Effect of Additive Oxides on the Viscosities of CaO-SiO_2-Al_2O_3 and CaO-Fe_2O_3 Melts

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ABSTRACT

The effects of MgO, TiO_2 or Fe_2O_3 on the viscosity of $40CaO$-$40SiO_2$-$20Al_2O_3$ /mass% slags have been measured by a rotating crucible viscometer. The viscosity of these quaternary slags decreased with increasing 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 effects of SiO_2, Al_2O_3 or MgO on the viscosity of $26.1CaO$-$73.9Fe_2O_3$ / mass% (CF) and $14.9CaO$-$85.1Fe_2O_3$ / mass% (CF_2) slags have been measured. Viscosity of calcium ferrite slags increased with increasing SiO_2, Al_2O_3 or MgO content. Al_2O_3 was found to be more effective for increasing the viscosity at the same content of additive oxide.

1. INTRODUCTION

The viscosity of molten slag varies widely, depending on temperature and composition. Several of the 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 recent 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 depend on published data range within ±25~50% /8/. Thus, the accuracy of measurements in viscosity for multicomponent slag and flux is of great importance for understanding the reaction behavior in the iron-making process.

In recent years, the amount of required 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 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 effects of adding MgO, TiO_2 or Fe_2O_3 on the viscosity of $40CaO$-$40SiO_2$-$20Al_2O_3$ /mass% slags relating to blast furnaces were investigated. In addition, the effects of adding SiO_2, Al_2O_3 or MgO on the viscosity of calcium ferrite melts, $26.1CaO$-$73.9Fe_2O_3$ /mass% (CF) and $14.9CaO$-$85.1Fe_2O_3$ /mass% (CF_2) relating to liquid phase sintering of ore were also measured.

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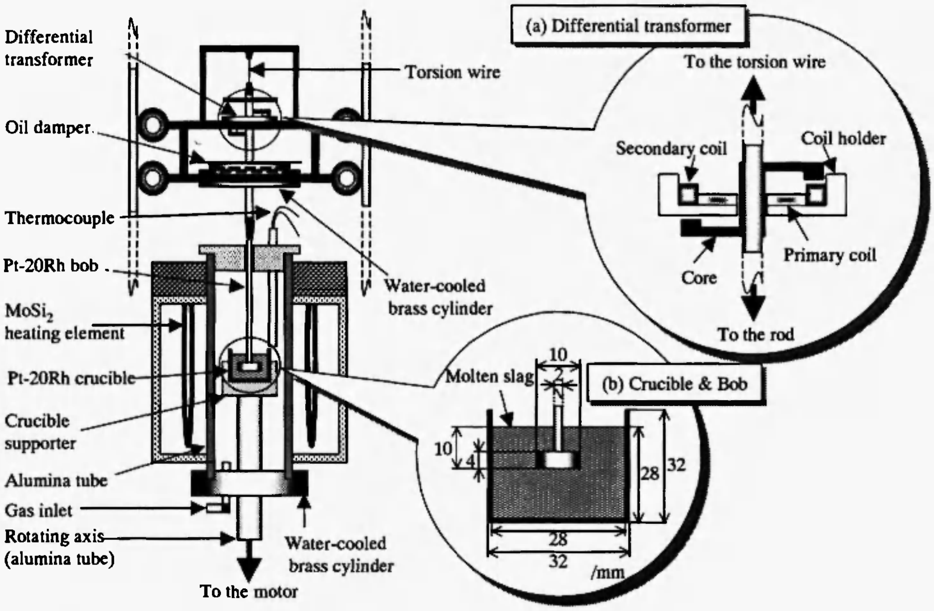

Fig. 1: Schematic illustration of the apparatus for viscosity measurement.

2. EXPERIMENTAL

2-1. 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%, 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 0.001-10 Pa·s at room temperature before the each measurement. Figure 2 shows examples of the calibration line. Calibrations of the viscometer were also made in the temperature range 1523-1823 K using reference slags (SRM2 type slags /8/). The compositions of the reference slags are given in Table 1. 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 2.

