Viscosity of Blast Furnace Type Slags

NORITAKA SAITO, NAOTO HORI, KUNIHIKO NAKASHIMA, and KATSUMI MORI

The effect of MgO, TiO_2, or Fe_2O_3 on the viscosity of 40CaO-40SiO_2-20Al_2O_3 (mass pct) slags has been measured by the rotating crucible viscometer. Viscosity of these quaternary slags decreased with an increase in the content of additive oxide. At the same content of additive oxide, the viscosity decreases from MgO, TiO_2 to Fe_2O_3. In addition, the effect of SiO_2 or Al_2O_3 on the viscosity of 26.1CaO-73.9Fe_2O_3 (mass pct) (CF) and 14.9CaO-85.1Fe_2O_3 (mass pct) (CF_2) slags has been measured. Viscosity of calcium ferrite slags increased with increasing SiO_2 or Al_2O_3 content. Al_2O_3 was found to be more effective for increasing the viscosity at the same content of the additive oxide.

I. INTRODUCTION

VISCOSITY of molten slag changes in wide range depending on temperature and composition. Several of factors in a blast furnace process, such as the rate of various reactions and the fluid flows, are affected by the properties of molten slag. Among them, it is well known that the viscosity is an important physical property for understanding the network structure of slag melts and for simulating the rate of various phenomena in high-temperature metallurgical processes. Numerous viscosity measurements have been carried out for binary or ternary slags in the last several decades.[1–7] Although practical slags related to the iron-making process are multicomponent systems, there are few data available on their viscosities. Furthermore, errors in the values of viscosity depending on published data range within ±25 to 50 pct.[8] Thus, the accuracy of measurements in viscosity for multicomponent slag and flux is strongly required for understanding of the reaction behavior in the iron-making process.

In recent years, the amount of demanded sinters in the blast furnace process has been increased to achieve high productivity. It is important to clarify the role of the liquid slag during the sintering process of ores, for the formation of liquid slags, and its flow controlling the strength and the reducibility of sinters in a blast furnace. However, there is no viscosity data available for this slag.

Here, the effect of adding MgO, TiO_2, or Fe_2O_3 on the viscosity of 40CaO-40SiO_2-20Al_2O_3 (mass pct) slags relating to blast furnace was investigated. In addition, the effect of adding SiO_2 or Al_2O_3 on the viscosity of calcium ferrite melts, 26.1CaO-73.9Fe_2O_3 (mass pct) (CF) and 14.9CaO-85.1Fe_2O_3 (mass pct) (CF_2) relating to liquid-phase sintering of ore, was also measured.

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II. EXPERIMENTAL

A. *Apparatus for Viscosity Measurement*

Figure 1 presents the schematic diagram of the outer cylinder rotating viscometer, which consists of a rotating system, a heating system, and a measuring system.[9] An electric resistance furnace with six U-shape $MoSi_2$ heating elements was employed for heating and melting. The differential transformer, as shown in Figure 1(a), was developed by improving a commercially available rotation angle detector. A crucible and a bob, both with Pt-20Rh (mass pct), were used in the experiments. The dimensions of the crucible and the bob are given in Figure 1(b).

The viscometer was calibrated using four silicone oil standards with viscosities of 0.001 to 10 Pa·s at room temperature before each measurement. Figure 2 shows examples of the calibration line. This figure reveals a liner relationship between the viscosity of silicone oil and the detected voltage by the differential transformer. Calibrations of the viscometer were also made in the temperature range 1523 to 1823 K using reference slags (SRM2 type slags[8]). The compositions of the reference slags are given in Table I. As shown in Figure 3, the results of high-temperature calibration fitted in with the recommended value[8] and had reproducibility. The experimental conditions used in this study are summarized in Table II.

B. *Sample Preparation*

Samples for viscosity measurement were prepared from reagent grade SiO_2, Al_2O_3, MgO, TiO_2, Fe_2O_3, and $CaCO_3$ powders (Sigma-Aldrich, Japan). These reagents were precisely weighed to form given compositions (*cf.* Table III), and mixed in an alumina mortar thoroughly. The sample was premelted in a resistance furnace using the Pt crucible for an hour. Then, the sample was crushed into powder and used for measurements.

C. *Viscosity Measurements*

The crucible filled with slag powder was placed in a crucible supporter in the furnace and heated to 1873 K. After then, the molten slag was kept at that temperature until the detected voltage value (viscosity) became constant. The measurements were carried out 3 times at every 50 K interval

