THE EFFECT OF Na_2O ON THE VISCOSITY OF MOULD FLUX

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ABSTRACT

Viscosity of mould flux is a key factor for controlling the lubrication. Although typical mould fluxes consist mainly of CaO, SiO_2 and CaF_2, Na_2O is also added to decrease the liquidus temperature and the viscosity. In order to investigate the effect of Na_2O on the viscosities of the mould fluxes, the viscosities of the Na_2O-CaO-SiO_2 and Na_2O-CaO-CaF_2-SiO_2 slags were measured over a temperature range between 1550 and 1750 K by the rotating cylinder method. The viscosity decreases with an increase in the ratio of (mol%Na_2O)/(mol%CaO) at a constant SiO_2 content. This is considered to be due to the breaking of the electrostatic bindings via Ca^{2+} by the substitution of one Ca^{2+} ion with two Na+ ions. The viscosity decreases with an increase in the ratio of (mol%CaF_2)/(mol%CaO) for the slags with lower Na_2O content, on the other hand, the viscosity slightly increases for the slags with higher Na_2O content. The reason for the latter may be that the reaction $Na_2O + CaF_2 \rightarrow CaO + 2NaF$ takes place in the slags with higher Na_2O content; the deficiency of Na_2O and the production of 2NaF leads to the polymerization of the silicate network as NaF works as a simple diluter, resulting in the viscosity increase.

INTRODUCTION

In order to optimize the metallurgical process, it is important to know the accurate thermophysical properties. Particularly, viscosity is one of the most important properties in various situations. Since viscosity is sensitive to the structure, viscosity has been also interesting from academic aspects. In continuous casting of steel, mould flux is fed on the top of molten steel in order to keep lubrication between the steel shell and the mould. Viscosity of mould flux is a key factor for controlling the lubrication. Although typical mould fluxes consist mainly of CaO, SiO_2 and CaF_2, Na_2O is also added to decrease the liquidus temperature and the viscosity. Typical commercial mould fluxes contain 1-20 mass% Na_2O. In the present study, the authors have investigated the effect of Na_2O on the viscosities of the mould fluxes so as to discuss it from the structural viewpoint. Hayashi et al. have measured the coordination environment of fluorine in the CaO-SiO_2-CaF_2-Na_2O glasses by 19 F MAS NMR over a wide composition range including the similar compositions to those of mould fluxes so as to determine the composition dependence of the coordination environment of F^-[1]. They have presented that most of F^- are fourfold-coordinated by Ca^{2+} for the samples having the value of $n_{Na}/(n_{Na} + n_{Ca}) \leq 0.3$, where n represents the cation fraction of each cation. On the other hand, the samples having the value of $n_{Na} / (n_{Na} + n_{Ca}) \geq 0.4$ contain F^- coordinated with both Na^+ and Ca^{2+} and F^- sixfold-coordinated by Na^+. Change in the coordination environment of F^- in terms of the composition could be relevant to the compositional dependence of the viscosities.

METHODOLOGY

Sample Preparation

The nominal compositions of the samples are given in Table 1. Samples were prepared from reagent grade SiO_2, CaF_2, Na_2CO_3 and CaO powders. The reagents were weighed to the desired compositions and mixed in an agate mortar. The mixtures were premelted at 1673 K for 30 min in an iron crucible, the dimensions of which are given in Figure 1. This sample and crucible were used in the viscosity measurements. In both the premelting process and the viscosity measurements, argon gas was employed. In order to prevent the iron crucible from oxidation, oxygen was removed from the gas by passing it through a column of magnesium turnings at 773 K.

Table 1: Chemical compositions of the samples (mol%)

	Na_2O	CaO	CaF_2	SiO_2
A	5.7	27.3	-	67.0
B	7.6	25.4	-	67.0
C	9.6	23.4	-	67.0
D	5.7	23.5	3.8	67.0
E	9.6	19.6	3.8	67.0