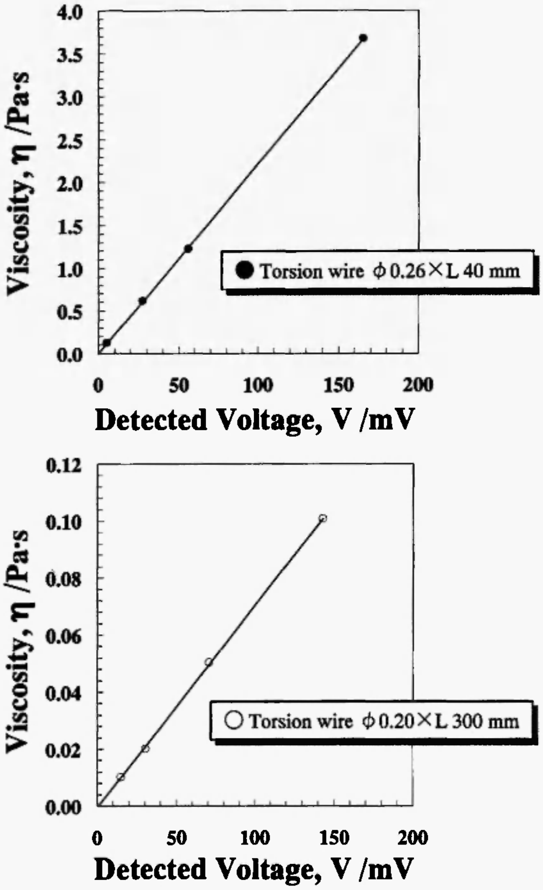

Fig. 2: Calibration lines for the evaluation of viscosity value.

Table 1

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
Slag1	63.0	14.3	20.2	0.630	0.550	0.140	0.380	—	—
Slag2	62.5	15.2	21.3	0.500	0.630	0.140	0.390	—	—

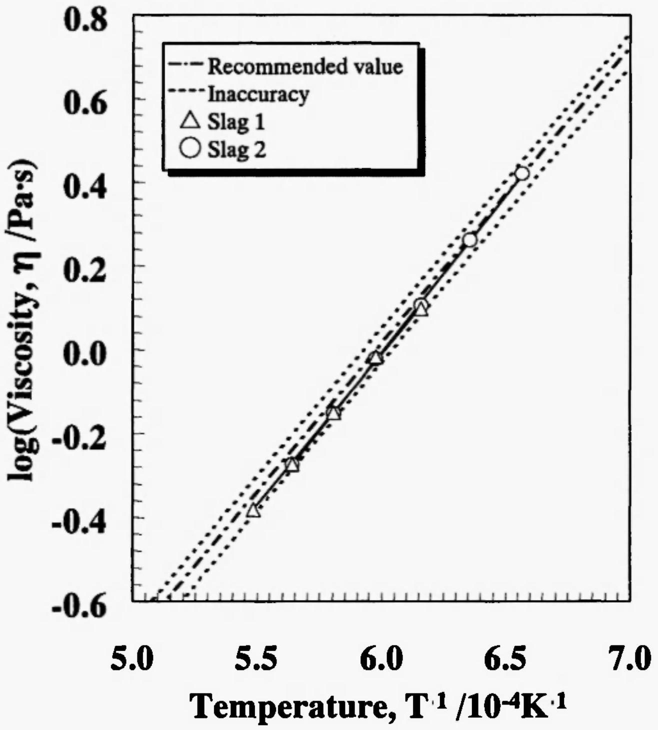

Fig. 3: Results of high temperature calibration using SRM2 type slag.

Table 2

Experimental conditions of viscosity measurement.

Atmosphere	Air Ar ($CaO-SiO_2-Al_2O_3-Fe_2O_3$ slag), 2.00 l /min.
Temperature range	1673~1873 K ($CaO-SiO-Al_2O_3$ system) 1573~1898 K ($CaO-Fe_2O_3$ system)
Diameter & length of torsion wire	φ0.200~0.430×40.0~50.0 mm ($CaO-SiO-Al_2O_3$ system) φ0.200×300 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 r.p.m. ($CaO-SiO-Al_2O_3$ system) 80.0 r.p.m. ($CaO-Fe_2O_3$ system)

2-2. 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 3), and mixed in an alumina mortar thoroughly. The sample was premelted in a resistance furnace using Pt crucible for an hour. Then the sample was crushed into powder and then used for measurements.

Table 3

Initial and final slag compositions for viscosity measurement.