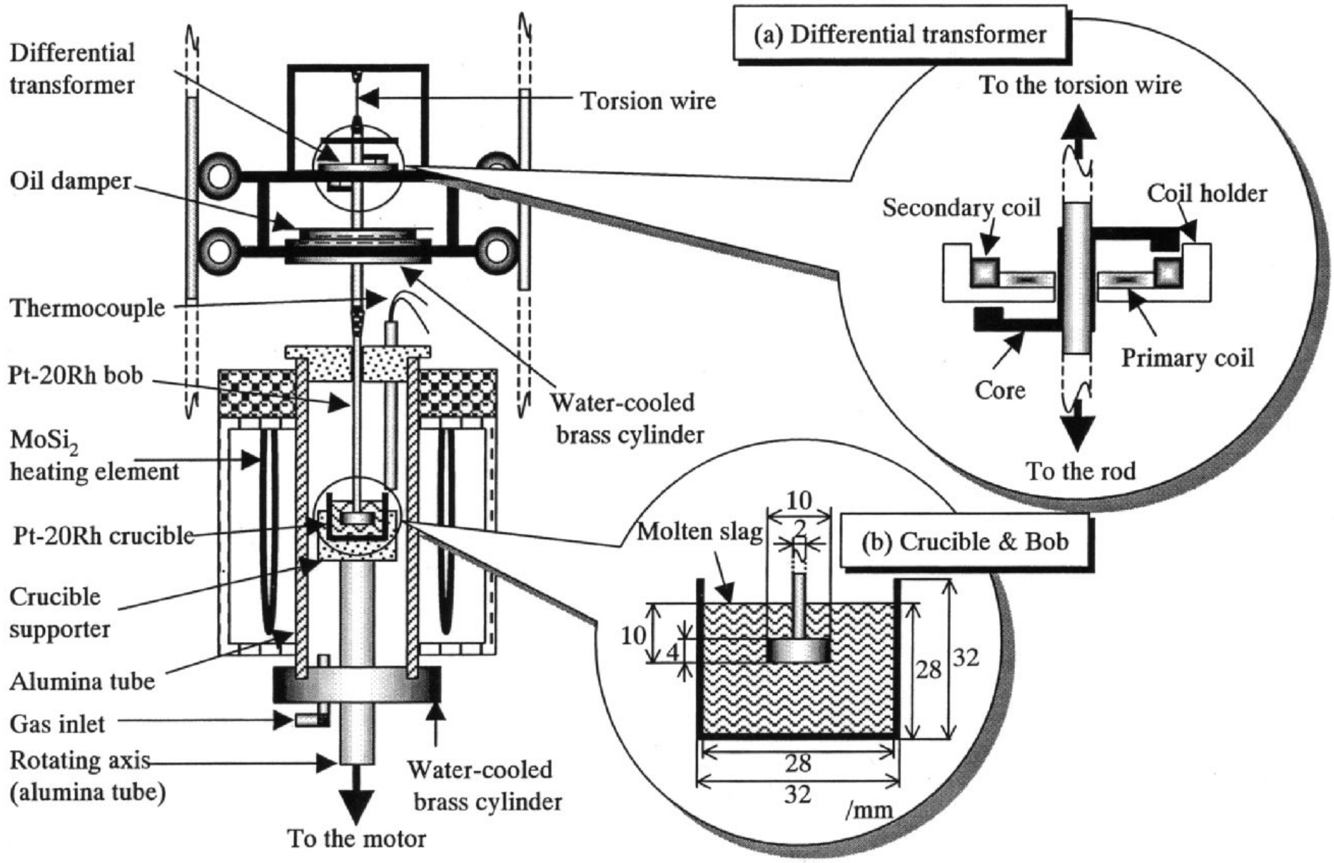


Fig. 1—Schematic illustration of the apparatus for viscosity measurement.

on cooling. Thereafter, the measurements were repeated at the same temperature on heating. The thermal equilibration time at each temperature setting point was chosen to be 30 minutes. The average value of these six measurements was used for the measured potential difference. An apparent viscosity was calculated based on the reference relationship between the viscosity and the potential difference, which was obtained by using various silicone oils beforehand (*cf.* Figure 2). Thereafter, these values were corrected for the thermal expansions of the crucible and the bob using the following equation:

$$\eta = \eta'/(1 + \alpha T)^3 \qquad [1]$$

where η, η', α, and T are viscosity, apparent viscosity, thermal expansion coefficient, and absolute temperature, respectively.

The scatter of the measured values between on cooling and on heating and the repetitive error of measurements were both within ± 3 pct. Table III shows the initial slag compositions and the summary viscosity data.

III. RESULTS AND DISCUSSION

A. *Effect of Holding Time on Isothermal Viscosity*

Figure 4 shows an example of the variation of viscosity with different holding times, and reveals the decrease of viscosity with holding time. It required no less than 8 hours to become constant for the viscosity of $13.4CaO-76.6Fe_2O_3-10SiO_2$ (mass pct) slag. CF_2-SiO_2 slags required a fairly long holding time to become constant value for viscosities, especially 11 hours for CF_2-15 mass pct SiO_2, 8 hours for CF_2-10 mass pct SiO_2, and 5.5 hours for CF_2-5 mass pct SiO_2. In other calcium ferrite slags and $CaO-SiO_2-Al_2O_3-(MgO, TiO_2$ or $Fe_2O_3)$ slags, a similar tendency can be seen, as shown in Figure 4, and holding times of 3 and 1.5 hours are required to become constant value for viscosities, respectively. Generally, it will take several hours to stabilize the viscosity value due to the time required for complete homogenization and thermal equilibration of melts.[10]

On the other hand, Nagata and Hayashi[11] have recently investigated the change of the oxygen coordination structures of both iron ions, Fe^{3+} and Fe^{2+}, in calcium-silicate ($40CaO-40SiO_2-20Fe_2O_3$ (mol pct)) slag during the equilibration process at various temperatures. And they have reported that the fraction of Fe^{3+} ions in octahedral symmetry to the total Fe^{3+} ions increased with holding time and became constant within 2 hours at 1773 K after equilibration operation. This result suggests that the decrease of the viscosity, as shown in Figure 4, is probably due to the increase in Fe^{3+} ions in octahedral symmetry with holding time, as Fe^{3+} ions in octahedral symmetry play the role of network modifier. Since calcium ferrite slags measured in this study contain a greater amount of Fe_2O_3 than slags used in their investigation, a much longer holding time would be necessary for stabilization of structures, particularly. Also, Al^{3+} and Ti^{4+} ions will have various oxygen coordination structures in CaO-SiO_2-Al_2O_3-(MgO, TiO_2 or Fe_2O_3) slags. Therefore, in the case of amphoteric oxides containing slag melting, it might be expected that they require a considerably long holding time for the homogenization and the equilibration of coordination structures.