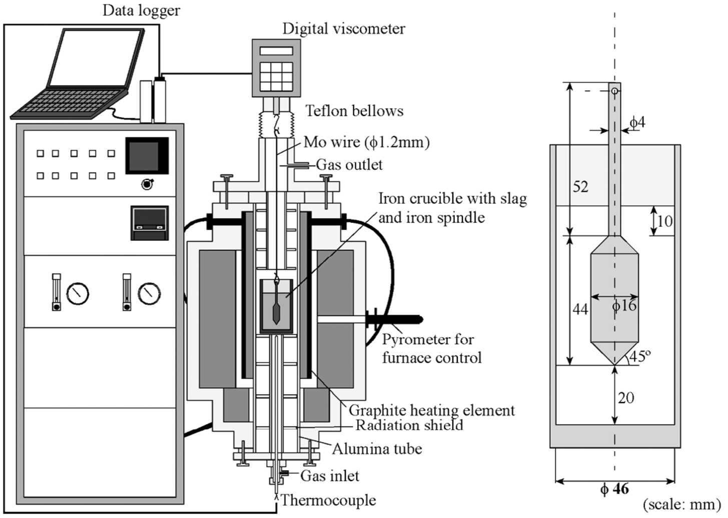

Figure 1: Experimental facilities for viscosity measurements

Measurement

The rotating cylinder method was used in the present study. A schematic diagram of the apparatus is shown in Figure 1. A Brookfield digital viscometer (model RVDV-II+) with the full scale torque of 7.187 10^{-4} N•m is controlled by a PC through a controller. The spindle is driven by a calibrated spring and, as the spindle is lowered in the molten sample, the viscous drag of the fluid against the spindle is measured by the spring deflection using a rotary transducer. The measured torque and related information are sent to a computer, which then calculates the viscosity of the fluid online. The equipment utilizes a high temperature furnace from the Laboratory Furnace Group 1000 Series supplied by Thermal Technology Inc. An optical pyrometer sensor coupled with an Eurotherm (model 818) digital controller controls the surface temperature. Temperatures were measured using a Pt-30Rh/Pt-6Rh thermocouple in an alumina sheath placed in contact with the base of the crucible. The crucible is placed within the uniform temperature (±3 K) zone of the furnace.

Measurements of viscosity in the present work were performed using pure iron spindles. The dimensions of the spindles are given in Figure 1. The experiment was started by placing the crucible containing premelted slag inside the reaction chamber. The spindle suspended by molybdenum wire was lowered until it hung ca. 10 mm above the slag surface. After the reaction chamber was flushed with argon for about 1 h, the sample was heated up to 1673 K for complete melting, kept at this temperature for 30 min and cooled at the rate of 5 K•min^{-1} to the desired temperature. When the temperature of the sample had established, the spindle rotating at a speed of 10-50 rpm was immersed into the slag. The tip of the bob was placed ca. 20 mm above the base of the crucible. The rotating speeds of 10, 20, 30, 40 and 50 rpm were used to confirm the linearity of the relation between the rotation speed and the measured torque. Figure 2 shows the typical relation between the rotation speed and the measured torque. Good linear relations were obtained for all measurements as can be seen in the figure. Most of the measurements were carried out during the cooling cycle to minimize any compositional changes in the melt. On the other hand, some of the measurements were carried out during the heating cycle to confirm the reproducibility of the experiment. The viscometer was calibrated using four standard silicon oils with viscosities of 0.5, 1, 5, 10 and 50 dPa•s at 298 K.

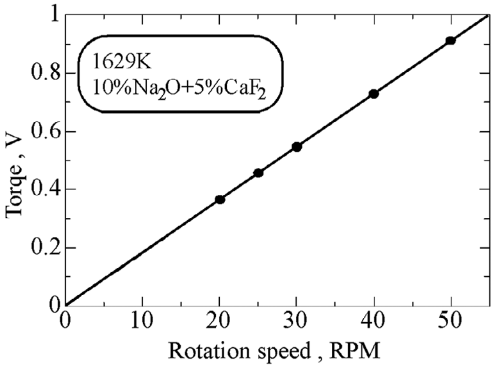

Figure 2: Typical relation between the rotation speed and the measured torque

RESULTS

The results of the viscosity measurements are presented in Table 2. Figure 3 shows the temperature dependence of viscosity for the Na_2O-CaO-SiO_2 system (samples A, B and C). The viscosity decreases with an increase in the ratio of (mol%Na_2O)/(mol%CaO) at a constant SiO_2 content. The viscosities of the Na_2O-CaO-SiO_2 system have been studied by a few research groups.[2] Figure 4 shows a comparison between present experimental results and the literature data. It can be seen that the present viscosity values are in agreement with the reported values although the compositional range of the present study is not covered by the previous studies. Figure 5 shows the temperature dependence of the viscosity for the samples A, C, D and E. It can be seen that the dependencies of viscosity on the ratio of (mol%CaF_2)/(mol%CaO) are contrary between Na_2O contents of 5.7 and 9.6 mol% at the same SiO_2 content: The viscosity decreases with an increase in the ratio of (mol%CaF_2)/(mol%CaO) for the slags with 5.7 mol% Na_2O, on the other hand, the viscosity slightly increases for the slags with 9.6 mol% Na_2O.

