Research Article

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Role of B_2O_3 on structure and shear-thinning property in $CaO-SiO_2-Na_2O$ -based mold fluxes

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Abstract: Most traditional mold fluxes are Newtonian fluids, and their constant viscosity has certain limitations in continuous casting. A new non-Newtonian fluid mold flux with shear-thinning behavior, *i.e.*, a mold flux with a relatively high viscosity at lower shear rates and a relatively low viscosity at higher shear rates, is required to satisfy the mold-flux performance requirements for high-speed continuous casting. The addition of a certain amount of B_2O_3 to a $CaO-SiO_2-Na_2O$ -based mold flux can result in a shear-thinning property. To obtain an improved understanding of the mechanism of this characteristic, a molecular-dynamics simulation method was used to study the microstructural changes of the mold flux. Structural changes of mold-flux samples were analyzed and verified by Raman spectroscopy. The results of the two methods were almost the same, both resulted from the addition of B_2O_3 and changed the microstructure and degree of polymerization of the mold flux, which resulted in the shear-thinning property of the mold flux. This non-Newtonian fluid mold flux was used in square-billet casting tests, and the quality of the slab was improved effectively.

Keywords: mold flux; non-Newtonian fluid; viscosity; degree of polymerization; shear-thinning

1 Introduction

Mold flux is important in the continuous casting of high-quality steel. In the lubrication region of the casting mold, and specifically at the meniscus and the area under the meniscus of the casting mold, the mold flux acts as a lubricant, and the shear rate can be as high as $100-1000\text{ s}^{-1}$. In this case, the viscosity (η) of the mold flux should be as low as possible to achieve a higher lubrication level. In addition, within the retention area of the casting mold, which is the molten-steel surface, a relatively high mold-flux viscosity is required to improve the slag-entrapment phenomenon, which decreases the occurrence of slag inclusions in the molten steel; the shear rate in this area is $10-40\text{ s}^{-1}$ [1–3].

A mold flux that exhibits a gradual decrease in viscosity with an increase in shear rate, can maintain a relatively high viscosity in the mold-retention area, which reduces the probability of the slag layer being involved in the molten steel, and promotes the flotation of slag inclusions and reduces slab defects. A relatively low viscosity exists in the lubrication area, which ensures that the mold flux can flow into and below the meniscus with time and maintain a certain liquid-slag-layer thickness. A good lubrication effect is achieved, which improves the heat transfer and billet quality, and reduces the frequency of bonding-steel leakage [4, 5]. The mold flux exhibits a shear-thinning property, which is a non-Newtonian fluid characteristic.

A Newtonian liquid is a liquid whose viscosity is independent of its shear rate. As the shear rate increases, the variation in viscosity is low or remains unchanged, and the traditional mold flux that is used in casting is a typical Newtonian fluid [6]. Therefore, traditional mold fluxes cannot resolve the contradiction above. A non-Newtonian fluid is a fluid whose viscosity changes with changes in shear rate [7]. Non-Newtonian fluids can be divided into two categories: one in which the viscosity increases gradually with an increase in shear rate, and demonstrates shear-thickening behavior, and the other in which the viscosity decreases gradually with an increase in shear rate, and demonstrates shear-thinning behavior. Based on the problems above, the urgent development of a non-

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Table 1: Main chemical composition of mold-flux sample after pre-melting (mass %)

Samples	CaO	SiO_2	Na_2O	Al_2O_3	MgO	CaF_2	Li_2O	B_2O_3
Blank-1	37.0	34.0	12.0	5.0	4.0	6.5	1.5	—
B-2	35.0	32.0	11.0	4.0	3.0	5.5	1.5	8.0
B-3	34.0	31.0	11.0	4.0	3.0	5.5	1.5	10.0
B-4	33.0	30.0	11.0	4.0	3.0	5.5	1.5	12.0
B-5	32.0	29.0	11.0	4.0	3.0	5.5	1.5	14.0

Newtonian fluid mold flux with shear-thinning properties is required.