B. *The Viscosity of 40CaO-40SiO$_2$-20Al$_2$O$_3$-(MgO, TiO$_2$ or Fe$_2$O$_3$) Quaternary Slags*

Figures 5 through 7 show the temperature dependence of the viscosity in 40CaO-40SiO_2-20Al_2O_3-(MgO, TiO_2 or Fe_2O_3) quaternary slags, respectively. The present result for 40CaO-40SiO_2-20Al_2O_3 (mass pct) slag is in good agreement with the results reported by Machin *et al.*[12] and Kozakevitch.[13]

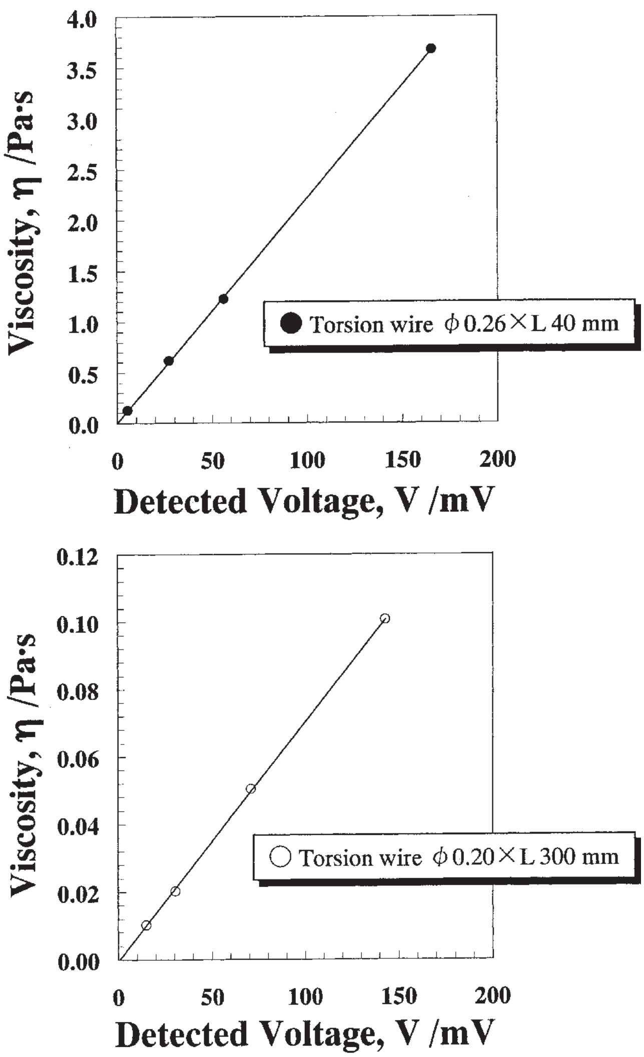


Fig. 2—Calibration curves for the evaluation of viscosity value.

The viscosity data can be described by an Andrade equation over the entire temperature region in this study.

$$\eta = A \exp\left(\frac{E_\eta}{RT}\right) \quad [2]$$

where A, E_η, R, and T are a constant, the apparent activation energy of viscous flow, the universal gas constant, and absolute temperature, respectively.

Figure 8 illustrates the effect of adding oxide (MgO, TiO_2, or Fe_2O_3) on the viscosity of 40CaO-40SiO_2-20Al_2O_3 (mass

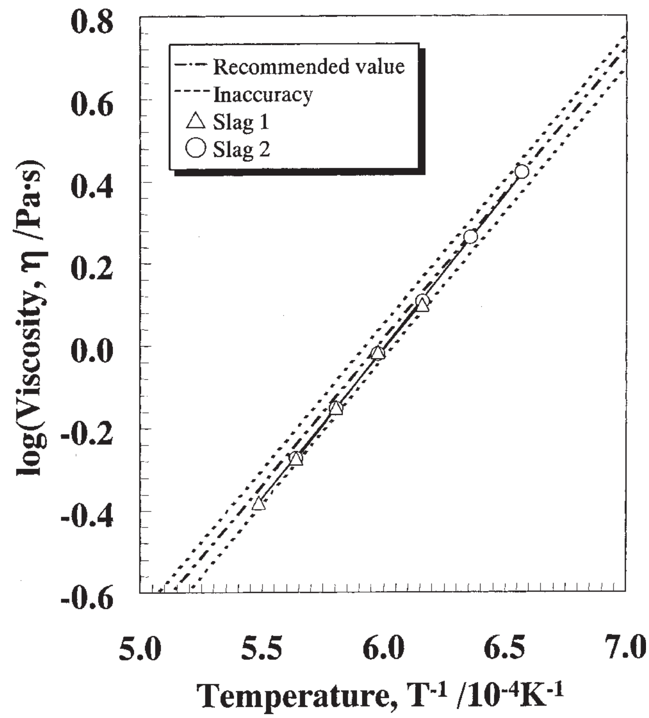


Fig. 3—Results of high-temperature calibration using SRM2 type slag.

Table II. Experimental Conditions of Viscosity Measurement

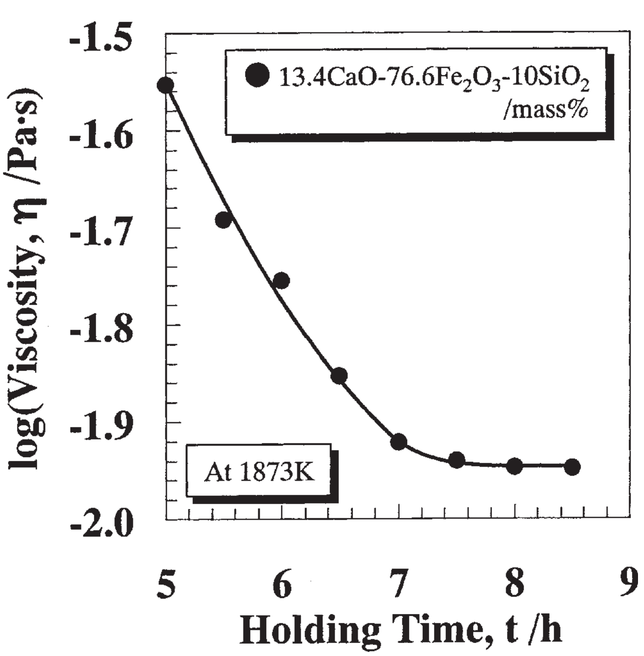
Atmosphere	Air Ar(CaO-SiO_2-Al_2O_3-Fe_2O_3 slag), 2.00 L/min
Temperature range	1673 to 1873 K (CaO-SiO-Al_2O_3 system) 1573 to 1873 K (CaO-Fe_2O_3 system)
Diameter and length of torsion wire	ϕ 0.200 to 0.430 × 40.0 to 50.0 mm (CaO-SiO-Al_2O_3 system) ϕ 0.200 × 300 mm (CaO-Fe_2O_3 system)
Viscosity of damper oil	0.300 Pa's
Sample weight	40.0 g
Immersion depth	10.0 mm
Revolution speed	60.0 rpm (CaO-SiO-Al_2O_3 system) 80.0 rpm (CaO-Fe_2O_3 system)

