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An Approach to Viscosity Calculations of Molten Iron and Its Dilute Binary Alloys[†]

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Abstract

Accurate theoretical values of viscosities are not available at present. Therefore, in this paper we propose an approach to viscosity calculations of liquid metals and dilute binary alloys.

Using the expression for liquid metals which has been derived by one of the authors, the calculated value of viscosity for molten iron at 1600°C is equal to 4.7 cP.

From the expression and experimental data, we present an attempt to calculate viscosities of dilute binary alloys from simple parameters. That is, viscosities of dilute iron-based binary alloys are approximately proportional to the square root of the product of atomic weight and melting point (°K), $(MT_m)^{\frac{1}{2}}$ of alloying elements.

Viscosities of molten iron due to one atomic pecent of various alloying elements at 1600°C are expressed as follows:

$$\eta_{\mathrm{Fe \cdot dil}} \approx \eta_{\mathrm{Fe}} + K[(MT_m)_X^{\frac{1}{2}} - (MT_m)_{\mathrm{Fe}}^{\frac{1}{2}}]$$

where, $K \approx 3.5 \times 10^{-5}$ (from experimental data).

We have obtained same relation for liquid mercury and its dilute amalgams as well.

Consequently, if the value K is obtained experimentally, the approximate values for viscosities of dilute alloys can be estimated.

1. Introduction

Viscosity of liquid metals and alloys is of interest as a physical quantity in non-equilibrium state as well as diffusion and thermal conduction. It is so not only from practical aspects but from the fundamental point of view. In particular, viscosity of dilute alloys is quite important as the data which are used for practical operations and the clue for theretical treatment of the viscosity of liquid alloys. Especially, experimental and theoretical studies on the viscosity of molten iron and its dilute, alloys are desired. Neverthless, few systematic studies have been made on this subject.[1,2]

Born and Green[3], and kirkwood and coworkers[4] have derived the expressions of viscosity of liquid as a function of intermolecular forces (potential) and pair correlation function based on statistical mechanical theory. At the present stage of statistical mechanics in regard to liquid, however, little is known about the molecular forces between same or foreigin molecules (atoms), and furthermole the mathematical treatment of their expressions is considerably complicated. It is, therefore, very difficult to apply these expressions in practice.

Though the strictness of physical treatments is sacrificed to a certain extent, it would be useful that viscosities of many liquid metals and dilute alloys can be estimated by simple expressions, from the partical standpoint.

In this paper, at first, the viscosity of pure molten iron at 1600°C was calculated from the expression which has been derived previously by one of the authors, and compared the values observed experimentally by a number of workers. Then, using the expression, an approach to viscosity calculations of dilute binary alloys has been proposed, and an expression for viscosities of molten iron with one atomic percent of various alloying elements at 1600°C was obtained with simple physical quantities.

2. Viscosity Calculation of Pure Molten Iron

Recently, we have discussed viscosity of liquid metals and have derived an expression within the following assumptions. All atoms in liquid state are regarded as equivalent harmonic oscillators · with the same frequency and momentum is transfered between the nearest neighbour atoms in adjacent layers. The expression[5] is given by:

$$\eta = \frac{4}{3} \nu P(T) m \rho^2 \int_0^a g(r) r^4 dr \tag{1}$$

and

$$P(T) = 1 - \int_{T \geq \alpha T_b} \sqrt{\frac{3}{8\pi}} \exp\left[-\frac{3}{8}\left(\frac{\alpha T_b}{T} - 1\right)^2\right] d\left(\frac{\alpha T_b}{T} - 1\right) \tag{2}$$

where, ν vibrational frequency of an atom in liquid state.

P(T): factor representing the probability which an atom in a state of vibration can stay at any position, that is, the life time of vibration.

m: atomic mass

ρ: average number of atoms per unit volume (number density)

g(r): radial distribution function (pair correlation function)

a: upper of the first peak in g(r)

T_b: boiling point (°K)

α: factor concerned with the energy needed to be able to move freely from a vibrating state to another site by translational motion (at the melting point, $\alpha \doteqdot 1 \sim 1.5$)

Now, we will calculate the viscosity of pure molten iron at 1600°C. At present, the characteristic frequency of vibration of liquid state is not estimated theoretically, therefore, to first approximation, Lindemann's formular[6] is used. The formular is:

$$\nu_m = C \sqrt{\frac{T_m}{M V_m^{\frac{2}{3}}}} \qquad (3)$$

where, ν_m is the fundamental frequency in solid state at the melting point, c is constant $(2.8 \times 10^{12} \sim 3.1 \times 10^{12})$, T_m is the melting point (°K), M the atomic weight and V_m the volume of a gram-atom at temperature T_m.

