TECHNICAL PAPERS*

THE ELECTRICAL CONDUCTIVITY OF SEVERAL FUNDAMENTAL SLAGS IN MOLTEN STATE**

*Kazumi Mori*** & Yukio Matsushita*****

I. Introduction

Hitherto the slag-metal interface-reactions had been interpreted on the basis of the molecular theory stating that molten slags consist of free or associated molecules. However this slag model was no more than a hypothesis, and had not yet shown an insight into the real construction of molten slags. In order to develop the theory of the slag-metal interface-reactions, it was at first necessary to understand the true characteristics of molten slags, which might be considered to be dissociated into ions. Recently the problem of ionic dissociation of molten slags had much attracted metallurgists' attention, and both the electrical conductivity and the electromotive force had been measured.¹⁾⁻⁵⁾ Since the systematic studies on the ionic construction of molten slags had been never sufficient, the authors measured the electrical conductivity of several fundamental slags, and consequently discussed the general constitution of molten slags, in particular consideration of the behaviours of the individual constituent.

II. Procedures of Measurement of Electrical Conductivity

The measurements of the electrical conductivity were carried out on the binary silicate slags $\text{Na}_2\text{O-SiO}_2$, CaO-SiO_2 , MnO-SiO_2 and FeO-SiO_2 , and besides on the ternary FeO-MnO-SiO_2 slags and moreover the binary $\text{CaO-Al}_2\text{O}_3$ slags. The procedures of the measurement were somewhat different corresponding to the binary or ternary systems aforementioned. Slags of the system $\text{Na}_2\text{O-SiO}_2$ were heated in a compact alundum crucible, and those of the systems CaO-SiO_2 , MnO-SiO_2 and $\text{CaO-Al}_2\text{O}_3$ in a graphite crucible. For the systems FeO-SiO_2 and FeO-MnO-SiO_2 an iron crucible itself functioned as the one electrode, while the other made of a pure iron

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*** Assistant Professor, Department of Metallurgy, Faculty of Engineering, Ibaragi University.

**** Assistant Professor, Department No. 4, The Institute of Industrial Science, University of Tokyo.

Fig. 1. Circuit for Measuring Electrical Conductivity of Molten Slags.

ments so as to avoid the oxidation of iron electrodes.

The resistance was measured making use of an alternating current-bridge method. The measurement circuit is illustrated in Fig. 1. The specific electrical conductivity could be determined according to the following equations,

$$\kappa = C/(R - R_i) \quad \dots\dots\dots (1)$$

where R is the measured total resistance, R_i is the resultant resistance of lead wires and electrodes and C is a cell constant. The C was obtained at room temperature by an aqueous solution of $N/10$ potassium chloride.

rod being immersed into the slag melt. For the systems $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{MnO}-\text{SiO}_2$ were again used the pairs of pure iron electrodes, but on the other hand, of which were taken place by the graphite electrodes for the systems $\text{CaO}-\text{SiO}_2$ and $\text{CaO}-\text{Al}_2\text{O}_3$. The experimental furnace was of a Tammann-type, except for the system $\text{Na}_2\text{O}-\text{SiO}_2$, whose slags were heated using an Elema-furnace. Temperature was indicated by a $\text{Pt}-\text{Pt} \cdot \text{Rh}$ thermocouple for the system $\text{Na}_2\text{O}-\text{SiO}_2$, but for the other systems an optical pyrometer corrected for the emissivity was selected. The constituents Na_2O , CaO and MnO were prepared from their own carbonates respectively and FeO only from oxalate, and besides SiO_2 and Al_2O_3 were made of the extra pure powders. The reading of the total resistance were recorded by temperature falls. For the system $\text{Na}_2\text{O}-\text{SiO}_2$ a nitrogen gas was constantly passed throughout the measure-

III. Results and Discussions

The specific electrical conductivity rose with increase of temperature, and this fact was characteristic of ionic conduction. In the systems MnO-SiO_2 , FeO-SiO_2 and FeO-MnO-SiO_2 the conductivities suddenly decreased in the neighbourhood of the solidifying temperature. This was due to the rapid rate of crystallization. Like the other authors' description, it was established that molten slags were highly ionized. Although the present data obtained never stated positively how much extent molten slags are ionized to, they might be favourably interpreted assuming complete ionization. The natural logarithm of the specific electrical conductivity ($\kappa : \Omega^{-1} \cdot \text{cm}^{-1}$) was linear, when it was plotted against the reciprocal of the absolute temperature ($T : ^\circ\text{K}$); namely the following equation was established,

$$\ln \kappa = Q/RT + B \dots\dots\dots (2)$$

where Q is the energy of activation, B is a constant independent of temperature and R is gas constant. The eq. (2) could be introduced theoretically on the basis of the theory of rate processes, and on the supposition that molten slags are completely ionized and all of the ions of but one sort take part in conduction.