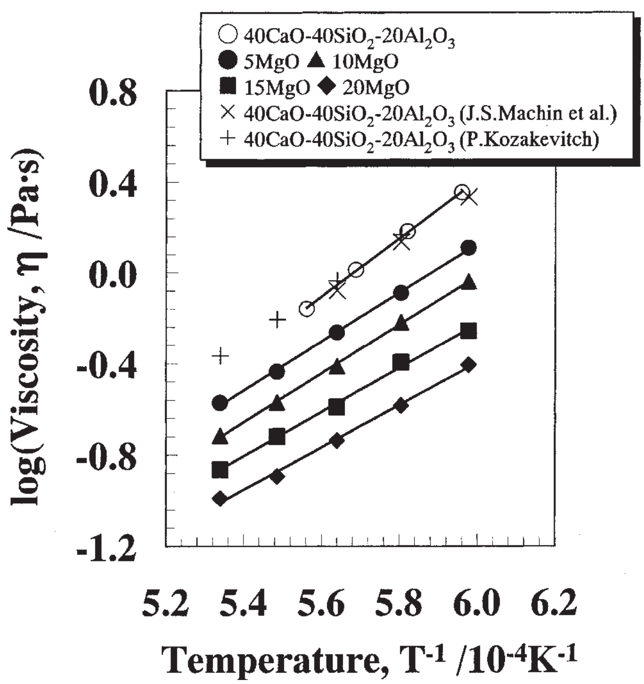
Table I. Chemical Composition of SRM2 Type Slags for Calibration at High Temperature

	SiO_2	Al_2O_3	Li_2O	K_2O	Na_2O	MgO	CaO	TiO_2	P_2O_5
SRM2	63.7	14.4	20.6	0.130	0.400	<0.1	0.400	<0.1	<0.01
Slag 1	63.0	14.3	20.2	0.630	0.550	0.140	0.380	—	—
Slag 2	62.5	15.2	21.3	0.500	0.630	0.140	0.390	—	—

Table III. Initial and Final Slag Compositions for Viscosity Measurement

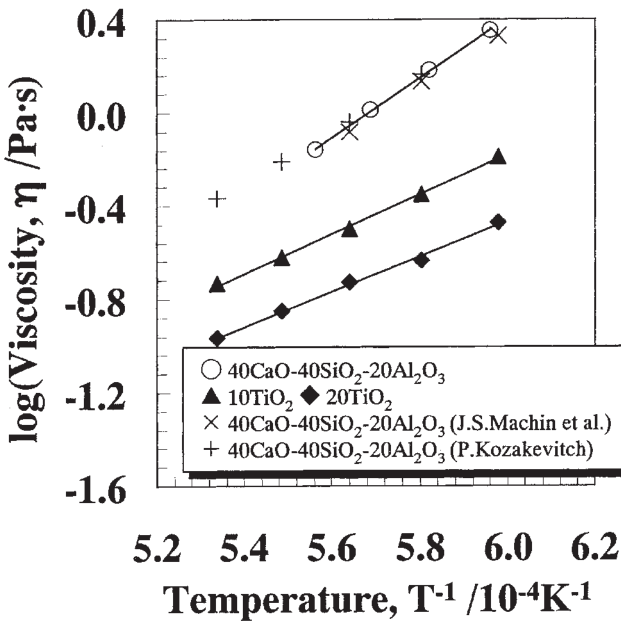
Chemical Composition (Mass Pct)						Viscosity (Pa·s) at Temperature (K)						
CaO	SiO_2	Al_2O_3	MgO	TiO_2	Fe_2O_3	1678	1718	1758	1798	—	—	—
40	40	20	—	—	—	2.253	1.519	1.028	0.693	—	—	—
CaO	SiO_2	Al_2O_3	MgO	TiO_2	Fe_2O_3	1573	1623	1673	1723	1773	1823	1873
38	38	19	5	—	—	—	—	1.284	0.812	0.545	0.366	0.267
36	36	18	10	—	—	—	—	0.913	0.604	0.387	0.269	0.193
34	34	17	15	—	—	—	—	0.552	0.402	0.257	0.190	0.137
32	32	16	20	—	—	—	—	0.392	0.260	0.183	0.128	0.102
36	36	18	—	10	—	—	—	0.648	0.448	0.317	0.239	0.185
32	32	16	—	20	—	—	—	0.338	0.231	0.187	0.141	0.109
36	36	18	—	—	10	—	—	0.629	0.437	0.313	0.241	0.183
32	32	16	—	—	20	—	—	0.248	0.180	0.129	0.108	0.090
28	28	14	—	—	30	—	—	0.166	0.131	0.107	0.089	0.071
24	24	12	—	—	40	—	—	0.089	0.075	0.070	0.061	0.054
26.1	—	—	—	—	73.9	0.0215	0.0153	0.0100	0.0072	0.0052	0.0040	0.0032
24.8	—	—	—	—	70.2	0.0276	0.0222	0.0179	0.0151	0.0130	0.0117	0.0102
23.5	10	—	—	—	66.5	—	0.0389	0.0318	0.0273	0.0235	0.0208	0.0184
22.2	15	—	—	—	62.8	—	—	0.0549	0.0438	0.0359	0.0296	0.0226
24.8	—	5	—	—	70.2	0.0334	0.0252	0.0176	0.0147	0.0124	0.0106	0.0087
23.5	—	10	—	—	66.5	0.0472	0.0371	0.0308	0.0264	0.0219	0.0196	0.0176
22.2	—	15	—	—	62.8	0.0670	0.0537	0.0429	0.0369	0.0299	0.0240	0.0219
14.9	—	—	—	—	85.1	—	—	0.0085	0.0054	0.0038	0.0026	0.0020
14.2	5	—	—	—	80.8	—	—	—	0.0142	0.0097	0.0077	0.0060
13.4	10	—	—	—	76.6	—	—	—	0.0209	0.0170	0.0142	0.0116
12.7	15	—	—	—	72.3	—	—	—	0.0261	0.0231	0.0215	0.0185
14.2	—	5	—	—	80.8	—	—	0.0143	0.0115	0.0078	0.0055	0.0044
13.4	—	10	—	—	76.6	—	—	—	0.0168	0.0137	0.0113	0.0095
12.7	—	15	—	—	72.3	—	—	—	0.0264	0.0226	0.0174	0.0161





