Basic Studies for Steelmaking by Physical Methods

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Some examples of basic studies related to steelmaking by physical methods, which have been carried out by the author and his group, are described on the estimation of some physical properties of liquid metals, a new concept of network parameter for slags and fluxes and a new viscosity measurement for metallurgical melts.

KEY WORDS: steelmaking; viscosity; diffusivity; network structure; slag; flux.

1. Introduction

A number of studies have been made to obtain fundamental information on metallurgical substances and their reactions related to steelmaking by means such as thermodynamics, kinetics, transport phenomena, fluid dynamics and mathematical modelling. However, those concerned with the physical properties of melts and their application are relatively few in spite of their practical importance.

The author has been concerned with some basic studies on physical and chemical properties of liquid metals and slags related to steelmaking for some years. In this paper examples will be given concerning (1) the estimation of some physical properties of liquid metals by model theory, (2) a new concept of “network parameter” for slags and fluxes and (3) a new measuring technique for the viscosity of metallurgical melts. Their application to industrial practice will also be described.

2. Estimation of Physical Properties of Liquid Metals Using Model Theory

To obtain reliable information on physical and chemical properties, generally, it is essential to determine their accurate values by precise measurements. The measuring techniques have progressed remarkably and the accuracy of the measured values has obviously been improving. Nevertheless considerable discrepancies still exist in the data measured by each investigator at present as a result of experimental uncertainty. As an example, Fig. 1 shows the viscosity of liquid iron as a function of temperature, which is important for process analysis in steelmaking,¹⁾ but it is very difficult to find out the most reliable value of the viscosity from the data in this figure.

In such a case it would be helpful to us in the course of the process analysis if we could estimate reliable values of physical properties of steel and slags theoretically or phenomenologically without undertaking experiments. Based on this concept the author and his colleagues have

derived some simple formulae describing some physical properties of liquid metals and alloys. In this paper viscosity and diffusivity of liquid iron and some iron based alloys calculated using these formula are introduced.

2.1. Estimation of Viscosity for Liquid Steel

Assuming that the mechanism of viscosity of liquid

Fig. 1. Viscosity of liquid iron as a function of temperature.

○: Measured by Morita and Iida.⁵⁾

△: Calculated using Eq. (1).

Identification numbers are: (1) Arsentiev *et al.*, (2) Barfield and Kitchener, (3) Nobohatskii *et al.*, (4) Romanov and Kochegarov, (5) Samarin, (6), (7) Ogino *et al.*, (8) Nakanishi *et al.*, (9) Vatolin *et al.*, (10) Froberg and Cakici, (11) Cavalier, (12) Saito and Watanabe, (13) Lucas, (14) Kawai *et al.*, (15) Thiele, (16) Avaliani *et al.*, (17) Wen Li-shi and Arsentiev, (18) Schenck *et al.*, (19) Froberg and Weber, (20) Narita and Onoe, (21) Krieger and Trenkler. (after Morita and Iida⁵⁾).

metals is based on the momentum transfer to make the mass velocity uniform, the following expression has been derived for the viscosity of liquid pure metals^{2,3)}

$$\eta \approx 4.5g(r_m)(1 - r_0/r_m) \frac{v_0 P(T)_m}{a} \dots\dots\dots (1)$$

$$P(T) = 1 - \int_w^\infty \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{W^2}{2}\right) dw,$$

$$W = \frac{\sqrt{3}}{2} \left(\frac{T_b - T}{T} \right)$$

where, η : viscosity of liquid,
 $g(r)$: pair correlation function,
 r_m, r_0 : the position of first peak and its left-hand edge in the $g(r)$ curve,
 v_0 : constant corresponding to the frequency of oscillation when no net displacement of the oscillating atom takes place,
 a : average interatomic distance,
 $P(T)$: probability function, and
 T_b : boiling point.

Table 1 shows a comparison of calculated and observed values of viscosity of 19 kinds of liquid pure metals at their melting points, where η_{cal}^a is the calculated viscosity by Eq. (1), η_{cal}^b that by using Andrade's empirical equation⁴⁾ which has been a representative expression of viscosity near the melting point, and η_{obs} observed viscosity.