The energy of activation of the system $\text{Na}_2\text{O-SiO}_2$ was somewhat small and of the order of 8~15 kcal/g-mol, and that of the system $\text{CaO-Al}_2\text{O}_3$ was the highest among the present systems and of the order of 25~47 Kcal/g-mol. The activation energy of viscosity was higher than that of conductivity; for instance 2~5 times as large as the latter for the system $\text{Na}_2\text{O-SiO}_2$ and 1.5~2 times for the system CaO-SiO_2 .^{(6), (7)} Accordingly it was evidenced that viscosity was mainly controlled by the ions of lower mobility and others conduction by those of higher mobility.

Fig. 2 illustrates the specific electrical conductivity of binary silicate slag systems, and Fig. 3 the conductivity and the energy of activation of the system $\text{CaO-Al}_2\text{O}_3$. In all of the systems the conductivity rose with increase of basic oxides at the constant temperature. Acidic oxides formed large size of negative ions of low mobility, and on the other hand basic oxides produced cations of high mobility, the latter controlling mainly the electrical conductivity. Additionally the experiments of electrolysis were carried out in the systems

Fig. 2. Electrical Conductivity of Binary Silicate Slags.

Fig. 3. Electrical Conductivity and Energy of Activation.
(CaO—Al₂O₃ System)

CaO-SiO₂ the rate of the rise of the conductivity with increase of CaO decreased beyond 50 mol %, agreeing with the results obtained by Bockris etc.⁽³⁾ (cf. Fig. 2). For the system Na₂O-SiO₂ the electrical conductivity (μ) equivalent to one gram-mole Na₂O rose from 392 at Na₂O 22.5 wt. % to 87.2 at Na₂O 50.3 wt. %.* It was apparent from these calculations that the mobility of Na⁺ became large with increase of Na₂O. In the system CaO-SiO₂ the increase of the mobility of Ca⁺⁺ with CaO decreased beyond 50 mol %, where the strong bonds were formed between Ca⁺⁺ and SiO₄.⁴

The plots $\log \kappa$ vs. $1/T$ of the system FeO-SiO₂ consisted of two straight lines, except for the composition near Fayalite, which suggested that the kinds of ions playing an important role in conduction were never but one. The energy of activation at higher temperatures was 1.5~2 times as large as that of at lower temperatures. Such intimate fact that near the composition of Fayalite the relationship between $\log \kappa$ and $1/T$ could be expressed by only one straight line and an abnormal change occurred in the viscosity-concentration curve⁽⁶⁾ indicated the formation of the characteristic constitution in molten state. The same characteristics as aforementioned appeared also in the system CaO-Al₂O₃. In the conductivity-concentration curve of this system a maximum value appeared at the composition corresponding to 5CaO · 3Al₂O₃, by which both the energy of activation Q and the constant B were divided into two groups (cf. Fig. 3). The same behaviours of Q and B were found in the system P₂O₅-SiO₂.⁽⁴⁾ Recently

CaO-SiO₂ and FeO-SiO₂. It was apparent that there existed appreciable differences of concentrations between near the part of anode and near that of cathode, and the concentration of CaO or FeO was higher near the cathode than near the anode, the results of which indicated that cations migrated to the cathode.

The fact that the electrical conductivity rose with increase of basic oxides was partly due to the increase of the number of cations. Further it was also controlled by the mobility of cations, and corresponding to this it was presumably expected for the conductivity-concentration curves to take various forms. For example, the conductivity of the systems Na₂O-SiO₂ and FeO-SiO₂ rose approximately linearly with increase of basic oxide mol %, but against these in the system

* $\mu = \kappa M/wd$, where M is the molecular weight of Na₂O, d is the density⁽⁶⁾ of the melt and w is a weight-percentage of Na₂O divided by 100.

Saito and Kawai⁽⁹⁾ reported on the viscosity of the system $\text{CaO-Al}_2\text{O}_3$, and the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ remained also even in molten state.

In the system FeO-MnO-SiO_2 , generally speaking, the conductivity decreased with increase of SiO_2 mol %. When MnO was substituted for FeO , the conductivity decreased slightly, except for high SiO_2 contents, where such degree of decreasing was more or less appreciable.

IV. Constitution of Molten Slags

For the purpose of studying the behaviours of the individual metallic oxide in molten slags, the electrical conductivity of the system sodium silicate-metallic oxides was measured. Samples were heated in an alundum crucible, an Elema-furnace being used in the systems containing FeO and MnO , samples were heated in the nitrogen atmosphere so as to avoid the oxidation as possible. Pure iron rods were used for electrodes. During measurements the oxidation of iron electrodes was suppressed by passing nitrogen gas. Temperature was measured by a Pt-Pt-Rh thermocouple. The concentration of the fundamental sodium silicate was Na_2O 32.45 mol % and SiO_2 67.55 mol %. Fig. 4 shows the specific electrical conductivity of the systems sodium silicate-metallic oxides at $1,200^\circ\text{C}$. When the added oxides were acidic, the concentration of mobile Na^+ decreased, the electrical conductivity being made lower than that of the fundamental system.

