Relation between the Viscosity and Electrical Conductivity of Molten Slag*

—Properties of Slag at Elevated Temperature (Part III)—

By Makoto KATO** and Susumu MINOWA**

Synopsis

Relation between the viscosity and the electrical conductivity in molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ or $[\text{CaO}(43)\text{-SiO}_2(43)\text{-Al}_2\text{O}_3(14)]$ -addition system was discussed in the data reported previously. Applying the equation, $\log \eta = a + b \cdot \log \kappa$, the viscosity coefficient was estimated from the conductivity. The estimated viscosity coefficient is well in agreement with the observed one.

I. Introduction

The relation between the electrical conductivity of materials and other physicochemical properties has been well examined at room temperatures,¹⁾⁻³⁾ whereas the knowledge on the interrelations of the properties of the melt at elevated temperatures are not available. Therefore, the properties of molten slag, especially the viscosity coefficient and the conductivity were both reported previously^{4),5)} by the present authors. In this paper, the relation between the viscosity and conductivity of molten slags is discussed basing on the observed data previously reported; and moreover, the equations for the relation of the viscosity and conductivity in some composition range are proposed.

II. Relation between the Viscosity and Conductivity of Molten Slag

1. $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ System

Three examples of the relation between the viscosity and conductivity are shown in Fig. 1 at various temperatures. Because the viscosity coefficient increased with conductivity decrease and the relation of $\eta \cdot \kappa \doteq \text{constant}$ (so-called Walden's law)⁶⁾ was in agreement with these data, the mechanism of viscous flow is supposed to be related with the mechanism of conduction. The flow unit in molten slag is in a large form at lower temperatures, because the viscosity increases with temperature lowering (the bridging of silicates or alumino-silicates is perhaps promoted with temperature lowering). This growth of network structure prevents the movement of conductive ions (mainly Ca^{2+}) and results in the conductivity decrease.

The relation between the viscosity coefficient and conductivity is shown in Fig. 2 at 1500°C. As the viscosity coefficient was inversely proportional to the conductivity, the mechanism of viscous flow or electric conduction is not expected to change substantially in this composition range.

Figure 3 shows the viscosity coefficient or the conductivity at 1500°C related with the ratio of $N_{\text{Al}_2\text{O}_3}/$

Fig. 1. Examples of the relation between the viscosity coefficient and conductivity of the same composition slag in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system

Fig. 2. Relation between the viscosity coefficient and conductivity of molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag at 1500°C

N_{CaO} . However, they were not related with $N_{\text{CaO}}/N_{\text{SiO}_2}$ or $N_{\text{CaO}}/(N_{\text{SiO}_2} + N_{\text{Al}_2\text{O}_3})$. The viscosity and

* Received June 6, 1968.

** The Government Industrial Research Institute (Nagoya), Hirate-cho, Kita-ku, Nagoya 462.

Fig. 3. $N_{\text{Al}_2\text{O}_3}/N_{\text{CaO}}$ dependence of the viscosity coefficient or the conductivity of molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ at 1500°C

conductivity in this slag composition are closely related with the behaviour of Al_2O_3 in molten slag. It has been pointed out by Kozakevitch⁷⁾ in his viscosity measurements on ternary melts, that Al_2O_3 shows the same effect on viscosity as SiO_2 in the composition range of low $\text{Al}_2\text{O}_3/\text{CaO}$ ratio and forms the network structure, in which the aluminium atom is located at the same position as silicon atom.

However, if Al_2O_3 shows the same effect as SiO_2 , the viscosity coefficient or the conductivity should be arranged with the ratio of $N_{\text{CaO}}/(N_{\text{SiO}_2} + N_{\text{Al}_2\text{O}_3})$. The behaviour of Al_2O_3 should be further examined.

The networks in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag are constructed mainly with SiO_2 and partly with Al_2O_3 , and are broken by CaO which controls the bonding of aluminium or silicon cation with oxygen anion. Therefore, CaO controls the size of silicate, aluminate, or alumino-silicate anion groups. Supposing that CaO reacts in compliance with anion group formers, the property dependence on Al_2O_3 content may be explained. Because bridging of anion groups is controlled by the relative quantities of CaO and other network formers. When the slag is in the composition range of $\text{SiO}_2 < \text{Al}_2\text{O}_3$, the interaction of cation with anion in molten slag is not much different from

the one in solid crystals.

