Effect of Basicity and B_2O_3 on the Viscosity and Structure of Fluorine-Free Mold Flux

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Abstract

The effect of basicity (weight ratio of CaO/SiO_2) and B_2O_3 on the viscosity and structure of Fluorine-free mold flux for the casting of medium carbon steels was conducted in this article, through the rotating cylinder method combined with the Fourier transform infrared (FTIR) spectroscopy. The results showed that, with the increase of basicity, the viscosity of mold flux was attenuated dramatically, and then kept constant or slight increased in the low temperature region. The reason could be explained as the degree of polymerization (DOP) of the network structure was first reduced significantly with the addition of basicity, and then the further depolymerization is less pronounced with the further increase of basicity. Beside the formation of high melting point substance leads to the slight increase of viscosity. Moreover, it suggested that the viscosity of mold flux is decreased with the addition of B_2O_3 content, due to the fact that B_2O_3 is a low melting point oxide which could substantially lower the break temperature of mold flux. The result of FTIR indicated B_2O_3 acts as network former, and tends to form $[BO_3]$ -triangular and $[BO_4]$ -tetrahedral structural units, which would connect with each other to form some simple network structure such as diborate or pentaborate. With the addition of B_2O_3 , the free oxygen ions (O^{2-}) would depolymerize the diborate structural unit, and the depolymerized diborate would link again with free $[BO_3]$ -triangular to form complex pentaborate groups. Moreover, the effect of above addition on the apparent activation energy for viscous flow and break temperature of mold flux also were discussed. The results obtained in this paper provide the detailed study of the structure evolution of Fluorine-free mold flux when B_2O_3 is added.

Key words: Mold flux; Fluorine-free; Basicity; B_2O_3 ; Viscosity; Structure

I. INTRODUCTION

It is well known that mold flux plays important roles in continuous casting, such as protecting the molten steel from oxidation, absorbing inclusions, providing thermal insulation, lubricating the strand, and controlling heat transfer between the mold and

1 shell.^[1-4] In conventional commercial mold flux, fluorides as an effective fluxing agent,
2 tends to work as a network breaker in silicate systems, to reduce the breaking
3 temperature and the viscosity of mold flux.^[5,6] Besides, fluorides would be necessary
4 for the formation of Cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$), a important crystalline phase, which could
5 precipitate in the mold flux film to effectively modify the horizontal heat transfer rate
6 from the molten steel to the copper mold. However, fluorides tend to cause many
7 problems, such as environmental pollution, corrosion of casting facilities, etc.^[7-10]
8 Therefore, it is of significant importance to develop the fundamental studies of F-free
9 mold flux system for continuous casting process.

10 Recently, series research of Wang et al.^[11-13] found that calcium borosilicate
11 ($\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$) appears the potential to replace Cuspidine for the development of F-free
12 mold flux system. As the major substance for the formation of calcium borosilicate
13 ($\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$) crystal phase, the basicity (weight ratio of CaO/SiO_2) of mold flux has
14 been regarded to affect the viscosity and structure of mold flux significantly. The study
15 of Takahira et al.^[14] found that the viscosity of traditional mold flux reduces with the
16 increase of basicity. Gao et al.^[15] also obtained the similar results in studying
17 SiO_2 - CaO - MgO - Al_2O_3 slag system. As another major substance for $\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$
18 crystal phase, B_2O_3 would also influence the viscosity and structure of molten mold
19 flux system. The studies of Qi et al.^[16] found that B_2O_3 could lower the viscosity of
20 mold flux due to the nature of its low melting point behavior. However, according to the
21 study of Sun et al.^[17], B_2O_3 would tend to act as a typical network forming oxide to
22 increase DOP of slag structure, which may lead to the increase of viscosity.

1 It is well known that viscosity, as one of the most important properties of mold flux,
2 would affect the lubrication of the mold oscillation, inclusion absorption and uniform
3 horizontal heat transfer in the mold, and it is usually affected by the variation of molten
4 structure. Therefore, it is necessary to research the relation between the viscosity and
5 slag structure.