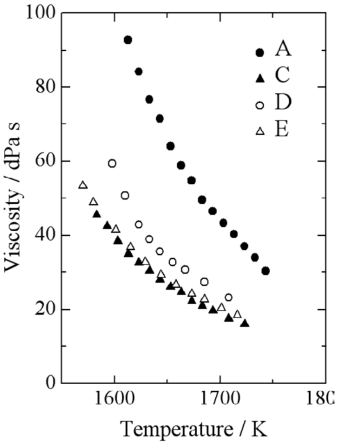

Figure 3: Temperature dependence of the viscosity for the Na_2O-CaO-SiO_2 system (samples A, B and C)

Table 2: Measured viscosity values of various slags

Sample	Temp., K	Viscosity ×dPa·s	Sample	Temp., K	Viscosity ×dPa•s
A	1743	30.31	C	1723	15.94
A	1733	33.93	C	1708	17.49
A	1723	37.05	C	1693	19.57
A	1713	40.25	C	1683	20.94
A	1703	43.30	C	1673	22.23
A	1693	46.49	C	1663	24.63
A	1683	49.56	C	1653	26.03
A	1673	54.79	C	1643	27.93
A	1663	58.91	C	1633	30.39
A	1653	64.12	C	1623	32.58
A	1643	71.48	C	1613	34.98
A	1633	76.73	C	1603	38.43
A	1623	84.16	C	1593	42.47
A	1613	92.80	C	1583	45.48
B	1733	23.64	D	1708	23.16
B	1723	25.41	D	1685	27.36
B	1713	27.87	D	1667	30.67
B	1703	29.97	D	1655	32.70
B	1693	31.95	D	1643	35.61
B	1683	34.42	D	1633	38.89
B	1673	36.76	D	1623	42.86
B	1663	39.85	D	1610	50.69
B	1653	43.36	D	1598	59.29
B	1643	46.86	E	1716	18.43
B	1633	50.59	E	1701	20.29
B	1623	54.77	E	1685	22.63
B	1613	59.10	E	1673	24.21
B	1603	64.70	E	1658	26.62
B	1593	70.57	E	1644	29.33
			E	1629	32.81
			E	1615	36.78
			E	1601	41.40
			E	1570	48.82
			E	1601	53.31

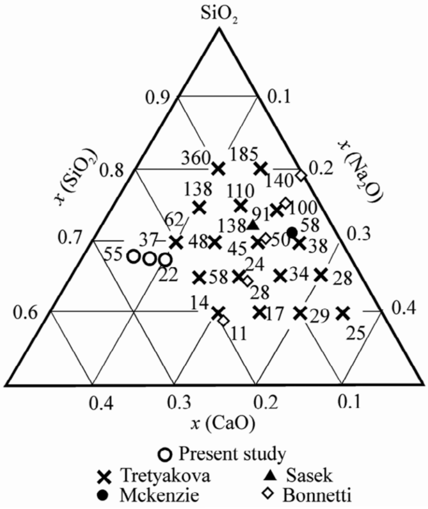

Figure 4: Comparison between present experimental results and the literature data [2]

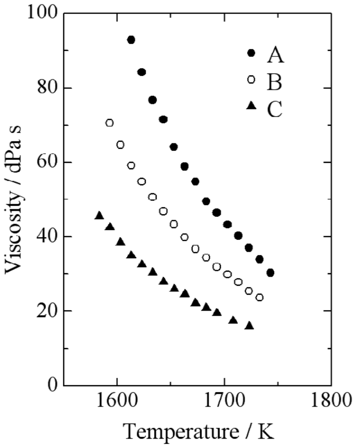

Figure 5: Temperature dependence of the viscosity for the samples A, C, D and E

DISCUSSION

Mechanism for Lowering the Viscosities of Slags by Substituting CaO with Na_2O in the Na_2O-CaO-SiO Slags

In silicate glasses the divalent calcium ions bind together the silicate anions by electrostatic forces as shown in Figure 6. When CaO is substituted with Na_2O, the electrostatic bindings via a divalent calcium ions are broken by two monovalent sodium ions. As this breaking reduces the resistance of flow due to the electrostatic bonds between the silicate anions through the divalent calcium ions, the viscosity is lowered.

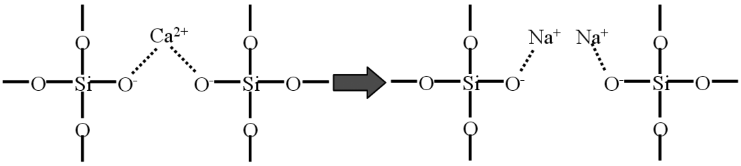

Figure 6: Structural change of the silicate network by the substitution of CaO with Na_2O

Effect of the Substitution of CaO with CaF_2 on the Viscosities of the Na_2O-CaO-CaF_2-SiO_2 Slags