pct) slags at 1873 K together with our previous data[9] for 50CaO-50SiO_2 (mass pct) slags. The horizontal axis shows the molar concentration of additive oxides. The viscosities of these quaternary slags decrease with increasing content of additive oxide. At the same content of additive oxide, the viscosity decrease from MgO, TiO_2 to Fe_2O_3. These variations of decreasing viscosity isotherm are similar to the previous work[9] for 50CaO-50SiO_2 slags.

It is known that Al_2O_3, TiO_2, and Fe_2O_3 are amphoteric oxide[3,14–16] and their behavior depend on the basicity of slags to which they are added.



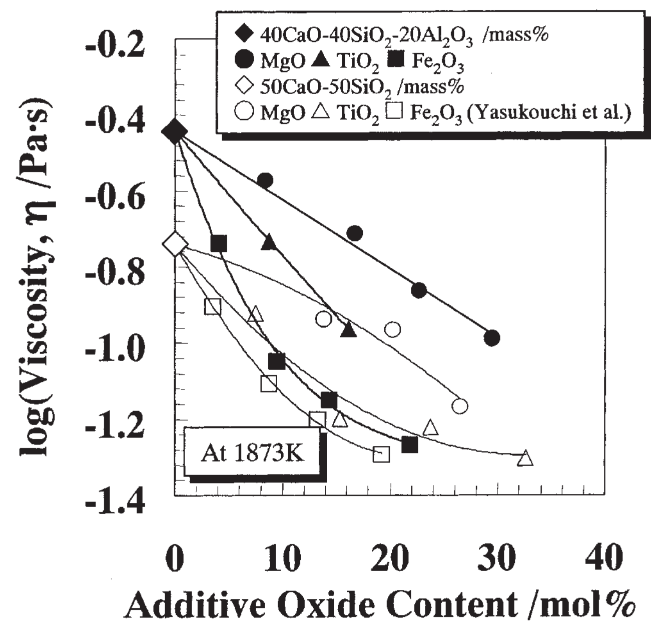
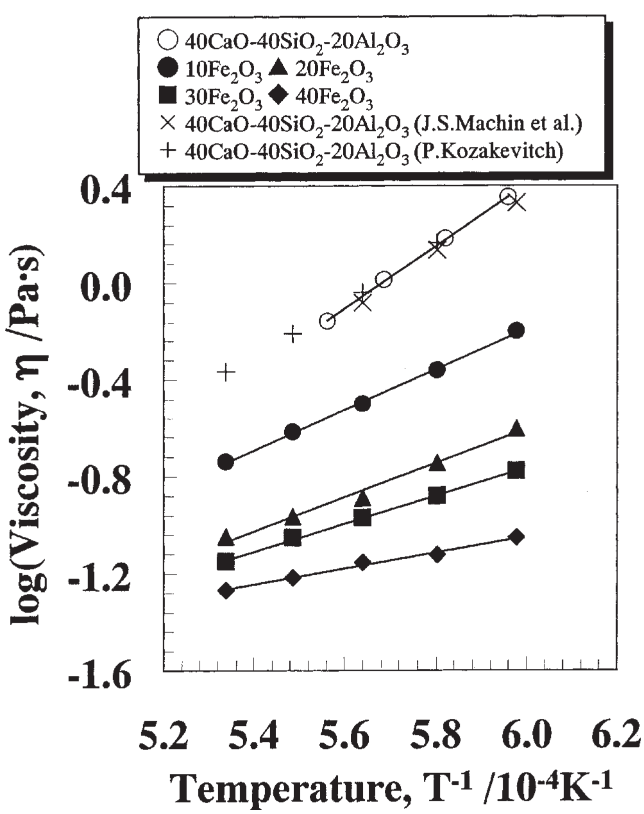


Fig. 8—Effect of additive oxide on the viscosity of $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2$ slags at 1873 K.



In the case of the mole ratio Al_2O_3/RO $<$ 1 (RO: basic oxide), Al_2O_3 would behave as acid oxide (network former), as described in References 14 and 17. Moreover, the viscosity of $50CaO-50SiO_2$ (mass pct) slag increased linearly with increasing Al_2O_3 content.[9] These results indicate that Al_2O_3 will behave as a network former in the present $40CaO-40SiO_2-20Al_2O_3$ (mass pct) slag.

Morinaga *et al.*[18] have investigated the electrical conductivity of the $CaO-SiO_2-TiO_2$ system. And they have suggested that, in the case of silicate melts with the ratio $CaO/SiO_2 = 1$, the percentage of Ti^{4+} ion in octahedral symmetry to the total Ti^{4+} ions is about 50 pct. Moreover, decreasing the ratio CaO/SiO_2 leads to increasing the percentage of Ti^{4+} ion in octahedral symmetry to the total Ti^{4+} ions, as described in Reference 18. Also, Morinaga *et al.*[15] and Sumita *et al.*[19] have reported that the oxygen coordination structure of Fe^{3+} ion can be determined by the ratio RO/Fe_2O_3 (RO: basic oxide). In this study, the structural analysis of quenched slag has not been done. It is expected that TiO_2 or Fe_2O_3 would behave as a network modifier in $40CaO-40SiO_2-20Al_2O_3$ slag. Therefore, the viscosity of these quaternary slags decreases with increasing TiO_2 or Fe_2O_3.

Since Fe^{3+} ion has a smaller cation-oxygen attraction[20] than that of the Ti^{4+} ion, at the same contents of TiO_2 and Fe_2O_3, the viscosity of $CaO-SiO_2-Al_2O_3-Fe_2O_3$ slags was lower than those of $CaO-SiO_2-Al_2O_3-TiO_2$ slags.