6 Although some research has been conducted to study the crystallization and heat
7 transfer behavior of F-free mold flux; however, there is very few of it focusing on the
8 structure and its related viscosity variation that caused by the absence of fluorides. As
9 the major component of the calcium borosilicate ($\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$) that has the potential to
10 replace the Cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) in fluorine free mold flux system, the effect of
11 basicity and B_2O_3 on the viscosity and the structure of F-free mold flux is urgent to be
12 conducted. Especially, how the evolution of the traditional silicate network structure
13 would be going when the network former B_2O_3 is added.

14 **II. MATERIALS and METHODS**

15 **2.1. Samples preparation**

16 The major chemical composition of each sample used in this study is listed in **Table**
17 **1**. All those samples were prepared from reagent grade chemicals of CaO, SiO_2 ,
18 Na_2CO_3 , B_2O_3 , and Li_2CO_3 et al, where the basicity was fixed at 1.10, 1.15 and 1.25,
19 respectively, and the content of B_2O_3 was varied at 4 wt%, 6 wt%, and 8 wt%. In the
20 preparation of experimental samples, the raw materials were firstly weighted according
21 to **Table 1**, and then they were mechanical fully mixed. Then the mixed samples were
22 heated at a heating rate of 25K/min in an induction furnace, and melted at 1773K

1 (1500°C) for 5 minutes to homogenize their chemical compositions. After that, the
 2 liquid slag was poured into a water-cooled copper plate to quench to achieve a fully
 3 glassy phase, and finally they were subjected to crushing and grounding into powder
 4 samples. All powder samples were tested by the X-ray diffraction (XRD, Rigaku
 5 TTRIII), and there is no characteristic signal occurring in the samples as shown in Fig 1,
 6 which indicates they are fully amorphous and can represent for the structure of each
 7 molten mold flux.

Table 1. The Chemical Compositions of mold fluxes.

Before experiment (wt%)							After experiment (wt%)					
Weighed amount using balance							XRF analysis					Calculated
Sample	R	CaO	SiO ₂	Na ₂ O	Li ₂ O	B ₂ O ₃	R	CaO	SiO ₂	Na ₂ O	Li ₂ O	B ₂ O ₃
A	1.10	40.86	37.14	8	2	6	1.10	40.84	37.15	7.99	2	5.89
B	1.25	43.33	34.67	8	2	6	1.25	43.4	34.72	7.97	2	5.84
C	1.15	41.72	36.28	8	2	6	1.15	41.8	36.38	7.97	2	5.83
D	1.15	42.79	37.21	8	2	4	1.15	42.8	37.17	7.95	2	3.94
E	1.15	40.65	35.35	8	2	8	1.15	40.68	35.38	7.96	2	7.92

Fig 1. XRD results of the pre-melted samples.

10 The major chemical component of each sample was analyzed by X-ray fluorescence

1 spectroscopy (XRF, S4 Pioneer; Bruker AXS; GmbH Karlsruhe, Germany); however,
2 the direct analysis of B and Li is unreliable. Work done by Janke et al.^[18] indicated that
3 as an effective fluxing agent, the vaporization of Li₂O in high temperature is very
4 limited. In addition, volatilization of Li was found only possible for commercial mold
5 powders that containing significant amounts of free carbon, such that lithium would be
6 reduced to its metallic form and vaporize.^[19] However, there is no carbon present in the
7 present study; thus, Li₂O was assumed to be constant. So, the percentage of B₂O₃ was
8 calculated according to the XRF results and the initial percentage of Li₂O. It was found
9 that the content doesn't change obviously, which indicates that there is no significant
10 evaporation in the current systems.

11 **2.2. Viscosity Measurement**

12 Viscosity is measured by using a Brookfield DV-II+viscometer (Brookfield Inc.
13 USA), through the rotating cylinder method, which is schematic shown in **Fig 2**. The
14 calibration measurement was carried out at room temperature by using standard oil
15 with known viscosity of 0.28 Pa.s.^[20]

16 When measuring the viscosity of those mold fluxes, the sample powders of 250 g
17 were placed in a graphite crucible. Then, the crucible was heated to 1773 K (1500 °C)
18 and held for 10 minutes to obtain a homogeneous melt in an electric resistance furnace.
19 Then, the bob was immersed into liquid slag bath and rotated **at a fixed speed with 12**
20 **r/min**. Each measurement was preformed during the cooling cycle, and the data of
21 viscosity versus temperature were collected every 5 s.