It is obvious that calculated values using Eq. (1) are much closer to the observed values than the values calculated by Andrade's equation, and this fact shows that Eq. (1) can be effectively used to estimate the viscosity of liquid pure metals. The calculated values of viscosity for liquid iron by Eq. (1) are also shown in **Fig. 1** with the measured values by the author's group.⁵⁾ The calculated values are a little lower than the author's measured values. Nevertheless this seems satisfactory

Table 1. Comparison of calculated and observed values for viscosity of liquid metals at their melting points.

Metal	Viscosity (mPa s)		
	η_{cal}^a	η_{cal}^b	η_{obs}
Na	0.68	0.62	0.70
Mg	1.22	1.39	1.25
Al	1.90	1.79	1.2-4.2
K	0.50	0.50	0.54
Fe	6.37	4.55	6.92
Co	5.93	4.76	4.1-5.3
Ni	5.64	4.76	4.5-6.4
Cu	4.07	4.20	4.34
Zn	2.65	2.63	3.50
Ga	2.00	1.63	1.94
Ag	3.53	4.07	4.28
Ln	1.97	1.97	1.80
Sn	2.04	2.11	1.81
Sb	2.23	2.68	1.43
Au	5.50	5.80	5.38
Hg	2.31	2.06	2.04
Tl	2.55	2.85	2.64
Pb	2.52	2.78	2.61
Bi	2.13	2.54	1.63

considering the uncertainty and discrepancy of the data reported by previous investigators.

On the other hand, the author and a colleague have derived another expression describing the viscosity of monoatomic liquids, such as metals, in terms of simple physical quantities by modifying Andrade's equation, as follows²⁾:

$$\eta = 1.8 \times 10^{-7} \frac{(MT_m)^{1/2}}{V_m^{2/3}} \cdot \frac{\exp(H_\eta/RT)}{\exp(H_\eta/RT_m)} \quad (\text{in SI unit}) \dots\dots\dots (2)$$

where, M : atomic weight, and

V_m : molar volume at melting point.

The calculated values by this equation agree well with measured values for metals whose melting points are rather low, but not with those for metals having higher melting points.

It would be helpful if those concerned with steelmaking practice could estimate the probable values of viscosity for molten steel and slags by simple calculations. From this standpoint the author and his colleague further derived some formulae expressing viscosity of liquid alloys.^{3,6,8)} The details of these formulae are omitted here because of space limitation. The calculated viscosity of liquid Fe-C alloy, as an example, is compared with the experimental data in **Fig. 2** and it is obvious the calculated result seems consistent with the experimental ones.

The viscosity of a multi-component dilute alloy, such as steel, η , can be evaluated by the following equation which can also be theoretically valid.²⁾

$$\eta = \eta_M + \sum_i \Delta\eta_i \dots\dots\dots (3)$$

where, η_M : viscosity of liquid pure metal M, and

$\Delta\eta_i$: change of viscosity due to component i in liquid M- i dilute binary alloy.

These expressions can be applied to estimate the viscosity of liquid steel. After a series of studies by the author's group, new formulae estimating the vis-

Fig. 2. Viscosities of liquid Fe-C alloys at 1823 K.

○ measured by Morita and Iida⁵⁾

----- calculated by Iida and Morita²⁾

— calculated by Hirai⁸⁾

① Arsentiev *et al.*, ② Vostryakov *et al.*, ③ Turovskii, Lyubimov, ④ Krieger, Trenkler, ⑤ Lucas, ⑥ Barfield, Kitchener, ⑦ Vatin *et al.*, ⑧ Krashennnikov, Filippov, ⑨ Wen Li-shi, Arsentiev.

Table 2. Comparison of calculated and observed values of solute diffusivity in liquid iron at 1873 K.

Solute	Calculated $\times 10^9 \text{ m}^2 \text{ s}^{-1}$	Observed $\times 10^9 \text{ m}^2 \text{ s}^{-1}$
C	4.8	4.0–20
Si	6.0	2.5–12
Mn	4.6	3.5–20
P	7.4	2.5
S	8.7	4.5–20
O	8.5	2.5–20
H	150	80–200
N	12	6–20
Ni	4.2	4.5–5.6
Co	4.2	3.5–5.0
Cr	4.3	3.0–5.0
Al	8.6	10
V	4.4	4.0–5.0
Mo	2.6	3.8–4.1

cosity of liquid metals and ionic melts were proposed by Hirai⁸⁾ and Du Sichen *et al.*⁹⁾ Their formulae are also useful in estimating the viscosity of metallurgical melts.