Few studies exist on non-Newtonian fluid mold fluxes, only a few researchers from Japan and South Korea [8, 9] have found that the addition of a certain amount of B_2O_3 to traditional mold flux can allow it to exhibit a shear-thinning property. With an increase in B_2O_3 content, the shear-thinning property increased and then decreased. This characteristic behavior results because B_2O_3 changed the degree of polymerization (DP) of the mold flux system.

B_2O_3 addition (as a type of fluxing agent) will reduce the mold-flux viscosity [10], but the specific law that decreases the mold-flux viscosity is unclear and it is not known if it will always decrease, and what an appropriate B_2O_3 addition is. Research is lacking in some microfields; it is not known whether the mold-flux structure will change to exhibit non-Newtonian fluid properties.

In this study, B_2O_3 was used as a key additive to verify whether it can yield non-Newtonian fluid characteristics in the mold flux. Different contents of B_2O_3 were added to the $CaO-SiO_2-Na_2O$ -based mold flux, and an improved rotary viscometer was used to detect and analyze the shear-thinning property of the mold flux.

To study how B_2O_3 addition into the mold flux results in structural changes and leads to the shear-thinning property of the mold flux, the microstructural change in the mold flux after B_2O_3 addition was studied by molecular-dynamics simulation. Molecular-structural changes in the mold-flux samples were analyzed by using high-temperature Raman spectroscopy. The non-Newtonian fluid mold flux was used in square-billet casting tests.

2 Preparation of non-Newtonian fluid mold flux and analysis of its shear-thinning property

2.1 Preparation of $CaO-SiO_2-Na_2O$ -based mold flux

Analytical reagent (AR)-grade CaO , SiO_2 , Na_2O , Al_2O_3 , MgO , CaF_2 and Li_2O were mixed in a certain ratio. The mixture was placed into a Pt crucible and heated to $1300^\circ C$ for 0.5 h to obtain a uniform and stable mold flux. The prepared mold flux was poured into a cold-steel sheet to obtain a slag with a full glass phase. The mold-flux samples were crushed and ground to smaller than 200 mesh. The prepared $CaO-SiO_2-Na_2O$ -based mold flux was defined as a Blank-1 sample.

2.2 Preparation of $CaO-SiO_2-Na_2O-B_2O_3$ -based mold flux

B_2O_3 (AR) was added to the $CaO-SiO_2-Na_2O$ -based mold flux in concentrations of 8%, 10%, 12%, and 14%, and mixed evenly. Mold flux was prepared by the method mentioned above. Samples with an increase in B_2O_3 content in the mold flux were defined as B-2, B-3, B-4, and B-5 samples. The chemical composition of the as-prepared mold-flux samples was determined by X-ray fluorescence spectroscopy. The test results are shown in Table 1.

The research results are based on the composition of the mold fluxes in Table 1.

2.3 Measurement of viscosity and analysis of shear-thinning behavior

The η values at rotation speeds of 50, 100, 150, and 200 r/min that correspond to shear rates ($\dot{\gamma}$) of 18, 35, 53, and $70 s^{-1}$ (shear rate = $0.35 \times$ rotation speed, where 0.35 represents the rotor coefficient), were measured using the

RTW-13-type melt physical-property comprehensive tester. The resultant $\eta-r'$ curves are presented in Figure 1(a). The Blank-1 sample showed a low degree of shear-thinning, whereas the B-2, B-3, B-4, and B-5 samples displayed a high degree of shear-thinning.

(a)

(b)

Figure 1: (a) Schematic diagram of viscosity change of mold-flux sample with shear-rate change; (b) schematic diagram of average viscosity of mold flux

The reduction ratio of the viscosity of the mold flux in the same range of shear-rate gradient change was used to measure the strength of the shear-thinning behavior, *i.e.*, the shear-thinning rate. The specific calculation equation is expressed as Eq. (1):

$$N = \frac{\eta_{\max} - \eta_{\min}}{\Delta r}, \quad (1)$$

where N represents the shear-thinning rate, $\eta_{\max}$ represents the viscosity at a shear rate of 18 s^{-1} , $\eta_{\min}$ represents

the viscosity at a shear rate of 70 s^{-1} , and $\Delta r'$ represents the variation in shear rates.