Fig. 4. Effect of Various Oxides on Specific Electrical Conductivity of Sodium Silicate.

Fig. 5. Relation Between Specific Electrical Conductivity and ϵ_M . (Sodium Silicate-Basic Oxide System)

On the other hand, if basic oxides were added, the concentration of mobile cations increased, resulting in the rise of the conductivity (except for CaO).

It was found that the ability of the added basic oxides to rise the electrical conductivity of sodium silicate decreased in the order of NiO , FeO , MgO , MnO , and CaO . This order was the same as the order of the radii of cations of the added basic oxides, except for Mg^{++} , and also as the order of ϵ_M (thermal energy per g-mol evolved when a solid oxide was formed from 1 g-atom metallic ion

and O^{--} equivalent to the former, both in the gaseous state) obtained by Huggins and Sun⁽¹⁰⁾ as illustrated in Fig. 5. ϵ_M was by definition the strength of the bond between metallic ion and oxygen ion, that is, the strength as the "base" of a metallic oxide. Hence the weaker was the "basic" strength of added oxides, the higher was the electrical conductivity. The cations tended to attract the oxygen ions of SiO_4 -tetrahedra, competing with the central Si^{4+} in tetrahedra, therefore it resulted in the reduction of the stability of bonds Si-O. The larger became the strength of bonds between cations and oxygen ions, the more decreased the stability of bonds Si-O, hence the more easily cations could move, resulting in the rise of conductivity.

The radii and valences of cations, which which were intimately connected with the strength of bonds between cations and oxygen ions, controlled the bonding strength between cations and SiO_4 -tetrahedra, or, in other words, determined the form of the SiO_4 -tetrahedra. Consequently the physico-chemical properties of molten slags might be properly explained in terms of those characteristic values of cations. In fact the viscosity of monosilicates decreased in the order of $CaO \cdot SiO_2$ ⁽⁷⁾, $MnO \cdot SiO_2$ ⁽¹¹⁾ and $FeO \cdot SiO_2$ ⁽⁸⁾, corresponding to the order of ionic radii of cations (by Goldschmidt)— $Ca^{++}(1.06 \text{ \AA}) > Mn^{++}(0.91 \text{ \AA}) > Fe^{++}(0.83 \text{ \AA})$. The orders of activities of SiO_2 and of the solubility curves of SiO_2 ^{(12), (13)} in several binary silicate melts were the same as the order of the bonding strength between oxygen ions and metallic cations.

V. Summary

The electrical conductivities of several binary and ternary fundamental slags were measured and discussed. The specific electrical conductivities were in general of the order of $0.1 \sim 1 \Omega^{-1} \cdot \text{cm}^{-1}$, and increased with temperature and with the concentrations of basic oxides added. The mechanism of conduction was mainly controlled by cations such as Na^+ , Ca^{++} , Mn^{++} and Fe^{++} etc. The characteristic constitution of molten slags corresponding to the compound Fayalite and $5CaO \cdot 3Al_2O_3$ was suggested. Being accompanied by the changes of mobility of cations with their concentrations, the conductivity-composition curves was expected to realize some marked features. Some intimate correlations existed between the physico-chemical properties of molten slags and the bonding strength, with which cations and oxygen ions interacted each other.

In this paper the experimental data of the electrical conductivities were discussed on the basis of an approximate model of molten slags. In studying the properties of molten slags, the most reliable way was presumably the method of statistical thermodynamics with consideration of the attraction between cations and anions. In Japan such investigation has just been started.⁽¹⁴⁾

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RESERCHES ON SPECIAL CAST STEELS

Hideo Mikashima, Dr. Eng.

The author investigated macro- and micro-structure of ten series of special cast steels, namely, Cr-Mo steels containing Si, Ni, or Ni and Mn as additional elements, Mn-Si steels containing Cr or W, and Cr-Mn-Si steels containing W, V, Ti, or Ti and Al. The change in structures and mechanical properties caused by normalizing and by the additional elements was also investigated.

I. The Structures of Special Cast Steels

To examine the macro-and micro-structure, the above mentioned steels were cast 45×60×100 mm in sand moulds. The macro-structure in the section were classified into three groups, i.e., a net-work structure, a fine structure and a cover dendritic structure. The range of chemical composition in which they appeared was tabulated in Tables I—III.

Table I. Elements which revealed a net work structure

Steel Series	Base Steel	1.0 Cr, 0.25 Mo		0.9 Mn, 0.6 Si	1.0 Cr, 1.0 Mn, 0.6 Si
	Additional Elements	0.3~3.0 Si	0~3.0 Ni	0.4~2.1 W	0.8~2.1 W
Conditions for Appearance of Net-Work Structure		4 C+Si<1.9	0.20~0.30 C, 3.0 Ni or 0.17~0.19 C, 2.0 Ni	0.19~0.22 C, 1.5~2.0 W	0.19~0.25 C, 1.0~2.1 W

* Kyūshū Institute of Technology.