There are few data available on the viscosity and the structural analysis for the slags with multiple amphoteric oxides coexisting. Further investigation of structural analysis is required.

When MgO behaves as a network modifier in Na_2O-SiO_2-MgO and $CaO-SiO_2-MgO$ slags, the viscosity decreases[17] and the electrical conductivity increases[14] with increasing MgO content, respectively. As such, it is natural that MgO will behave as a network modifier and decrease the viscosity of slag.

Figure 9 shows the relationship between the content of additive oxide and the apparent activation energy of viscous flow calculated according to Eq. [1]. The horizontal axis shows the molar concentration of additive oxides.

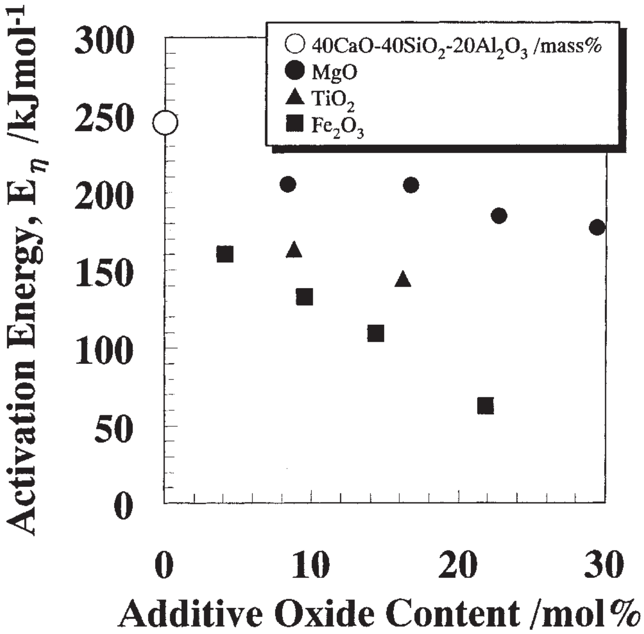


Fig. 9—Effect of additive oxide on the apparent activation energy of viscous flow of $CaO-SiO_2-Al_2O_3$ slags.

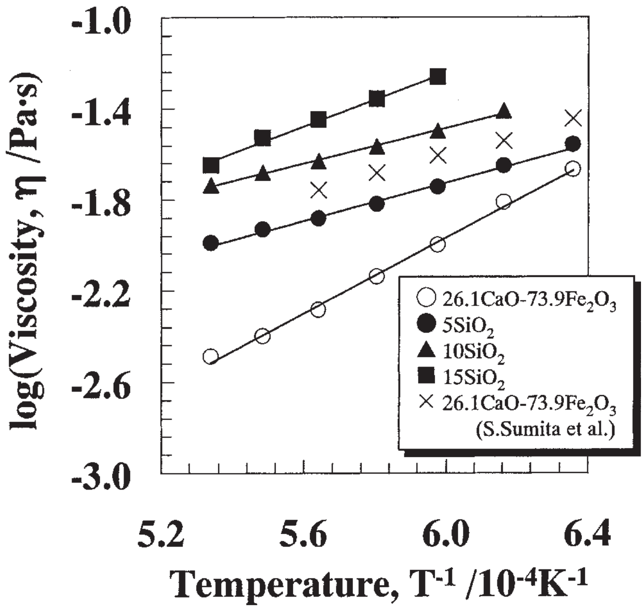


Fig. 10—Temperature dependence of the viscosity of $CF-SiO_2$ slags.

The apparent activation energy of viscous flow decreases with increasing content of additive oxide in any system. This result also indicates that the structural unit for viscous flow of slags becomes smaller with increasing MgO, TiO_2, or Fe_2O_3 content.

C. *The Viscosity of CF-(SiO_2 or Al_2O_3) and CF_2-(SiO_2 or Al_2O_3) Ternary Slags*

Figures 10 through 13 show the temperature dependence of the viscosity of $CF-SiO_2$, $CF-Al_2O_3$, CF_2-SiO_2, and $CF_2-Al_2O_3$ ternary slags, respectively. The present results of CF

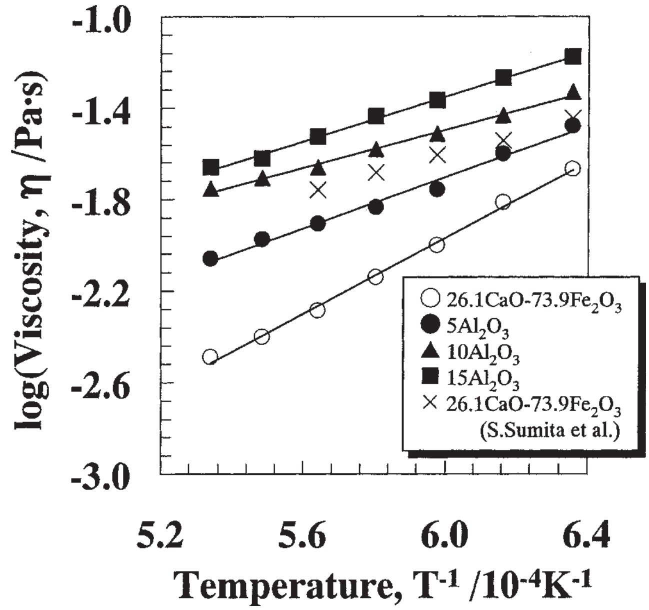


Fig. 11—Temperature dependence of the viscosity of $CF-Al_2O_3$ slags.