The calculation results of the shear-thinning rate for each mold-flux sample are presented in Table 2. The minimum shear-thinning rate of the Blank-1 sample was 0.00050, whereas the maximum shear-thinning rate of the B-4 sample was 0.00104. Therefore, we concluded that the B-4 sample exhibited the strongest shear-thinning behavior and that of the Blank-1 sample was weakest. An increase in B_2O_3 content in the mold flux resulted in an initial increase and then decrease in shear-thinning behavior.

Table 2: Shear-thinning rate of mold-flux samples

Sample number	Shear-thinning rate
Blank-1	0.00050
B-2	0.00096
B-3	0.00098
B-4	0.00104
B-5	0.00094

Figure 1(b) shows the average viscosity of the mold-flux sample. The average viscosity of the mold flux that contains B_2O_3 was significantly lower than that of the blank sample. When the content of B_2O_3 changed from 8% to 12%, the average mold-flux viscosity increased gradually. However, when the content of B_2O_3 exceeded 12%, the average viscosity of the mold fluxes decreased rapidly. Therefore, it is necessary to conduct an in-depth study on the molecular structure of the mold flux in this process.

3 Molecular-dynamics simulation

After B_2O_3 addition into the $\text{CaO-SiO}_2\text{-Na}_2\text{O}$ -based mold flux, the changes in radial distribution function, coordination number and proportion of the Si-O atoms were calculated by molecular-dynamics simulation. The structural-change information and the DP of the mold flux during the process were analyzed, and the influence of B_2O_3 addition on the shear-thinning property of the mold flux was studied further [11–15]. The temperature change with time in the simulation process is shown in Figure 2.

Table 3 shows the composition of the simulated slag system. Table 4 shows the number of atoms, side length, and density of the box.

Figure 3 shows the simulation results with 12% B_2O_3 . To observe the molecular structure more clearly, one crys-

Figure 2: Schematic diagram of temperature variation with time

Table 3: Slag compositions

Slag sample	Alkalinity	Composition (mass %)			
		CaO	SiO ₂	Na ₂ O	B ₂ O ₃
1	1.1	48	43	9	0
2	1.1	44	39	9	8
3	1.1	43	38	9	10
4	1.1	41	38	9	12
5	1.1	40	37	9	14

Figure 3: Simulated cell diagram with 12% B_2O_3 content

tal cell was selected for observation. The O atoms are red, the Si atoms are blue, the Ca or Na atoms are white, and the B atoms are green. The crystal cell shows that mainly Si and B atoms are involved in bonding. One Si atom connects to four O atoms. Two connection types exist between the B and O atoms; one B atom connects to four O atoms (majority), and one B atom connects to three O atoms (minority). Ca or Na atoms have the least number of bonds, but

(a) Radial distribution function

(b) coordination number

Figure 4: B_2O_3 content of 12%, radial distribution function and coordination number

a high coordination number of O atoms (up to six), which results in their weak control over O atoms.

3.1 Analysis of radial-distribution function and coordination number of $CaO-SiO_2-Na_2O-B_2O_3$ -based mold flux

Figure 4 shows the calculated radial-distribution-function and coordinate-distribution diagrams for a 12% B_2O_3 addition (i.e., the B-4 sample). The abscissa that corresponds to the first peak of the radial distribution function in Figure 4(a) was the bond length that corresponds to the atoms in the mold flux. The bond lengths of B-O, Si-O, Ca-O, and Na-O were 1.35 Å, 1.625 Å, 2.25 Å, and 2.35 Å, respectively. The bond lengths of each atomic pair in the quaternary

Table 4: Simulated particle number and box side length

Number	Number of particles					The length of the box/Å	Density/g·cm ⁻³
	Ca	Si	Na	B	O		
1	997	834	337	0	2832	5000	2.758
2	868	718	320	252	2842	5000	2.733
3	838	690	316	312	2844	5000	2.727
4	786	680	312	368	2854	5000	2.709
5	757	655	308	424	2856	5000	2.702

slag system show that the binding capacity of the B and O atoms was strongest, followed by Si atoms and then relatively weak Ca and Na atoms, where Na was the weakest.