Fig 2. The schematic figure of viscosity viscometer.

2.3. FTIR Spectroscopy

In order to understand the influence of basicity and B_2O_3 on the structure of mold flux, the as-quenched samples were analyzed by using FTIR (Nicolet 6700). The quenched samples were pulverized into powders with the size less than 100 micron diameter. Then 2.0 mg of each sample powders mixed with 200 mg KBr (reagent grade) were pressed into thin section disk for FTIR test. The FTIR measurement was conducted by a spectrophotometer equipped with a KBr detector, and the spectra were recorded in the range of 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} . The wavenumber of the FTIR transmission spectra region of the samples are mainly between 1600 to 400 cm^{-1} ,^[21-23] and the assignments of the detected absorption bands representing for the corresponding structure are summarized in **Table 2**.

Table 2. Assignments of FTIR bands.

Wavenumber (cm ⁻¹)	Assignments	References
400-600	T-O-T bond bending vibrations (T denotes Si, Ca, or Na elements et al.)	[17]
600-800	B-O-B bond bending vibrations in pentaborate	[24-27]
~760	B–O–B bond bending vibrations from pentaborate groups	[24]
800-1200	Assigned [SiO ₄]-tetrahedral stretching vibration and [BO ₄]-tetrahedral stretching vibrations	[17,22,24-26]
~900	B-O bond in [BO ₄]-tetrahedral units in diborate	[25,26]
1200-1600	[BO ₃]-tri-hedral stretching vibrations	[24-26]
~1250	Stretching vibration of B-O bonds in boroxol rings	[24-26,28]
~1350	Stretching mode of [BO ₃]-tri-hedral and [BO ₂ O ⁻]-tri-hedral in boroxol rings (O ⁻ : non-bridging oxygen atom)	[24-26,28]

III. RESULTS AND DISCUSSION

3.1. Effect of basicity on the viscosity and its correlation to the structure

Fig 3 shows the viscosity of mold flux at different temperatures varying with basicity at fixed 6 wt% B₂O₃ content. It can be seen that the viscosity is firstly getting reduced significantly when the basicity is increased from 1.10 to 1.15, and then keeps relatively constant, except a slight increase at low temperature region in the range from 1.15 to 1.25.

It is well known that the depolymerization of the structure results in a lower viscosity. With the increase of basicity, the amount of CaO (basic substance) in the sample is increased, and the availability of free oxygen ions (O²⁻) increases as well due to the dissociation of CaO. Therefore, the free oxygen ions (O²⁻) would react with the bridged oxygen (O⁰) in the silicates and tend to decrease the complex Si-O structure within the slag structure. Thus, the viscosity of mold flux should be decreased with the increase of basicity.

Fig 3. Viscosity of the F-free mold flux versus basicity at different temperatures.

However, when excess free oxygen ions (O^{2-}) are supplied with the further increase of basicity (1.15 to 1.25), the depolymerization effect would not be pronounced especially at low temperature region, as many existing complex network structures have already been depolymerized into simpler and smaller network units.

On the other hand, the increase of basicity tends to promote the formation of high melting substance Ca_2SiO_4 . Thus the liquidus temperature of the slag would be improved due to the excessive formation of Ca_2SiO_4 , and it leads to the reduction of superheat degree of the slag melt, which in turn increases the viscosity for the system that with a higher basicity. Therefore, the viscosity for high basicity mold flux is depending upon the balance between the depolymerization of structure and the decrease of superheat degree. The finding is in agreement with the results of Lee who conducted the influence of basicity on the viscosity of blast furnace slags. ^[29]

In connection with the viscosity, the FTIR results of the as-quenched samples with varied basicity are shown in **Fig 4**, where the assignments of each band is shown in

Table 2.