Chemical compositions /mass%												
Initial						Final						
CaO	SiO_2	Al_2O_3	MgO	TiO_2	Fe_2O_3	CaO	SiO_2	Al_2O_3	MgO	TiO_2	Fe_2O_3	FeO
40	40	20				40.4	39.8	19.8				
38	38	19	5			39.6	37.0	18.1	5.34			
36	36	18	10			36.0	35.8	17.1	11.0			
34	34	17	15			34.7	34.2	16.0	15.1			
32	32	16	20			32.4	31.7	15.8	20.1			
36	36	18		10		37.2	35.1	17.0		10.6		
32	32	16		20		34.1	31.9	15.0		19.0		
36	36	18			10	37.9	35.3	16.5			7.79	2.45
32	32	16			20	33.1	32.1	14.1			14.3	6.44
28	28	14			30	28.3	28.3	12.6			23.0	7.87
24	24	12			40	23.4	23.5	11.3			30.1	11.7
26.1					73.9	25.8					73.7	0.498
24.8	5				70.2	25.2	4.0				70.0	0.808
23.5	10				66.5	24.1	9.1				65.9	0.842
22.2	15				62.8	22.7	14.3				62.2	0.869
24.8		5			70.2	24.7		4.7			70.1	0.485
23.5		10			66.5	23.5		9.9			66.1	0.487
22.2		15			62.8	23.0		14.6			61.9	0.489
25.4			2.5		72.1	25.0			2.3		72.7*	
24.8			5		70.2	24.1			4.7		71.3*	
24.1			7.5		68.4	24.0			6.8		69.2*	
14.9					85.1	15.7					83.5	0.829
14.2	5				80.8	14.4	4.7				79.9	1.057
13.4	10				76.6	13.9	9.1				75.9	1.098
12.7	15				72.3	12.8	14.2				71.8	1.160
14.2		5			80.8	14.2		5.1			79.9	0.832
13.4		10			76.6	13.8		9.6			75.7	0.858
12.7		15			72.3	12.6		14.9			71.4	1.052
14.5			2.5		83.0	15.1			2.2		82.7*	
14.2			5		80.8	15.0			4.5		80.5*	

*Fe_tO

2-3. Viscosity Measurements

The crucible filled with slag powder was placed in a crucible supporter in the furnace and heated up to 1873K.

After then, the molten slag was kept at that temperature until the detected voltage value (Viscosity) became constant.

The measurements were carried out three times at every 50K interval 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 min. 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%.

After the viscosity measurements, the quenched slags were used for chemical analysis. Since slags with Fe_2O_3 contain some amount of FeO, the fraction of Fe^{3+} and Fe^{2+} were determined by EDTA titration method. Table 3 shows the initial and the final slag compositions.

3. RESULTS AND DISCUSSION

3-1. Effect of holding time on isothermal viscosity

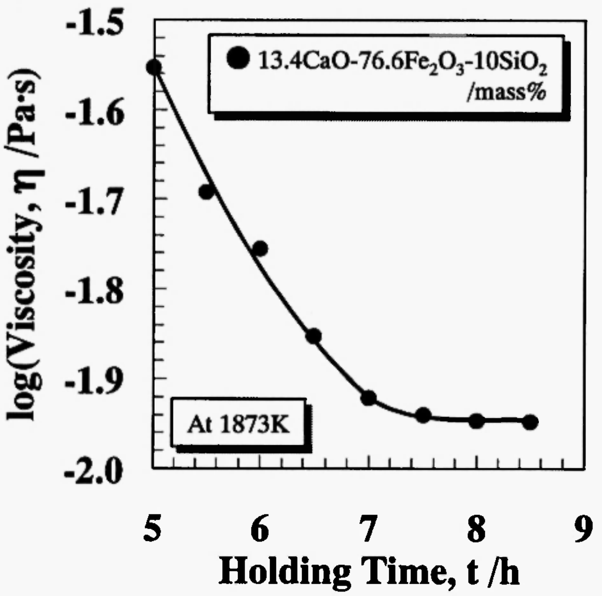

Fig. 4: An example of the variation of viscosity with different holding time.

Figure 4 shows an example of the variation of viscosity with different holding time, and reveals the decrease of viscosity with holding time. It required no less than 8 hours to become constant for the viscosity of $13.4CaO\text{-}76.6Fe_2O_3\text{-}10SiO_2$ /mass% slag. $CF_2\text{-}SiO_2$ slags required a fairly long holding time to become constant value for viscosities, especially, 11 hours for CF_2-15mass%SiO_2, 8 hours for CF_2-10mass%SiO_2 and 5.5 hours for CF_2-5mass%SiO_2. In other calcium ferrite slags and $CaO\text{-}SiO_2\text{-}Al_2O_3$-(MgO, TiO_2 or Fe_2O_3) slags, the 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 viscosity value due to the time required for complete homogenization and thermal equilibration of melts /10/.

On the other hand, Nagata *et al.* /11/ have recently investigated the change of the oxygen coordination structures of both iron ions, Fe^{3+} and Fe^{2+}, in calcium-silicate ($40CaO\text{-}40SiO_2\text{-}20Fe_2O_3$ /mol%) slag during the equilibration process at various temperatures. They 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 1773K after equilibration operation. This result suggests the decrease of the viscosity, as shown in Figure 4, will be due to the increased 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 larger 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, it might be expected that they require a considerably longer holding time for the equilibration of coordination structures.