Figure 4(b) shows that the coordination-number platform of the Si–O bond was stable and long, and its average coordination number was ~4. Therefore, the connection mode of the Si–O bond in the mold flux of the system was mostly the [SiO₄] tetrahedral structure. The coordination-number platform of the B–O bond was long and relatively stable, and its average coordination number was ~3.5. The B–O bond also existed as a [BO₃] triangle and [BO₄] tetrahedron. The Na–O bond had no obvious coordination-number platform, and its bond length was largest. This result indicates that the Na atom had the weakest constraint on O, which was why Na₂O as a network exosome oxide would provide more free oxygen atoms. The coordination-number platform of the Ca–O bond was similar to that of the Na–O bond, which indicates that the Ca atom had a similar effect to the Na, but the bond length of the Ca–O bond was smaller, which indicates that it had a strong attraction to the O atom.

3.2 Influence of B₂O₃ on microstructure and shear-thinning property of CaO–SiO₂–Na₂O-based mold flux

To study changes in the structure of the [B–O] and other components of the mold flux after B₂O₃ addition to the CaO–SiO₂–Na₂O-based mold flux so as to exhibit a shear-thinning property, the coordination information of different B₂O₃ contents on the Si–O and B–O bonds in the slag system was obtained by simulation calculation, and the coordination structure diagram is shown in Figure 5.

As shown in Figure 5, the coordination structures of Si–O and B–O were relatively stable, but showed some differences. The Si–O coordination number showed that the coordination number of Si–O was maintained at ~4. As shown in Figure 5(a), the average coordination number of the Si–O structure decreased with an increase in B₂O₃ con-

(a) Si–O **(b)** B–O**Figure 5:** Influence of B₂O₃ on coordination number

tent in the mold flux. During this process, B atoms that had been added to the mold flux replaced some Si atoms and combined with O atoms to result in a slight decrease in Si–O coordination number. It was also confirmed that the affinity of B and O atoms was stronger than the Si.

Figure 6: Proportion of O connected to Si atom

As shown in Figure 5(b), when the content of B_2O_3 changed to 8%–12%, the average coordination number of the B–O bond increased gradually and approached 4. The proportion of $[BO_4]$ tetrahedron structure in the mold flux increased gradually, which led to an increase in DP of the mold flux. When the B_2O_3 content reached 14%, the average coordination number of the B–O bond decreased, which indicates that the proportion of $[BO_3]$ triangular structure contained in the slag began to increase and lead to a decrease in DP of the mold flux. The DP of the mold flux was largest when the B_2O_3 content was 12%.

To study the influence of B_2O_3 on the degree of aggregation of the Si–O tetrahedron in the mold flux, a search was conducted by programming with the O atom at the center and the Si–O bond length (1.625 Å) as the radius. The search results are shown in Figure 6. N represents the number of Si atoms that are combined with one O atom (*i.e.*, coordination number). The 2-coordinated Si (bridging oxygen) and 1-coordinated Si (non-bridging oxygen) were connected mainly with O atoms, and the DP of the mold flux could be analyzed from the coordination number of O atoms. An increase in B_2O_3 content resulted in an increase in number of bridging oxygens and a decrease in the number of non-bridging oxygens. The number of non-bridging oxygens represents the degree of fracture in the system, whereas the number of bridging oxygens represents the DP. When the content of B_2O_3 in the mold flux was 12%, the number of bridging oxygens in the system was highest and the DP of the mold flux was highest.

According to calculations in previous experiment, when the B_2O_3 content changed within the range of 8%–14%, the shear-thinning property of the mold flux increased and then decreased, and when the content of B_2O_3 was 12% (B-4 sample), the shear-thinning property

Figure 7: (a) B-4 sample Raman spectrum at 1300°C, (b) B-4 sample peak resolution spectra at 1300°C

reached a maximum. This was the same as the change in trend of the DP of the mold flux, which indicates that when the B_2O_3 content changes in the above range (8%–14%), the strength of the shear-thinning property of the mold flux was in positive proportion to the DP.