When the small addition of CaO is made, CaO reacts with SiO_2 preferentially and breaks the silica network. The flow units of this melt are supposedly in a large form as alumino-silicate or silicate anion groups which are controlled by the amount of CaO . When the CaO addition increases, CaO reacts not only with silica networks but also with alumino-silicate networks with excess CaO over some silica equivalent. The flow units may be small in form of silicate or aluminate anion groups which are also dependent on the amount of CaO in the melt. The relative size of flow units is determined by ratio of CaO to SiO_2 . Further the quantitative relation of flow units is controlled by Al_2O_3 and CaO contents. Thus, the properties of the slag are affected by the anion group which is mainly constructed by the silicate anion groups and subsidiary aluminate anion groups. The above speculation is consistent with the coefficients a and b of Eq. (3) determined by $N_{\text{Al}_2\text{O}_3}$ and $(N_{\text{SiO}_2} - N_{\text{CaO}})$ in the following estimation.

Figure 4 shows the relation between the activation energies for viscous flow and for electric conduction. E_η was larger than E_κ , and $E_\eta/E_\kappa \doteq 1.37$ is given in Fig. 4. This is perhaps caused by the size difference between the flow unit and the conductive ions. The former is in a rather large form as silicate or alumino-silicate anion groups and the latter is mainly Ca^{2+} cation as

Fig. 4. Relation between the activation energy for viscous flow and for the electrical conduction of molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag

Table 1. ΔF_f° and ΔH_f° for the formation of binary compounds in CaO , SiO_2 , and Al_2O_3 system, at $1800^\circ\text{K}^{8)}$

Reaction	ΔH_f° (cal/mol)	ΔF_f° (cal/mol)
$3\text{CaO (c)} + \text{Al}_2\text{O}_3 \text{ (c)} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \text{ (c)}$	-3 900	-15 290
$\text{CaO (c)} + \text{Al}_2\text{O}_3 \text{ (c)} \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \text{ (c)}$	-4 550	-11 910
$\text{Al}_2\text{O}_3 \text{ (c)} + \text{SiO}_2 \text{ (c)} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \text{ (c)}$ (silimanite)	-47 870	-44 900
„ (andalusite)	-41 270	-39 750
„ (kyanite)	-39 470	-34 920
$\text{CaO (c)} + \text{SiO}_2 \text{ (c)} \rightarrow \text{CaO} \cdot \text{SiO}_2 \text{ (c)}$ (Wollastonite or pseudo-wollastonite)	-21 150	-19 640
$2\text{CaO (c)} + \text{SiO}_2 \text{ (c)} \rightarrow 2\text{CaO} \cdot \text{SiO}_2 \text{ (}\hat{\text{c}}\text{)}$	-23 190	-33 860
$3\text{CaO (c)} + \text{SiO}_2 \text{ (c)} \rightarrow 3\text{CaO} \cdot \text{SiO}_2 \text{ (c)}$	-22 230	-32 470

charge carrier. As E_η showed the linearity in relation with E_κ , the mechanism of the viscous flow and the electric conduction may not change in this composition range.

2. [CaO(43)-SiO₂(43)-Al₂O₃(14)]-Oxide (FeO, MnO, MgO, V₂O₅, Cr₂O₃, P₂O₅, or TiO₂) System

Walden's law was almost valid in this oxide-added system. The relation between the viscosity coefficient and the conductivity at 1500°C is shown in Fig. 5. V₂O₅ and Cr₂O₃ showed the different influence on structural change from other oxides. The conductivity of slag did not change at 1500°C by addition of other oxides, but the conductivity of slag was very much affected by the addition of V₂O₅ or Cr₂O₃ at the same temperature.