3-2. The viscosity of 40CaO-40SiO_2 -20Al_2O_3-(MgO, TiO_2 or Fe_2O_3) quaternary slags

Figures 5-7 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% slag is in good agreement with the results reported by Machin et al. /12/ and Kozakevitch /13/. The viscosity data can be described by an Arrhenius type equation over the entire temperature region in this study.

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

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

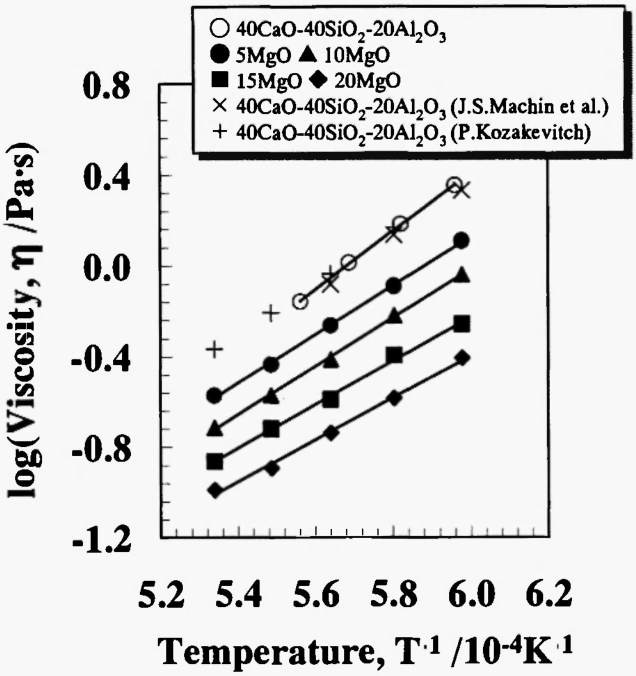

Fig. 5: Temperature dependence of the viscosity of CaO-SiO_2-Al_2O_3-MgO slags.

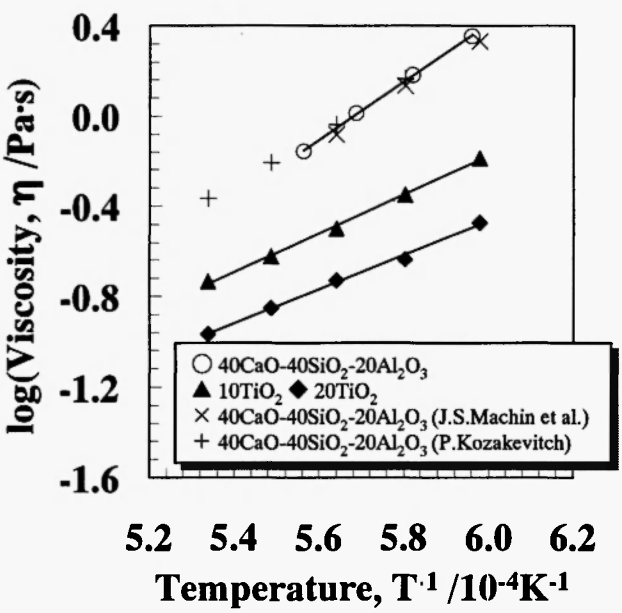

Fig. 6: Temperature dependence of the viscosity of CaO-SiO_2-Al_2O_3-TiO_2 slags.

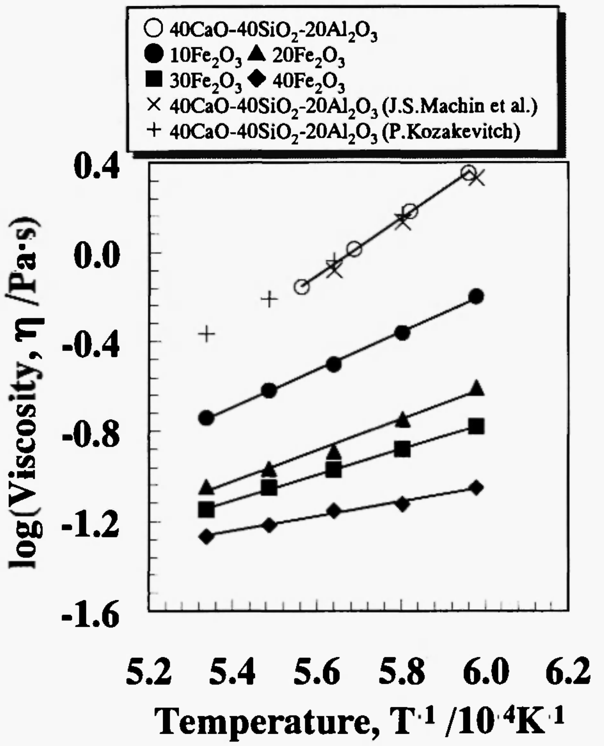

Fig. 7: Temperature dependence of the viscosity of CaO-SiO_2-Al_2O_3-Fe_2O_3 slags.