4 Quantitative analysis by high-temperature Raman spectroscopy

The B-2, B-3, B-4, and B-5 samples were characterized by high-temperature Raman spectroscopy at 1300°C. Figure 7(a) presents the Raman spectrum of the B-4 sample, in which the B_2O_3 content was 12%. Figure 7(b) shows the peak deconvolution spectrum of the B-4 sample, as obtained by using the PEAKFIT software, in the Raman shift range from 1200 to 800 cm^{-1} .

Table 5: Peak relative-area ratios and DP obtained from Raman data through Gaussian fitting

Sample number	Basicity (CaO/SiO ₂)	DP (C ₃ /C ₂)	Best-fitted Gaussian peak area ratio			
			C ₀	C ₁	C ₂	C ₃
B-2	1.1	0.86	0.148	0.272	0.312	0.268
B-3	1.1	0.88	0.126	0.290	0.311	0.273
B-4	1.1	0.96	0.145	0.285	0.291	0.279
B-5	1.1	0.84	0.162	0.269	0.309	0.260

Figure 7(a) shows two relatively obvious peak values in the range of Raman displacement of 600–400 cm⁻¹ and 1200–800 cm⁻¹, respectively. Among them, the spectral peak with a Raman displacement of 600–400 cm⁻¹ contained some simple Si–O_b–Si or Si–O_{nb} connection structures [16, 17]. However, the spectral peak of Raman displacement for 1200–800 cm⁻¹ contained some Q_n structural units and [BO₄] tetrahedral structural units [16, 17]. A small peak occurred where the Raman displacement was 1450–1300 cm⁻¹, which contained a two-dimensional [BO₃] triangular structure [16, 17].

Figure 7(b) shows abundantly dispersed anion structural-unit (Q_n) information around the Raman shift at 1200–800 cm⁻¹. The peaks at 860, 936, 1000, and 1110 cm⁻¹ correspond to the Q₀ (SiO₄⁴⁻ stretching of the monomer structural unit), Q₁ (Si₂O₇⁶⁻ stretching of the dimer structural unit), Q₂ (SiO₃²⁻ stretching of the chain structural unit), and Q₃ (Si₅O₅²⁻ stretching of the sheet-like structural unit) [16, 17], where Q represents the [SiO₄] tetrahedron unit and *n* represents the number of bridging oxygen atoms in each tetrahedron [18]. However, one addition structural unit, Q₄ (SiO₂ moganite) was not detected in the Raman spectra because its concentration in the mixed silicate was low. Figure 8 shows the molecular diagrams of all five anion structural units.

Figure 8: Molecular diagrams of all five scattered anion structural units

The DP and molecular concentration within the mold flux were calculated from the Raman spectroscopic data. The polymerization reaction in the mold flux is represented by Eqs. (2) to (4):

$$K = \frac{[\text{SiO}_3^{2-}] \cdot [\text{SiO}_2]}{[\text{Si}_2\text{O}_5^{2-}]} = \frac{C_2 \cdot C_4}{C_3}, \quad (3)$$

$$C_4 = K \cdot \frac{C_3}{C_2}, \quad (4)$$

where *K* is the equilibrium constant, C₂ and C₃ represent the concentration of Q₂ and Q₃, respectively, and C₄ represents the concentration of the molecular polymerization units. According to Eq. (4), the C₄ could be calculated from C₃/C₂; therefore, in this work, C₃/C₂ was considered to represent the DP of the equilibrium system that was established through the reactions among the silicate structural units within the mold flux [19, 20].

To analyze the changes in Q_n structural units and the variation law of DP in the CaO–SiO₂–Na₂O–B₂O₃ mold flux, the relative areas of each anion structural unit in the B-2, B-3, B-4, and B-5 samples were best-fitted to a Gaussian function. The results are presented in Table 5.

As shown in Table 5, when the content of B₂O₃ in the slag changed from 8% to 12% (samples B-2 to B-4), the relative proportional area (C₂) of the structural unit of Q₂ decreased gradually, and the relative proportional area (C₃) of the structural unit of Q₃ increased gradually. At this point, C₃/C₂ increased gradually, that is, the DP of the mold flux increased gradually. However, when the content of B₂O₃ in the slag changed from 12% to 14% (samples B-4 to B-5), C₂ increased and C₃ decreased. At this point, C₃/C₂ decreased, that is, the DP of the mold flux decreased. Therefore, when the content of B₂O₃ in the slag changed from 8% to 14% (samples B-2 to B-5), the DP of the mold flux increased initially and then decreased, and reached a maximum for the B-4 sample. The experimental results were consistent with the molecular-dynamics simulation results.