Fig. 5. Relation between the viscosity coefficient and conductivity of molten [CaO(43)-SiO₂(43)-Al₂O₃(14)]-oxide addition slag

Fig. 6. Relation between the activation energy for viscous flow and for electrical conduction of molten [CaO(43)-SiO₂(43)-Al₂O₃(14)]-oxide addition slag

The relation between the viscosity coefficient and the conductivity was linear in the quaternary system. This linearity may be caused by carrier increase due to the oxide addition, but not by the structural change. Figure 6 shows the relation of E_η with E_κ and $E_\eta/E_\kappa \cong 1.76$. This ratio was a little larger than the one in ternary system. This may be caused by the decrease of E_κ due to the fact that the ionic radius of cation⁸⁾ added as oxides is smaller than that of Ca²⁺. From this reason, the slags containing V₂O₅ and Cr₂O₃ showed the different tendency from the others.

3. [CaO(43)-SiO₂(43)-Al₂O₃(14)]-Fluoride (NaF, CaF₂, MgF₂, or AlF₃) System

Walden's law was also valid in the slag containing fluorides, or in the melt of the same composition. The relation between the viscosity coefficient and the conductivity was similar to the ternary system as shown in Fig. 7, though the slag containing NaF showed rather high conductivity. This is caused by the electronic conduction in addition to ionic one, as mentioned previously.¹¹⁾

The relation between E_η and E_κ differed from the one in the ternary system, as shown in Fig. 8. E_η was nearly equal to E_κ and the line of this relation did not intersect the zero point. The apparent activation energy of conduction becomes small, when the electronic conduction increases in the slag containing much fluorides. Moreover, because the fluoride is a strong network modifier,⁹⁾ the network structure is broken down to small sizes.

Fig. 7. Relation between the viscosity coefficient and conductivity of molten [CaO(43)-SiO₂(43)-Al₂O₃(14)]-fluoride addition slag

Fig. 8. Relation between the activation energy for viscous flow and for electrical conduction of molten [CaO-(43)-SiO₂(43)-Al₂O₃(14)]-fluoride addition slag

4. Influence of Additions on the Relation of E_η with E_κ of Molten CaO(43)-SiO₂(43)-Al₂O₃(14) Slag

Figure 9 shows the shift of E_η - E_κ relation with increasing additions, when the E_η - E_κ relation of mother slag was taken as a reference value. The directions of the shift correspond to the groups classified previously¹¹⁾ with conductivity data. This is an information for structure of slag melts.

Fig. 9. The shift of E_η - E_κ relation of mother slag by the addition

III. Conversion of the Viscosity Coefficient to the Conductivity

1. Derivation of the Conversion Equation

The following equations are valid for the viscosity coefficient and conductivity of molten slags, as mentioned previously.¹¹⁾

$$\eta = A_\eta \exp(E_\eta/RT) \dots \dots \dots (1)$$

$$\kappa = A_\kappa \exp(-E_\kappa/RT) \dots \dots \dots (2)$$

Therefore, Eq. (3) is derived from the combination of Eq. (1) with (2).¹⁰⁾

$$\log \eta = a + b \cdot \log \kappa \dots \dots \dots (3)$$

where,

$$a = \log A_\eta + (E_\eta/E_\kappa) \cdot \log A_\kappa$$

$$b = -(E_\eta/E_\kappa)$$

Table 2 shows the results of calculation based on the observed data of CaO-SiO₂-Al₂O₃ system, for the purpose of confirming Eq. (3).

Because Eq. (3) is well in agreement with the results obtained in Table 2, the viscosity coefficients are able to be converted from the conductivity and *vice versa*, when the coefficients a and b are determined.

Estimated viscosity coefficients are compared with the measured values and the coefficients a and b were determined for the given slag compositions.

2. CaO-SiO₂-Al₂O₃ System

In this system, the properties of slag were obviously influenced by the Al₂O₃ content and the ratio of CaO and SiO₂ contents, as mentioned above. The constants a and b become as follows in this system.

$$a = (1/2) \cdot N_{\text{Al}_2\text{O}_3}, \quad b = -[1.37 + 2(N_{\text{SiO}_2} - N_{\text{CaO}})]$$

Therefore, the viscosity coefficient can be related to the conductivity by the following equation.

$$\log \eta = (1/2) \cdot N_{\text{Al}_2\text{O}_3} - [1.37 + 2(N_{\text{SiO}_2} - N_{\text{CaO}})] \cdot \log \kappa \dots (4)$$

Figure 10 shows the comparison of the observed viscosity coefficient and the values calculated by Eq. (4).