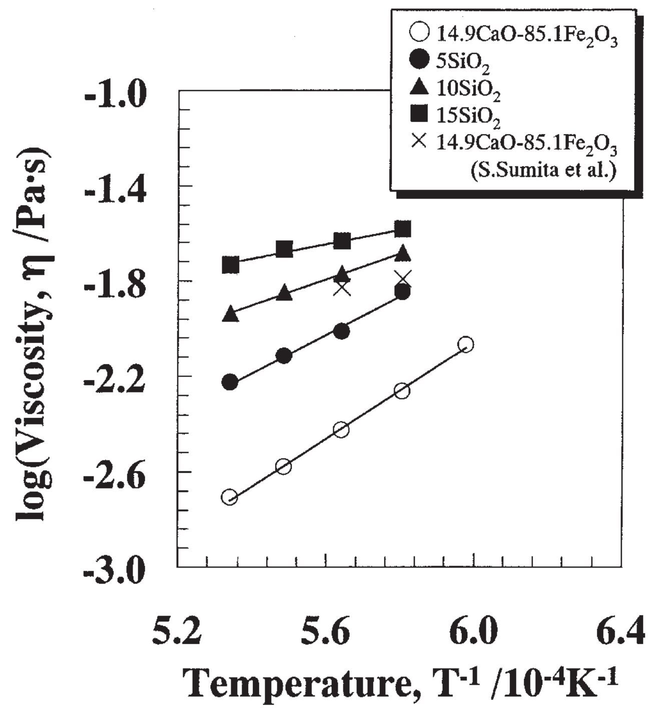


Fig. 12—Temperature dependence of the viscosity of CF_2-SiO_2 slags.

and CF_2 are not in good agreement with the results reported by Sumita *et al.*[19] Generally, the errors in values of viscosity depending on published data range within ± 25 to 50 pct [8] In the case of rotating crucible viscometer, several instrumental factors cause errors,[21] *i.e.*, the lean of rotating axis, the variation of immersion depth, and so on. However, their work with the experimental conditions is not published; the difference in values between our result and reported results is, in part, due to the holding time, as mentioned earlier.

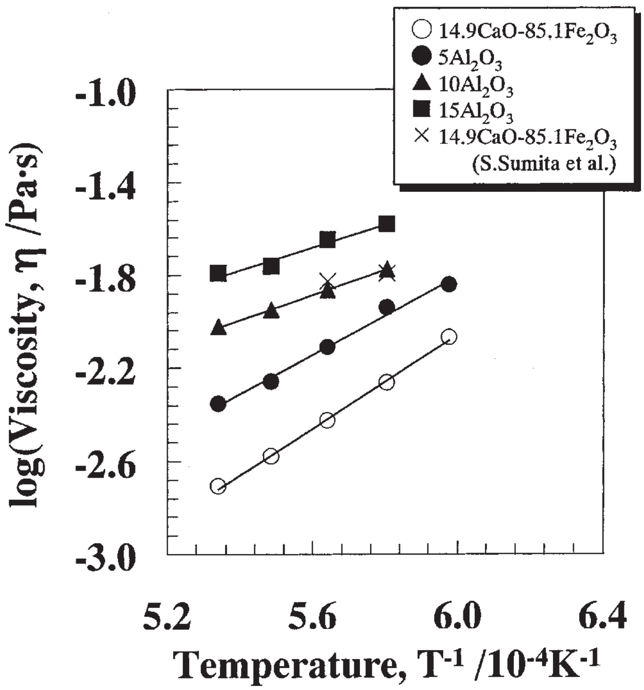


Fig. 13—Temperature dependence of the viscosity of CF_2-Al_2O_3 slags.

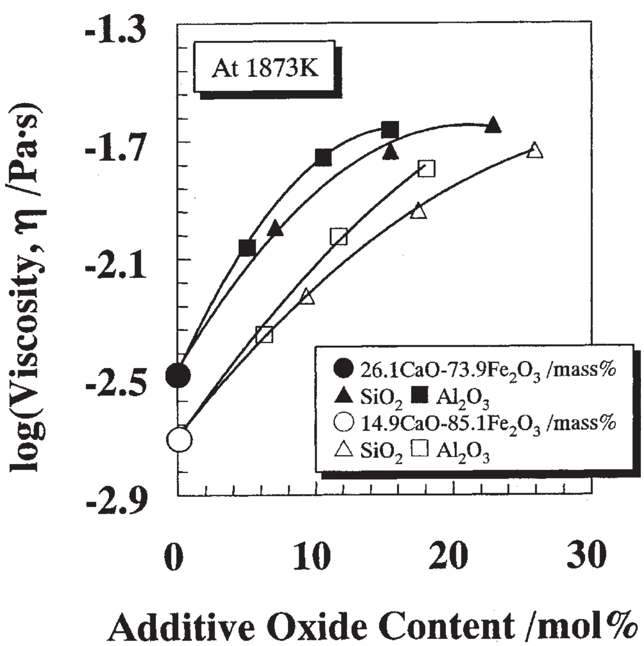


Fig. 14—Effect of additive oxide on the viscosity of CaO-Fe_2O_3 slags at 1873 K.

The viscosity data can be described by an Andrade Eq. [1] over the entire temperature region in this study, as shown in Figures 10 through 13.

Figure 14 illustrates the effect of adding oxide (SiO_2 or Al_2O_3) on the viscosity of CF and CF_2 slags at 1873 K. The horizontal axis shows the molar concentration of additive oxides. The viscosity of these calcium ferrite slags increases with an increase in the content of additive oxide. At the same content of additive oxide, Al_2O_3 is more effective for

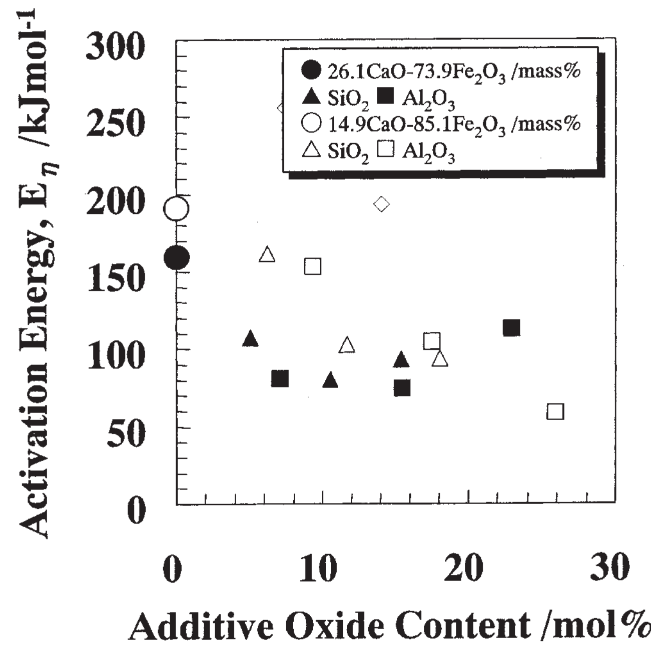


Fig. 15—Effect of additive oxide on the apparent activation energy of viscous flow of CaO-Fe_2O_3 slags.