Fig 4. Effect of basicity on the results of FTIR spectra of the as-quenched samples

It could be observed that the absorbance peak of the T-O-T bond bending vibrations in the region of 400-600 cm^{-1} and the B-O-B bond bending vibrations from pentaborate in 600-800 cm^{-1} become less pronounced with the increase of basicity, due to the more presence of free oxygen ions (O^{2-}) that react with the bridged oxygen (O^0) of T-O-T and B-O-B bond within the slag structure, **resulted in** the depolymerization of the T-O-T and B-O-B bond.

The B-O asymmetric stretching vibrations of $[\text{BO}_4]$ -tetrahedral is located in the absorption region 800-1200 cm^{-1} , and this region also represents the stretching vibration of the $[\text{SiO}_4]$ -tetrahedral. It seems that the signal of the absorption region in this range becomes less noticeable with the increase of basicity, also suggesting the depolymerization of network structure of slag melts.

The absorption region of 1200-1600 cm^{-1} represents the asymmetric stretching vibrations of $[\text{BO}_3]$ -triangular, and it becomes weakening and broadening, which

1 indicates that the characteristic network of $[\text{BO}_3]$ -triangular melt structure has been
2 broken. In detail, the band at around 1250 cm^{-1} , assigned to the asymmetric stretching
3 vibration of B-O bonds in $[\text{BO}_3]$ -triangular of boroxol rings, becomes less pronounced
4 with the increase of basicity. Also the intensity of the band at around 1350 cm^{-1} ,
5 generated by the asymmetric stretching modes of $[\text{BO}_3]$ -triangular and
6 $[\text{BO}_2\text{O}^-]$ -triangular in boroxol rings, attenuates gently with the increase of basicity. The
7 variation trend of these two bands indicates the structures of $[\text{BO}_3]$ -triangular and
8 $[\text{BO}_2\text{O}^-]$ -triangular are gradually broken in the melts with the increase of basicity.

9 It implies from above results of the FTIR, the increase of basicity not only makes the
10 complex silicate structure being depolymerized, but also causes the variation of borate
11 structure, leading to the reduction of mold flux viscosity.

12 **3.2. Effect of B_2O_3 on the viscosity and its correlation to the structure**

13 **Fig 5** shows the viscosity of mold flux at different temperatures versus B_2O_3 content
14 at fixed basicity of 1.15, where it can be observed that the viscosity decreases
15 continuously with the addition of B_2O_3 . The melting point of B_2O_3 is 723 K (450°C),^[30]
16 and the addition of B_2O_3 could combine with many kinds of oxides to form eutectics
17 with low melting points, which substantially lower the break temperature of mold flux.
18 Thus, the superheat is increased, leading to the reduction of mold flux viscosity.

Fig 5. Viscosity of the F-free mold flux system versus B₂O₃ content

The FTIR spectra results of above samples are shown in **Fig 6**. It could observe that the general pattern of bending vibration of T-O-T, in the absorption region of 400-600 cm⁻¹, becomes less pronounced with the addition of B₂O₃, as B was introduced into the network structure to substitute for other elements. However, the absorption region 600-800 cm⁻¹ assigned to the bending vibrations of B-O-B in pentaborate, becomes more pronounced, indicating there are more B elements introduced into the network and formed pentaborate structure.

The absorption region in the range of 800-1200 cm⁻¹ is weakening and the peak of 900 cm⁻¹ representing B-O bond in [BO₄]-tetrahedral units in diborate is flattening, which suggests simple diborate structural units and traditional silicate tetrahedral structure is resolved, with the addition of B₂O₃. Furthermore, the band at 1250 cm⁻¹, assigned to the asymmetric stretching vibration of B-O bonds in [BO₃]-triangular of boroxol rings, becomes less pronounced with the addition of B₂O₃ content. However, the band at 1350 cm⁻¹, generated by the asymmetric stretching mode of [BO₃]-triangular

1 and $[\text{BO}_2\text{O}^-]$ -triangular in boroxol ring, becomes more and more prominent. The reason
 2 could be explained as follows.