3. [CaO(43)-SiO₂(43)-Al₂O₃(14)]-Oxide Addition System

In this system, Eq. (3) was also used. By trial and error method, a and b were determined as follows.

$$a = (1/2) \cdot N_{\text{Al}_2\text{O}_3} \pm N$$

$$b = -[1.76 + 2(\Sigma N_{\text{former}} - \Sigma N_{\text{modifier}})]$$

Fig. 10. Calculated viscosity coefficient compared with observed one, in molten CaO-SiO₂-Al₂O₃ slag

Table 2. Comparison between the observed viscosity coefficient and calculated one based upon the observed conductivity with Eq. (3) at 1500°C

No.	η_{obs} (poise)	$\log \eta_{\text{obs}}$	κ_{obs} (ν/cm)	$\log \kappa_{\text{obs}}$	$\log A_\eta$	$\log A_\kappa$	$-b$	a	η_{cal} (poise)
9	6.60	0.820	0.341	-0.467	-5.37	5.22	1.10	0.347	7.2
10	7.84	0.894	0.242	-0.616	-7.85	5.85	1.36	0.080	8.2
11	11.2	1.05	0.203	-0.693	-8.25	6.15	1.36	0.107	11
12	4.92	0.692	0.547	-0.262	-6.43	4.45	1.50	0.234	5.8
13	2.47	0.393	0.648	-0.188	-5.02	3.31	1.55	0.105	2.5
14	4.65	0.668	0.517	-0.287	-5.27	4.28	1.30	0.278	4.5
15	3.90	0.591	0.527	-0.278	-7.20	4.70	1.57	0.162	4.0
16	2.78	0.444	0.706	-0.151	-5.29	4.95	1.13	0.297	2.9
17	4.40	0.644	0.415	-0.382	-5.23	4.14	1.31	0.184	4.8
18	4.77	0.679	0.423	-0.374	-6.70	4.14	1.64	0.072	4.8

Fig. 11. Calculated viscosity coefficient compared with observed one, in molten [CaO(43)-SiO₂(43)-Al₂O₃-(14)]-oxide addition slag

where $\pm N$ is a molar fraction of added oxides and a positive sign is adopted for network former (Cr_2O_3 , P_2O_5) and a negative sign for modifier (FeO , MnO , MgO , V_2O_5 , TiO_2), according to the previous work. ΣN_{former} represents $(N_{\text{SiO}_2} + N_{\text{added former}})$ and $\Sigma N_{\text{modifier}}$, $(N_{\text{CaO}} + N_{\text{added modifier}})$. The value 1.76 is the ratio of E_η/E_κ in Fig. 6. Thus, the viscosity coefficient can be estimated from the following equation with the measured conductivity.

$$\log \eta = [(1/2) \cdot N_{\text{Al}_2\text{O}_3} \pm N] - [1.76 + 2(\Sigma N_{\text{former}} - \Sigma N_{\text{modifier}})] \cdot \log \kappa \dots (5)$$

The comparison of the estimated viscosity coefficients with the measured ones is shown in Fig. 11. Because, V_2O_5 or Cr_2O_3 is different from other oxides in their influence on slag structure, Eq. (5) may not be used for the slag containing them.

4. [CaO(43)-SiO₂(43)-Al₂O₃(14)]-Fluoride Addition System

In this system, it was difficult to determine the coeffi-

Fig. 12. Calculated viscosity coefficient compared with observed one, in molten [CaO(43)-SiO₂(43)-Al₂O₃-(14)]-fluoride addition slag

cients a and b , satisfactorily for all fluorides, due to the loss of fluorine, too small viscosity, and participation of the electronic conduction.¹¹⁾ The unification into only one equation is difficult because of the difference in fraction of the electronic conduction and of the constitution of flow unit with fluoride contents. However, the coefficients a and b were determined.

$$a = (1/2) \cdot N_{\text{Al}_2\text{O}_3} - N_{\text{fluoride}}$$

$$b = -[1.06 + 2(N_{\text{SiO}_2} - \Sigma N_{\text{modifier}})]$$

where $\Sigma N_{\text{modifier}}$ represents $(N_{\text{CaO}} + N_{\text{fluoride}})$, and the value 1.06 one of E_η/E_κ in Fig. 8. Therefore,

$$\log \eta = [(1/2) \cdot N_{\text{Al}_2\text{O}_3} - N_{\text{fluoride}}] - [1.06 + 2(N_{\text{SiO}_2} - \Sigma N_{\text{modifier}})] \cdot \log \kappa \dots (6)$$

Figure 12 shows the comparison of the estimated viscosity coefficient with the measured one. The estimation for the slag containing much fluorides was close to the measured one, while that for viscous slag was not.