increasing the viscosity than other additions. Kou *et al.*[22] have investigated the viscosity of Na_2O-SiO_2-Al_2O_3 and CaO-SiO_2-SiO_2 systems using a rotating crucible viscometer. They have reported that, in the case of melts with high basicity, Al^{3+} ion formed oxygen tetrahedron like Si^{4+} ion, and the value of SiO_2 equivalence of Al_2O_3 was about 1.65. In this study, the basicity of CF and CF_2 slags will be fairly high, it is very natural that almost all of the Al_2O_3 added would behave as a network former in calcium ferrite slag. Therefore, the viscosity of Al_2O_3 containing slag is higher than that of SiO_2 containing slag.

Figure 15 shows the relationship between the content of additive oxide and the apparent activation energy of viscous flow based on Eq. [1]. The horizontal axis shows the molar concentration of additive oxides. The apparent activation energy of viscous flow decreases with increasing content of additive oxide in any systems. However, the viscosity increases with an increase in the addition contents. At this point, it is difficult to estimate the structure of these calcium ferrite slags solely from the data of viscosity.

Further investigations such as spectroscopy, density, and surface tension measurements are required for the clarification of structure of calcium ferrite slags.

IV. CONCLUSIONS

The effect of adding MgO, TiO_2, or Fe_2O_3 on the viscosity of 40CaO-40SiO_2-20Al_2O_3 (mass pct) slags and that of adding SiO_2, Al_2O_3, or MgO on the viscosity of CF (Mono calcium ferrite 26.1CaO-73.9Fe_2O_3 (mass pct)) and CF_2 (Hemi calcium ferrite 14.9CaO-85.1Fe_2O_3 (mass pct)) have been measured by the outer cylinder rotating viscometer.

1. Slags shortly after melting showed some higher values of viscosity, but the viscosity decreased with the holding

time and became constant in 1.5 to 11 hours depending on slag compositions.

2. Viscosity of CaO-SiO_2-Al_2O_3 slags decreased with increasing MgO, TiO_2, or Fe_2O_3. At the same content of additive oxide, the viscosity decreases in order of Fe_2O_3, TiO_2, and MgO. The apparent activation energy of viscous flow decreases with increasing the content of additive oxide in any systems.
3. The viscosity of calcium ferrite slags increased with increasing the content of SiO_2 or Al_2O_3. At the same content of additive oxide, Al_2O_3 is effective for increasing the viscosity more than others. The apparent activation energy of viscous flow decreased with increasing the content of additive oxide in any systems.

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REFERENCES

1. J.O'M. Bockris and D.C. Lowe: *Proc. R. Soc. (London) A*, 1954, vol. A226, pp. 423-35.
2. *Handbook of Physico-chemical Properties at High Temperatures*, ISIJ, Tokyo, 1988.
3. S. Sumita, T. Mimori, K. Morinaga, and T. Yanagase: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1980, vol. 44, pp. 94-99.
4. H. Schenk and M.G. Frohherg: *Arch. Eisenhuttenwes.*, 1961, vol. 33, pp. 421-25.
5. E.T. Turkdogan and P.M. Bills: *Am. Ceram. Soc. Bull.*, 1960, vol. 39, pp. 682-87.
6. E.E. Hoffmann and K. Nabin: *Arch. Eisenhuttenwes.*, 1961, vol. 32, pp. 199-208.
7. Y. Shiraishi and T. Saito: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1965, vol. 29, pp. 614-32.
8. T. Iida and Y. Kita: *Boundary*, 1996, vol. 10, p. 34.
9. T. Yasukouchi, K. Nakashima, and K. Mori: *Testu-to-Hagané*, 1999, vol. 85 (8), pp. 125-31.
10. F.-Z. Ji, Du. Sichen and S. Seetharaman: *Metall. Mater. Trans. B*, 1997, vol. 28B, pp. 827-34.
11. K. Nagata and M. Hayashi: *J. Non-Cystalline Solids*, 2001, vol. 282, pp. 1-6.
12. J.S. Machin, T.B. Yee, and D.C. Hanna: *J. Am. Ceram. Soc.*, 1952, vol. 35, pp. 322-25.
13. P. Kozakevitch: *Rev. Metall.*, 1960, vol. 57, pp. 149-58.
14. H. Ito, K. Morinaga and T. Yanagase: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1963, vol. 27, pp. 182-91.
15. K. Morinaga, Y. Suginohara, and T. Yanagase: *Tech. Rep. Kyushu Univ.*, 1975, vol. 48, pp. 859-65.
16. T. Nakamura, K. Morinaga, and T. Yanagase: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1977, vol. 41, pp. 1300-08.
17. M. Kawahara, Y. Ozima, K. Morinaga, and T. Yanagase: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1977, vol. 41, pp. 618-23.
18. K. Morinaga, Y. Suginohara, and T. Yanagase: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1974, vol. 48, pp. 658-62.
19. S. Sumita, K. Morinaga, and T. Yanagase: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1982, vol. 46, pp. 369-77.
20. Y. Awakura, S. Ban-ya, T. Ejima, K. Itagaki, E. Kato, Y. Kawai, K. Mori, Z. Morita, K. Ogino, H. Itao, M. Shimoji, T. Yanagase, and T. Yokokawa: *Physical Chemistry of Metals*, The Japan Institute of Metals, Sendai, 1996.
21. Y. Shiraishi: *Kinzoku*, 1999, vol. 69, pp. 117-24.
22. T. Kou, K. Mizoguchi, and Y. Suginohara: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.)*, 1978, vol. 42, pp. 775-81.