2.2. Estimation of Solute Diffusivity for Liquid Steel

It is known that there is a close relation between viscosity and diffusivity.¹⁰⁾ This suggests that it may be possible to estimate the probable value of diffusivity when the viscosity value is definite. Based on this idea, we derived some formulae expressing self and solute diffusivity of liquid metals and alloys.²⁾ The calculated values of diffusivity of various solute elements in liquid iron at 1873 K are compared with their measured values in Table 2, and it is obvious that the calculated values are consistent with the measured ones.

3. Network Parameter for Slags and Fluxes

Since some kinds of liquid slags and fluxes have a so-called network structure their viscosity values will be higher than those for hypothetical melts of the same composition but without a network structure. This is due to the structure having a mass effect on the viscosity as a flow unit. Consequently we defined a “network parameter ψ ” which can reflect the magnitude of this network structure of slags and fluxes quantitatively¹¹⁾:

$$\psi = \log \left(\frac{\eta}{\eta_0} \right)^2 \approx \log \frac{M^*}{M} \dots \dots \dots (4)$$

where η is the viscosity of melts experimentally obtained, η_0 is the viscosity of hypothetical melts having no network structure which can be calculated by Eq. (2). M and M^* are the mass of flow unit respecting with and without network structure. Therefore when η is known we can determine the value of ψ by Eq. (4). Then, we investigated the network parameter of some slags related to steelmaking, and found that rather simple relations would exist between the network parameter and the lattice energy, the optical basicity and the sulphide capacity of slags, as shown in Figs. 3, 4 and 5.

Fig. 3. Relationship between network parameter and lattice energy for molten slags at 1773 K.
 ○ CaO–SiO₂, △ CaO–MgO–SiO₂, □ Al₂O₃–MgO–SiO₂

Fig. 4. Relationship between network parameter and optical basicity for molten slags at 1773 K.
 ○ CaO–SiO₂, ● CaO–Al₂O₃–SiO₂, × SiO₂–BaO

Fig. 5. Relationship between network parameter and sulphide capacity for molten slags at 1773 K.
 ○ CaO–SiO₂, ● CaO–Al₂O₃–SiO₂, ■ CaO–MnO–SiO₂, ▲ CaO–Al₂O₃–SiO₂–MgO

4. Oscillating-plate Viscometer

The author and his group developed an oscillating-plate viscometer to measure the viscosity of high temperature melts instantaneously and continuously.^{12–14)} Figure 6 shows a schematic diagram of an oscillating-plate viscometer originally made by the author's group.

Fig. 6. Schematic diagram of an oscillating-plate viscometer.

 Fig. 7. Variation of $\log(\rho\eta)$ with temperature.

The viscosity measurement is based on the principle that when a plate is sinusoidally oscillated in a liquid the amplitude of the oscillating plate changes depending on the viscosity of the liquid, and the viscosity can be determined by the following equation.

$$\rho\eta = k \left(\frac{E_a}{E} - 1 \right)^2 \quad \dots\dots\dots (5)$$

where ρ is the density of melt, η is the viscosity of melt, E_a and E are the amplitude of oscillating-plate in the air and in the melt, respectively, and k is the instrumental constant determined experimentally.

It has become possible to detect rapidly and continuously the change of viscosity of melts undergoing chemical reaction using this viscometer. This instrument can be used for both academic measurements of viscosities on a laboratory scale and plant scale measurements of viscosities of mold powders used in continuous casting and slags or fluxes in the steelmaking practice. Figure 7 shows an example of the measured values of viscosity for mold flux¹⁵⁾ in which the viscosity and the solidification temperature are measured instantaneously. These values provide us useful information for the continuous casting operation.

5. Summary

Examples of studies related to steelmaking by physical methods were given concerning the estimation of viscosity and diffusivity of liquid metals, the new concept of "network parameter" for slags and fluxes, and the new oscillating plate viscometry for metallurgical melts.

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