IV. Summary

In molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ and $[\text{CaO}(43)\text{-SiO}_2(43)\text{-Al}_2\text{O}_3(14)]$ -addition system, the relation between the viscosity and the conductivity was examined. And moreover, the viscosity coefficient was estimated

from the measured conductivity using Eq. (3). The results obtained are as follows:

(1) The relation, $\eta \cdot \kappa \doteq \text{const.}$, is valid in the same composition slag.

(2) In CaO-SiO₂-Al₂O₃ system, the Al₂O₃ contents and the ratio of CaO and SiO₂ mainly control the properties of slag. The ratio of the activation energy for viscous flow and for conduction is about 1.37.

(3) In [CaO(43)-SiO₂(43)-Al₂O₃(14)]-oxide (FeO, MnO, MgO, V₂O₅, Cr₂O₃, P₂O₅, TiO₂) system, the ratio of E_η/E_κ is about 1.76, but in the slag containing Cr₂O₃ or V₂O₅ the ratio is different and they indicated the extraordinary influence on slag structure.

(4) In the quaternary system containing fluoride (NaF, CaF₂, MgF₂, AlF₃), the electronic conduction seems to be involved in determining the ratio.

(5) The introduction of the equation, $\log \eta = a + b \cdot \log \kappa$, enables to convert the viscosity coefficient to the conductivity, in the same composition range.

(6) In this slag composition range, the coefficients a and b are presented as follows.

In ternary system, $a = (1/2) \cdot N_{\text{Al}_2\text{O}_3}$, $b = -[1.37 + 2(N_{\text{SiO}_2} - N_{\text{CaO}})]$

In quaternary system (oxide addition),

$$a = (1/2) \cdot N_{\text{Al}_2\text{O}_3} \pm N$$

$$b = -[1.76 + 2(\Sigma N_{\text{former}} - \Sigma N_{\text{modifier}})]$$

In quaternary system (fluoride addition),

$$a = (1/2) \cdot N_{\text{Al}_2\text{O}_3} - N_{\text{fluoride}}$$

$$b = -[1.06 + 2(N_{\text{SiO}_2} - \Sigma N_{\text{modifier}})]$$

REFERENCES

- 1) J. O'M. Bockris and B. E. Conway: Modern Aspects of Electrochemistry, (1954), F. C. Tompkins ed.
- 2) Ariyama *et al.*: Kaimen-Gensho-Koshi-Kekkan (Bussei-Butsurigaku Koza 10), (1959), Kyoritsu Shuppan, Tokyo.
- 3) I. Oshida: Ekitai-no-Denki Bussei, (1964), Maki-Shoten, Tokyo.
- 4) M. Kato and S. Minowa: *Tetsu-to-Hagané*, **51** (1965), 1849; **52** (1966), 582; 584; 586.
- 5) M. Kato and S. Minowa: *Tetsu-to-Hagané*, **52** (1966), 580; **52** (1966), 1436; 1438; 1441.
- 6) Electrochemical Soc. Japan: Denki-Kagaku Binran, (1953), 219, Maruzen, Tokyo.
- 7) P. Kozakevitch: Phys. Chem. Process Metallurgy, 1, International Symposium Pittsburgh, (1959), 97, Interscience publishers, New York.
- 8) J. F. Elliot, M. Gleiser, and V. Ramakrishna: Thermochemistry for Steelmaking, (1963), 300-304; 682, Addison-Wesley Pub. Co. Inc., Mass.
- 9) P. Kozakevitch: *Rev. Mét.*, **51** (1954), 569.
- 10) Soc. Chem. Eng. Japan: Bussei-Josu 3-shu, (1965), 369, Maruzen, Tokyo.
- 11) M. Kato and S. Minowa: *Trans., ISIJ*, **9** (1969), 31; 39, (in this issue).