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

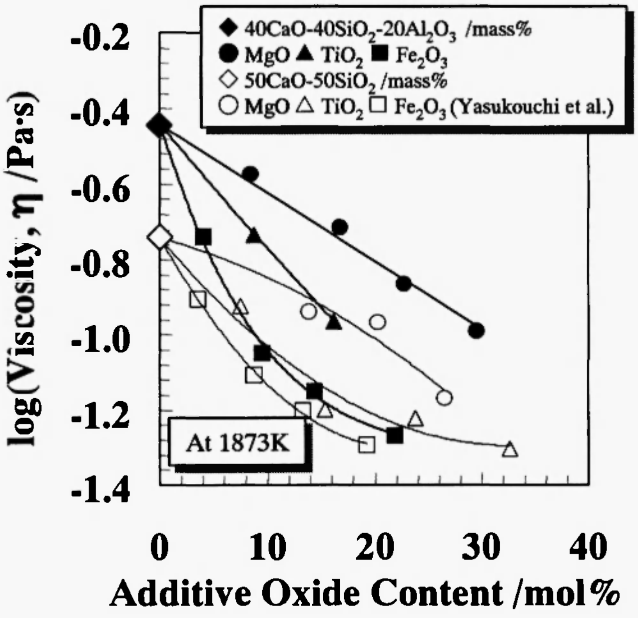

Fig. 8: Effect of additive oxide on the viscosity of $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2$ slags at 1873K.

$20Al_2O_3$ /mass% slags at 1873K together with our previous data /9/ for $50CaO-50SiO_2$ /mass% 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 decreases 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.

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% 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% slag.

Morinaga et al. /18/ have investigated the electrical conductivity of $CaO-SiO_2-TiO_2$ 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%. Moreover, decreasing the ratio CaO/SiO_2 lead to the 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 have not been done. It is expected that TiO_2 or Fe_2O_3 would behave as network modifier in $40CaO-40SiO_2-20Al_2O_3$ slag. Therefore, the viscosity of these quaternary slags decrease with increasing TiO_2 or Fe_2O_3.

Since Fe^{3+} ion has smaller cation-oxygen attraction /20/ than that of 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 coexisted. Further investigation of structural analysis is required.

When MgO behaves as network modifier in Na_2O-SiO_2-MgO and $CaO-SiO_2-MgO$ slags, namely 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 equation (2S). 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. This result also indicates that the structural unit for viscous flow of slags became smaller with increasing MgO, TiO_2 or Fe_2O_3 contents.

3-3. The viscosity of CF-(SiO_2, Al_2O_3 or MgO) and CF_2-(SiO_2, Al_2O_3 or MgO) ternary slags.

Figures 10-15 show the temperature dependence of the viscosity of $CF-SiO_2$, $CF-Al_2O_3$, CF-MgO, CF_2-SiO_2, $CF_2-Al_2O_3$ and CF_2-MgO ternary slags, respectively. The present results of CF and CF_2 are not in good agreement with the results reported by Sumita *et al.* /19/, and these differences could be caused by the holding time before measurements, as shown in Figure 4. Generally, the errors in values of viscosity depending

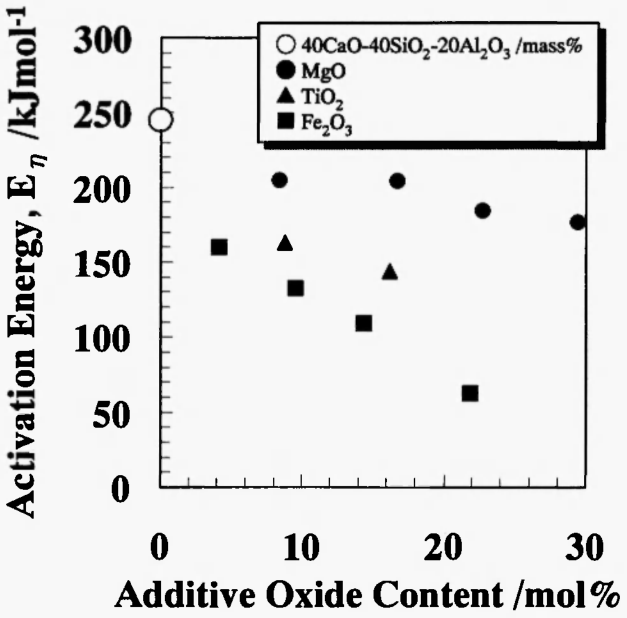

Fig. 9: Effect of additive oxide on the apparent activation energy of viscous flow of CaO-SiO_2-Al_2O_3 slags.