The simulation and experimental results indicated that when the B₂O₃ content varied from 0% to 12%, most of the B₂O₃ existed in the mold flux as a three-dimensional [BO₄] tetrahedral structure, whereas a few existed as two-dimensional [BO₃] triangular structures. This occurs mainly because the alkali-metal oxide Na₂O in the slag has a relatively weak control of the O atoms, and it is easy to

provide free O atoms. The bonding ability between the B and O atoms is strongest, so the free O atom in the slag will bond preferentially with the B atom to form a three-dimensional $[BO_4]$ tetrahedron structure, which will increase the DP in the mold flux. The reaction principle is shown in Figure 9.

Figure 9: Schematic diagram of polymerization

When the content of B_2O_3 changes from 12% to 14%, the content of B_2O_3 exceeds the content of Na_2O (11%), the CaO with the highest content in the mold flux begins to play a role as a network-modifying oxide. This decomposes most three-dimensional $[BO_4]$ tetrahedral structures into two-dimensional $[BO_3]$ triangular structures, and results in a decreased DP of the mold flux. The reaction principle is shown in Figure 10. Therefore, the DP of sample B-4 (B_2O_3 content of 12%) is highest in the $CaO-SiO_2-Na_2O-B_2O_3$ non-Newtonian fluid mold flux.

Figure 10: Schematic diagram of depolymerization

In conclusion, the shear-thinning property of the mold flux is related directly to the DP, and the DP is related to the amount of B_2O_3 . When the content of B_2O_3 varies from 0% to 12%, the DP of the mold flux increases, and the shear-thinning property increases. When the content of B_2O_3 varies from 12% to 14%, the DP of the mold flux decreases, and the shear-thinning property decreases. The results show that when the B_2O_3 content was 12%, the shear-thinning property of the mold flux was strongest.

5 Applications to continuous casting

During continuous casting, the mold flux is critical as a lubricating agent at the mold wall where the shear rate is

assumed to range between 100 and 1000 s^{-1} . In this case, the low viscosity of the mold flux is desirable to maximize the lubrication capacity [9]. Figure 11 shows the conceptual effect of the $CaO-SiO_2-Na_2O-B_2O_3$ non-Newtonian fluid mold flux (B-4 sample) during continuous casting.

Figure 11: Schematic diagram showing conceptual effect of $CaO-SiO_2-Na_2O-B_2O_3$ non-Newtonian fluid mold flux during continuous steel casting

To verify the practical application of a non-Newtonian fluid mold flux with shear-thinning properties, samples Blank-1 and B-4 (after compounding with a certain amount of carbon) were used separately in square-billet casting tests at the multifunctional continuous-casting experimental stage. The section size of the casting mold was $100\text{ mm} \times 100\text{ mm}$, the pulling rate was 1.9 m/min , and the slag consumption was 0.2 kg/t . The as-cast steel composition is presented in Table 6.

Figure 12 shows the casting-slab surface morphology when samples Blank-1 and B-4 were used. The surface of the Blank-1 as-cast slab was rough, with a relatively serious slag-sticking phenomenon, which causes problems in subsequent rolling and molding steps. The surface of

Table 6: Composition of as-cast low-carbon steel mass%

C	Si	Mn	P	S
0.01–0.08	≤ 0.008	≤ 0.15	≤ 0.02	≤ 0.02

the B-4 as-cast slab was relatively smooth, where the slag sticking phenomenon improved visibly. The casting quality, however, was improved substantially. This improvement in casting quality is attributed primarily to the B-4 sample showing a strong shear-thinning, which resulted in a relatively low viscosity in the lubricating area at a high shear rate, and lead to a significant improvement in its lubricating ability (Figure 11), so that the casting quality was improved visibly.

