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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ULOGA KOMBINOVANJA MgO I Al_2O_3 NA VISKOZNOST I NJIHOV UTICAJ NA STRUKTURU KALUPNOG FLUKSA BEZ FLUORA

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Apstrakt

Korišćenjem FactSage proračuna, Furijeove transformacije infracrvene spektroskopije (FTIR), rotacionih viskozimetara i rendgenske difrakcije (XRD), potvrđen je kombinovani uticaj MgO i Al_2O_3 na strukturu kalupnog fluksa bez fluora. Viskoznost šljake na 1300 °C smanjena je sa 2-10 wt% MgO, dok je veća količina Al_2O_3 povećala ukupnu viskoznost. Trend eksperimentalnih rezultata bio je u saglasnosti sa modelima Ribouda i Iide, dok su vrednosti FactSage proračuna bile relativno više. Na viskoznost šljake je veći uticaj imala mreža Si-O nego od struktura Al(B)-O, a MgO imao je dvostruki efekat na strukturu šljake. Krive viskoznosti i temperature promenile su se od alkalne ka kiselinskoj šljaci kada je Al_2O_3 povećan od 8 wt% na 12 wt%, dok trend nije bio uniforman sa dodatkom 2-10 wt% MgO. Svi FactSage proračuni i XRD obrasci pokazali su da povećanje sadržaja MgO postepeno podstiče rast kristala $Ca_3MgSi_2O_8$ i $Ca_{11}Si_4B_2O_{22}$, dok dodatak Al_2O_3 inhibira precipitaciju kristala.

Ključne reči: *Kalupni fluks; Bez fluora; Struktura; Viskoznost; Kristalizacija*