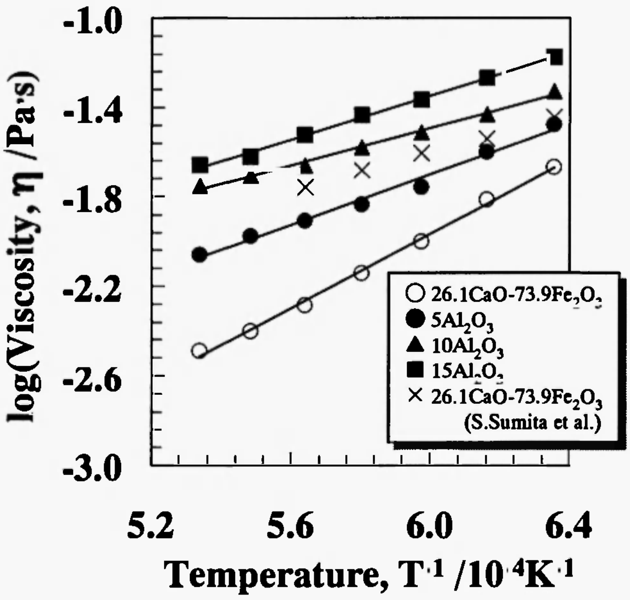

Fig. 11: Temperature dependence of the viscosity of CF-Al_2O_3 slags.

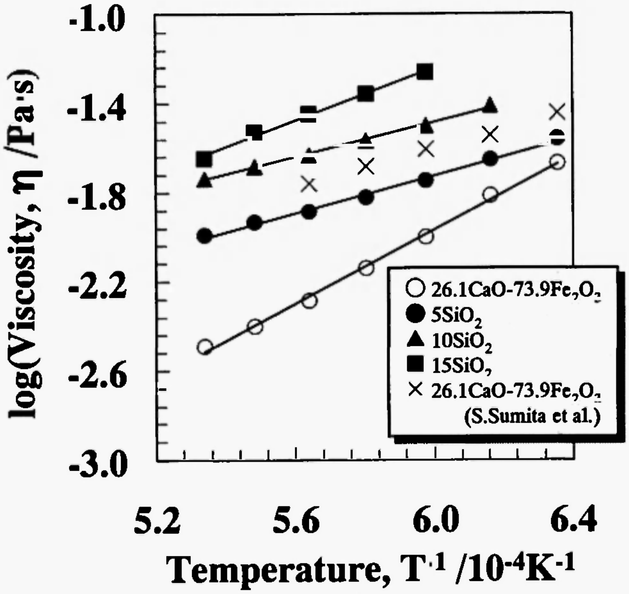

Fig. 10: Temperature dependence of the viscosity of CF-SiO_2 slags.

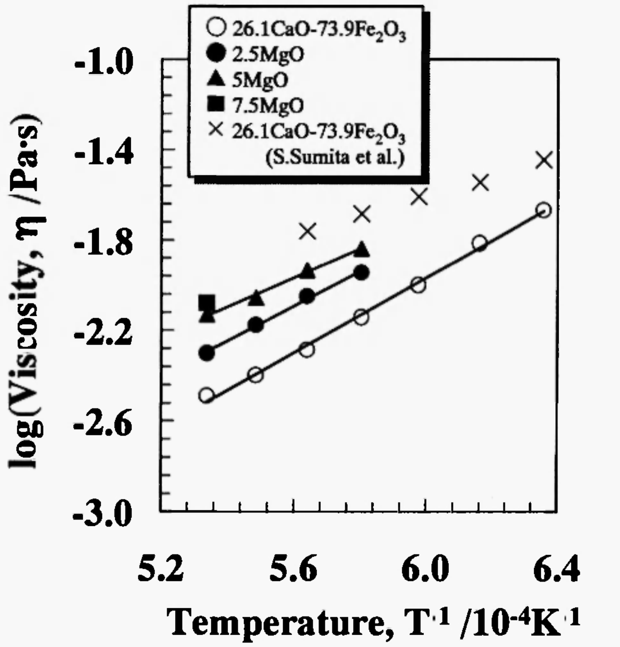

Fig. 12: Temperature dependence of the viscosity of CF-MgO slags.

on published data range within±25~50% /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 in which the experimental conditions are not published, the different of values between our result and reported results is, in part, due to the holding time as mentioned earlier.