3

4 **Fig 6. Effect of B_2O_3 on the results of FTIR spectra of as-quenched samples**

5 As network former, B_2O_3 could decompose and form many $[\text{BO}_3]$ -triangular and
 6 $[\text{BO}_4]$ -tetrahedral structural units, then these $[\text{BO}_3]$ -triangular structural units would
 7 connect with $[\text{BO}_4]$ -tetrahedral structural units to form some simple network structure
 8 such as diborate structural units^[31-33], which is schematically illustrated in **Fig 7**. With
 9 the addition of B_2O_3 , there would be more simple borate structural units formed, as
 10 suggested by the signal ($600\text{-}800\text{ cm}^{-1}$) that the bending vibrations of B-O-B in
 11 pentaborate becomes more pronounced. Meanwhile, the existing free oxygen ions (O^{2-})
 12 would interact with the bridged oxygen between the $[\text{BO}_3]$ -triangular structural unit and
 13 the $[\text{BO}_4]$ -tetrahedral structural unit to depolymerize the diborate structural units,
 14 which could be clarified by the band at 1250 cm^{-1} , where the asymmetric stretching
 15 vibration of B-O bonds in $[\text{BO}_3]$ -triangular of boroxol rings dissociated. Eventually, the
 16 dissociated simple diborate units would connect with extra $[\text{BO}_3]$ -triangular or

1 [BO₄]-tetrahedral units to form more complex pentaborate groups, it could be testified
 2 by the band at 760 cm⁻¹ where assigned B–O–B bond bending vibrations from
 3 pentaborate groups. Thus, the stretching mode of [BO₃]-tri-hedral and
 4 [BO₂O⁻]-tri-hedral in more complex boroxol rings is strengthened, as shown by the
 5 signal of band at 1350 cm⁻¹ in **Fig 6**. The schematic illustration for the above process is
 6 shown in **Fig 8**.

7
 8 **Fig 7. The schematic illustration for simple borate structural units**

9
 10 **Fig 8. The schematic illustration for the formation of complex borate structure**

11 From above results, B₂O₃ acts as a typical network former in the present study, which

tends to increase the DOP of borate structure and results in an increasing viscosity of above systems. However, B₂O₃ is a low melting point oxide, which could substantially lower the break temperature of mold flux system, as verified from the results in the following **Section 3.3.2**. Thus, with the decrease of break temperature, the superheat degree is increased; leading to the reduction of the melts viscosity. Furthermore, once [BO₃]-tri-hedral (a simple two dimensional structure) introduces into three dimensional complex structure, it would greatly reduce the symmetry of the current structure, and the present borate structure has preferentially connected to the near Si atoms and introduced into the silicate networks, which could lower the uniformity of the networks.^[34] Thus, the strength of the whole structure is weakened; thereby the viscosity of mold flux is getting reduced with the addition of B₂O₃.

3.3. Effect of B₂O₃ on the apparent activation energy for viscous flow and the break temperature

3.3.1. Effect of B₂O₃ on the apparent activation energy

Actually, the variation of the viscosity could be related to the apparent activation energy for viscous flow, and the relationship between the apparent activation energy and temperature, is usually described by the Weymann–Frenkel equation:

$$\eta = \eta_0 \cdot \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

where η is the viscosity of mold flux, η_0 is the pre-exponent factor, T is the absolute temperature, R is the gas constant and E_a is the apparent activation energy. The activation energy represents the change of the frictional resistance for viscous flow. By rearranging Eq.(1), the value of E_a can be determined as the slope of the plotting $\ln\eta$

1 versus $1/(RT)$ from Eq.(2).

$$2 \quad \ln \eta = \ln \eta_0 + \frac{Ea}{RT} \quad (2)$$

3 According to Eq.(1) and Eq.(2), the apparent activation energy for viscous flow
 4 could be calculated from the slope of the natural logarithm of viscosity as a function of
 5 $1/RT$. The results of the calculation are provided in **Fig 9** and **Table 3**.

6
 7 **Fig 9. Plots of $\ln \eta$ VS $1/RT$ with the variation of B_2O_3 content**

Table 3. The apparent activation energy (Ea) and break temperature (T_{br}) of mold fluxes.