Figure 12: Surface morphologies of casting slabs: (a) Blank-1 sample, (b) B-4 sample

6 Conclusions

1. The shear-thinning property of the $\text{CaO-SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ non-Newtonian fluid mold flux differed from that of the $\text{CaO-SiO}_2\text{-Na}_2\text{O}$ -based mold flux. When the B_2O_3 content varied from 0% to 12%, the DP increased because of the increasing proportion of $[\text{BO}_4]$ tetrahedron structures in the mold flux. When the B_2O_3 content changed at 12%–14%, its content exceeded the Na_2O content in the slag. CaO in the mold flux as a network-modifying oxide promotes the depolymerization reaction so that the proportion of $[\text{BO}_3]$ triangular structure increases and results in a decrease in DP. When the content of B_2O_3 was 12%, the DP of the mold flux was highest and the shear-thinning property was strongest.
2. Blank-1 and the B-4 mold-flux samples were used in laboratory square-billet casting tests. The slag-sticking phenomenon on the surface of the billet with sample Blank-1 was relatively serious; however, the phenomenon decreased and the surface quality of the billet improved significantly when the B-4 sample was used. This new type of mold flux has good application prospects in the field of low carbon-steel casting.

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References

- [1] S.H. Shin, D.W. Yoon, J.W. Cho, and S.H. Kim, *J. Non-Cryst. Solids*, 425 (2015) 83-90.
- [2] S.H. Shin, J.W. Cho, and S.H. Kim, *J. Non-Cryst. Solids*, 423 (2015) 45-49.
- [3] S.H. Shin, J.W. Cho, and S.H. Kim, *J. Am. Ceram. Soc.*, 97 (2014) 3263-3269.
- [4] X.Z. Ma, *Steelmak.*, 1 (1996) 7-10.
- [5] T.M. Ye, W.J. Xiao, J.P. He, J.P. Wang, and Z.F. Zhao, *Steelmak.*, 25(2009)12-15.
- [6] Y. Gu, R.Z. Liu, K. Wu, Y. Zhao, S.Q. Li, X. Gao, and G.J. Sun, *Spec. Steel.*, 25 (2004) 18-21.
- [7] H.X. Mao, C.G. Bai, G.B. Qiu, D.F. Chen, L.Y. Wen, and L.Y. Dong, *J. Cho. Uni.*, 28 (2005) 52-55.
- [8] K. Watanabe, K. Tsutsumi, M. Suzuki, H. Fujita, S. Hatori, T. Suzuki, and T. Omoto, *ISIJ Int.*, 54 (2014) 865-871.
- [9] H.S. Seung, W.C. Jung and H.K. Seon, *Mater. Des.*, 76 (2015) 1-8.
- [10] D.M. Li, M.T. Shao, X.L. Yang, and C.M. Diao, *Application Technology of Mold Flux for Continuous Casting*, Metallurgical Industry Press, Beijing (2008).
- [11] S. Won and F. Tsukihashi, *ISIJ Int.*, 44 (2007) 1817-1825.

- [12] Y.Q. Wu, Study on the microstructure of silicate melt and its relationship with macroscopic properties, Shanghai University (2004).
- [13] Y.H. Wen, R.Z. Zhu, F.X. Zhou, and C.Y. Wang, *Adv. Mec.*, 33 (2003) 65-73.
- [14] Q. Wang and Y. Sun, *Shanxi. Coal.*, 3 (2009) 46-47.
- [15] M.R. An, Effects of twin and stack-layer faults on mechanical properties of nanocrystalline metal materials, Xi'an University of Posts and Telecommunications (2013).
- [16] A. Bachar, C. Mercier, A. Tricoteaux, A. Leriche, and C. Follet, *Non-Cryst. Solids.*, 358 (2012) 693-701.
- [17] M. Bradley, *Curve fitting in Raman and IR spectroscopy: basic theory of line shapes and applications*, Thermo Fischer Scientific, Madison (2007), pp. 376-379.
- [18] E. Dolekcekic, M.J. Pomerpocy, and S. Hampshire, *J. Eur. Ceram. Soc.*, 27 (2007) 893-897.
- [19] J.H. Park, *Metall. Mater. Trans. B*, 44 (2013) 938-942.
- [20] J.H. Park, *Met. Mater. Int.*, 19 (2013) 577-581.