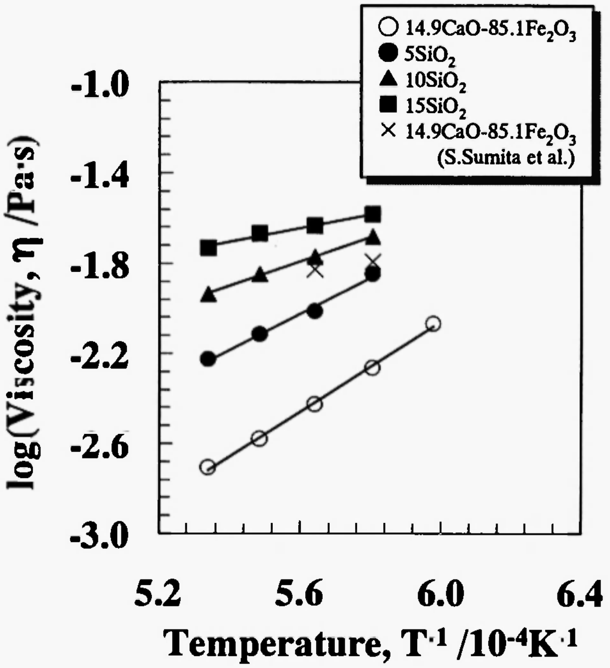

Fig. 13: Temperature dependence of the viscosity of CF_2-SiO_2 slags.

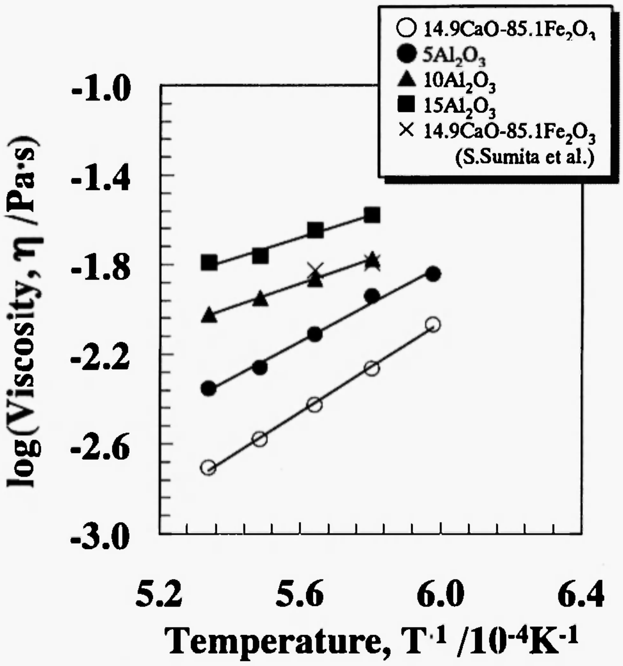

Fig. 14: Temperature dependence of the viscosity of CF_2-Al_2O_3 slags.

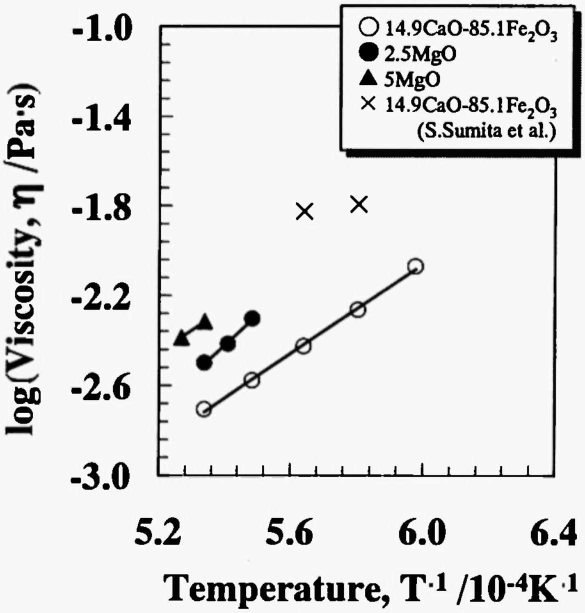

Fig. 15: Temperature dependence of the viscosity of CF_2-MgO slags.

The viscosity data can be described by an Arrhenius type equation (2) over the entire temperature region in this study as shown in Figure 10-15.