Sample	C	D	E
Ea (KJ/mol)	182.99 ± 8.86	382.28 ± 34.36	173.76 ± 16.29
T_{br} (°C)	1191	1232	1183

8 As shown in **Fig 9** and **Table 3**, through comparing Sample C ($B_2O_3=6$ wt%) with D
 9 ($B_2O_3=4$ wt%) and E ($B_2O_3=8$ wt%), it suggests that the activation energy decreases
 10 with the addition of B_2O_3 , which indicates that the resistance for viscous flow decreases.
 11 The result is consistent with the one discussed in **Section 3.2** that the addition of B_2O_3
 12 tends to greatly reduce the resistance of viscous flow process, and therefore causes the

1 apparent activation energy decreased.

2 3.3.2. Effect of B_2O_3 on the break temperature

3 Break temperature is defined as the temperature at which there is a significant change
4 of viscosity during the cooling cycle, and it represents the transition zone from the fully
5 liquid region to the solid-liquid co-existing region.^[35,36] The break temperature is a key
6 parameter to indicate the rheological property of mold flux, which determines the
7 thickness of the solid and liquid layer in the gap of shell/mold wall. **Fig 10** shows the
8 viscosity-temperature curves for mold fluxes with different B_2O_3 contents, and the
9 break temperature obtained from the viscosity-temperature curves are listed in **Table 3**.

10

11

Fig.10 Viscosity changes with different B_2O_3 contents for F-free mold fluxes

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It can be seen from **Fig 10** and **Table 3** that the sample D ($B_2O_3=4$ wt%) has the highest break temperature of 1232 °C (1503 K), followed by the sample C ($B_2O_3=6$ wt%) and the sample E ($B_2O_3=8$ wt%), which indicates that the break temperature reduces with the addition of B_2O_3 . The reason is that boron is network former in silicate structure, which is similar to silicon; so the crystallization of mold flux can be

1 suppressed by the addition of B_2O_3 that would in turn lower the break temperature.^[20]

2 Besides, boron can react with other element to form low melting point compound,
3 which also could make the break temperature of mold flux lower.^[37]

4 **IV. CONCLUSIONS**

5 The effect of basicity (weight ratio of CaO/SiO_2) and B_2O_3 on the viscosity and
6 structure of Fluorine-free mold flux was conducted in this article, and the specific
7 conclusions are summarized as follows:

8 (1) With the increase of basicity, the viscosity of mold flux was attenuated dramatically,
9 and then kept constant or slight increased in the low temperature region. It is
10 because the degree of polymerization (DOP) of the network structure was first
11 reduced significantly with the addition of basicity, and then the further
12 depolymerization is less pronounced with the further increase of basicity. Besides,
13 the formation of high melting point substance leads to the reduction of superheat of
14 the slag melts and slight increase of viscosity.

15 (2) The viscosity was decreased obviously with the addition of B_2O_3 content, as B_2O_3
16 could substantially lower the break temperature of mold fluxes, and the addition of
17 B_2O_3 could greatly reduce the symmetry and the uniformity of the networks which
18 decrease the strength of the whole structures. The result of FTIR indicated B_2O_3
19 could form $[BO_3]$ -triangular and $[BO_4]$ -tetrahedral structural units, and these units
20 can connect to form some simple structures such as diborate or pentaborate
21 structural units. With further addition of B_2O_3 , the diborate structural units could be
22 depolymerized, and would link with free $[BO_3]$ -triangular units to form complex

pentaborate groups.

(3) The apparent activation energy for Sample C ($B_2O_3=6$ wt%), Sample D ($B_2O_3=4$ wt%) and Sample E ($B_2O_3=8$ wt%) is 182.99 ± 8.86 KJ/mol, 382.28 ± 34.36 KJ/mol, and 173.76 ± 16.29 KJ/mol respectively. Their respective break temperatures are 1191°C , 1232°C , and 1183°C . It showed that the activation energy and the break temperature of mold flux were attenuated with the addition of B_2O_3 content.

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