Recently, it has been known that CaF_2 works as a simple diluter and the addition of CaF_2 does not influence the polymerization in the CaO-CaF_2-SiO_2 slags [3, 4, 5]. As for the structural role of CaF_2 in the CaO-SiO_2-CaF_2-Na_2O glasses, Hayashi et al. have measured the coordination environment of fluorine in the CaO-SiO_2-CaF_2-Na_2O glasses by 19F MAS NMR over a wide composition range.[1] They have presented that most of F^- are fourfold-coordinated by Ca^{2+} for the samples having the value of $n_{Na} / (n_{Na} + n_{Ca}) \leq 0.3$, where n represents the cation fraction of each cation, while F^- are coordinated with both Na^+ and Ca^{2+} for the samples having the value of $n_{Na} / (n_{Na} + n_{Ca}) \geq 0.4$. Hayashi *et al.* [3] have presented the mechanism for lowering the viscosities of the CaO-CaF_2-SiO_2 slags by CaF_2 addition using the structural model proposed by Baak and Olander [6] and Bills [7].

Figure 7 shows the structural change of the silicate network by the substitution of CaO with CaF_2 in accordance with their report. Since the present compositional change is not the CaF_2 addition to the slags with a constant basicity of (mol%CaO)/(mol%SiO_2) but the substitution of CaO with CaF_2 in the slags with a constant SiO_2 content, the trend of the viscosity change is determined by the competition of (i)polymerization of the silicate network by the deficiency of CaO and (ii) breaking of the electrostatic bindings $O^-–Ca^{2+}–O^-$ by two CaF^+ ions.

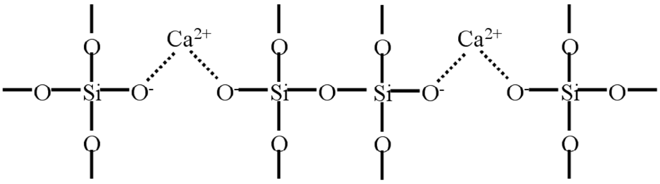

Figure 7: Structural change of the silicate network by the substitution of CaO with CaF_2

The present results indicate that the effect of (ii) is dominant at least for the viscosities of the slags with 5.7 mol% Na_2O. However, with respect to the viscosities of the slags with 9.6 mol% Na_2O, the effect of (i) not (ii) may govern the viscosity since the viscosity increases with an increase in the ratio of (mol%CaF_2)/(mol%CaO). A more likely possibility for the viscosity increase of the slags with 9.6 mol% Na_2O is that some of F^- ions are coordinated with Na^+ instead of Ca^{2+} in the slags. This means that the following reaction takes place in the slags:

$$Na_2O + CaF_2 \rightarrow CaO + 2NaF \quad (1)$$

When this reaction occurs, the compositional change *the substitution of CaO with CaF_2 in the slags with a constant SiO_2 content corresponds to the compositional change the substitution of Na_2O with 2NaF in the slags with a constant SiO_2 content*. Since NaF works as a simple diluter, the substitution of Na_2O with 2NaF leads to the polymerization of the silicate network as shown in Figure 8, resulting in the viscosity increase.

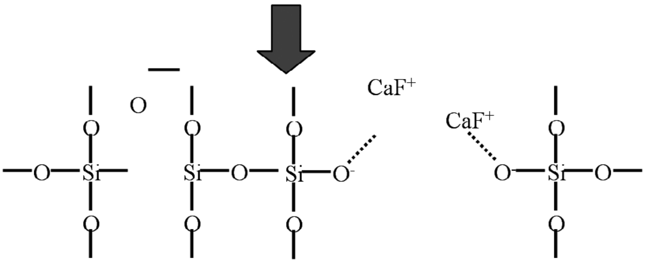

Figure 8: Structural change of the silicate network by the substitution of Na_2O with 2NaF

CONCLUSIONS

In order to investigate the effect of Na_2O on the viscosities of the mould fluxes so as to discuss it from the structural viewpoint, the viscosities of the Na_2O-CaO-SiO_2 and Na_2O-CaO-CaF_2-SiO_2 slags were measured over a temperature range between 1550 and 1750 K by the rotating cylinder method.

- The viscosity decreases with an increase in the ratio of (mol%Na_2O)/(mol%CaO) at a constant SiO_2 content. This is considered to be due to the breaking of the electrostatic bindings via Ca^{2+} by the substitution of one Ca^{2+} ion with two Na^+ ions.
- The viscosity decreases with an increase in the ratio of (mol%CaF_2)/(mol%CaO) for the slags with 5.7 mol% Na_2O, on the other hand, the viscosity slightly increases with an increase in the ratio of (mol%CaF_2)/(mol%CaO) for the slags with 9.6 mol% Na_2O. The reason for the latter may be that the reaction $Na_2O + CaF_2 \rightarrow CaO + 2NaF$ takes place in the slags: Since NaF works as a simple diluter, the deficiency of Na_2O and the production of 2NaF leads to the polymerization of the silicate network, resulting in the viscosity increase.

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