Figure 16 illustrates the effect of adding oxide (SiO_2, Al_2O_3 or MgO) on the viscosity of CF and CF_2 slags at 1873K. The horizontal axis shows the molar concentration of additive oxides. The viscosity of these

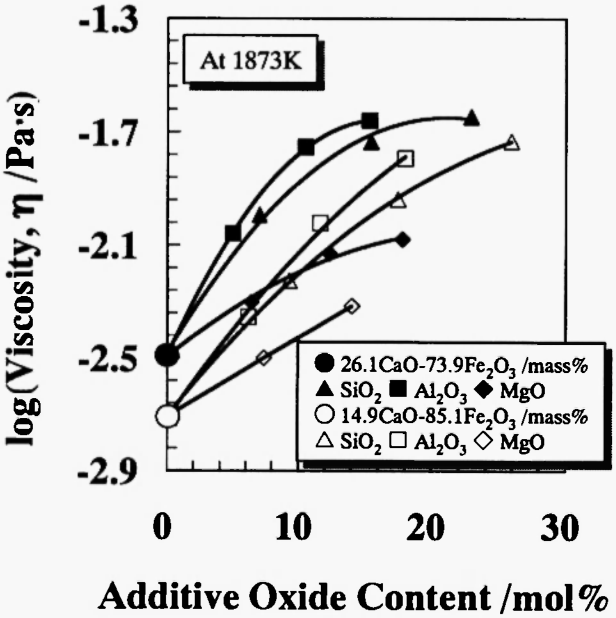

Fig. 16: Effect of additive oxide on the viscosity of CaO-Fe_2O slags at 1873K.

calcium ferrite slags increases with increasing the content of additive oxide. At the same content of additive oxide, Al_2O_3 is more effective for increasing the viscosity than other additions. Kou *et al.* /22/ have investigated the viscosity of $Na_2O\text{-}SiO_2\text{-}Al_2O_3$ and $CaO\text{-}SiO_2\text{-}SiO_2$ systems using rotating crucible viscometer, and they have reported that, in the case of melts with high basicity, Al^{3+} ion formed oxygen tetrahedron, likewise 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.

As shown in Figure 8, MgO is effective in decreasing the viscosity of silicate slags. However, in calcium ferrite systems, the viscosity of CF and CF_2 slags increases with increasing MgO content. Structural analyses have not yet been done for these slags. Since adding MgO will raise the liquidus temperature of calcium ferrite slags, it is very probable that the viscosities of these slags increase with MgO content.

Figure 17 shows the relationship between the content of additive oxide and the apparent activation energy of viscous flow based on equation (2). 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 increasing addition contents. On this point, it is difficult to estimate the structure of these calcium ferrite slags solely from the data of viscosity.

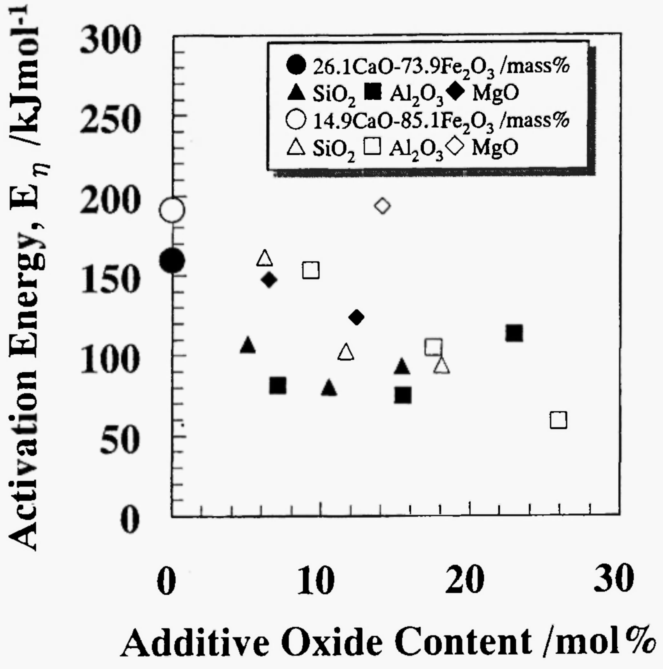

Fig. 17: Effect of additive oxide on the apparent activation energy of $CaO\text{-}Fe_2O$ slags.

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

4. CONCLUSIONS

The effect of adding MgO, TiO_2 or Fe_2O_3 on the viscosity of $40CaO\text{-}40SiO_2\text{-}20Al_2O_3$ /mass% slags and that of adding SiO_2, Al_2O_3 or MgO on the viscosity of CF (Mono calcium ferrite $26.1CaO\text{-}73.9Fe_2O_3$ /mass%) and CF_2 (Hemi calcium ferrite $14.9CaO\text{-}85.1Fe_2O_3$ /mass%) 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 1.5-11 hours depending on slag compositions.
2. Viscosity of $CaO\text{-}SiO_2\text{-}Al_2O_3$ 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, Al_2O_3 or MgO. 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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