The calculated value of ν_m from the equation (3) is equal to 7.95×10^{12} (sec^{-1}). Value for the density of molten iron at 1600°C is from Lucas[7]: 6.94 (g.cm^{-3}). Atomic mass, m, is equal to 9.28×10^{-23} (g), and number density, is equal to 7.48×10^{22} (number). The integration concerned with radial distribution function: $\int_0^a g(r) r^4 dr$ could be done by following assumption. In our phenomenological theory, the radial distribution function is introduced as a measure to estimate the number of atoms participating in the momentum transfer between the nearest neighbour atoms (the coordination numbers of atoms). By considering nearest neighbour interactions, this concept is useful in making a first order approximation to the macroscopic behaviour of liquid such as viscosity. But it is not yet well-defined how the area under the first peak of atomic radial distribution function is designated. In present work, the coordination numbers of atoms have been estimated by the method as shown in **Fig. 1.** That is, a corresponds to the first minimum on the right hand side of the first peak in g(r). This method is considered the best mathematical one. The result of the integration is equal to 9.72×10^{-39} (cm^5). The observed value for the radial
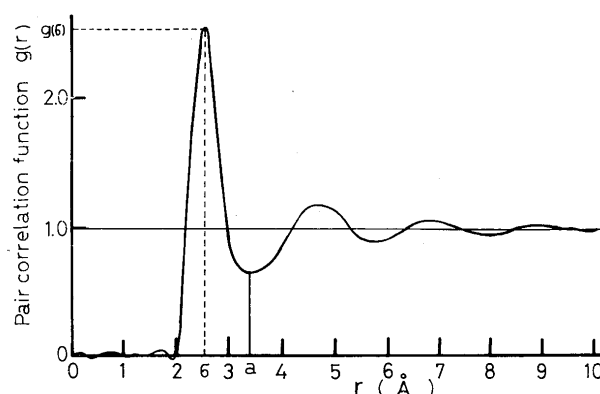

Fig. 1. Pair correlation function of molten iron at 1620°C (see Ref. 8).

distribution function of molten iron at 1620°C is from Waseda and Suzuki[8].

When the vibrating frequency of atoms is estimated from the Lindemann's formaular, p(T)<1 is resonable, because the strength of the interaction between atoms in solid state is stronger than in liquid state. When the vibrational frequency of atoms in liquid is calculated by the Limdemann's formular, P(T) is equal to $0.8 \sim 1$ for alkali metals, tin, lead and and other metals. That is, if the frequency of atoms is determined from the Limdemann's formular and P(T) is equal to $0.8 \sim 1$, the calculated values of viscosity of liquid metals at the melting point are in good agreement with experimental data.

Now, when P(T) is equal to 0.9 for molten iron at the melting point, 1.4 is obtained for the factor α from the equation (2), and P(T) is equal to 0.88 at 1600°C. From those results, the calculated value of visicosity for molten iron at 1600°C is equal to 4.7 cP. The calculated value is equal to 5.3cP, when P(T) is equal to 1 at 1600°C, and 4.3cP when P(T) is equal to 0.8, respectively. Viscosity of molten iron as determined by a number of workers and the calculated values are shown in **Fig. 2.**

3. An Approach to Viscosity Calculations of Dilute Bibary Alloys

From experimental data, for the majority of liquid metals, the integral term in the equation (1) can be expressed approximately in the following form:

$$\int_0^a g(r) r^4 dr \approx 0.35 g(\sigma) \sigma^5 \qquad (4)$$

where, σ is the averege interatomic distance. Furthermore, using a relationship $\rho \sim 1/\sigma^3$, the equation (1) is approximated by:

$$\eta \approx 0.47 \nu P(T) mg(\sigma) \cdot \frac{1}{\sigma} \qquad (5)$$

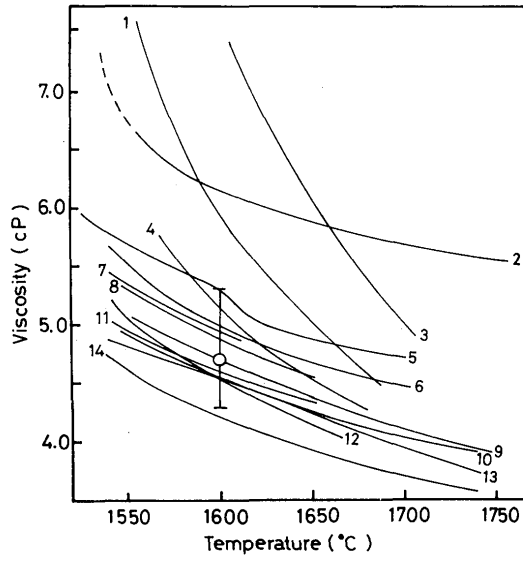and, using the Lindemann's formular for ν, we have

Fig. 2. Viscosity of molten iron as determined by a number of
workers and calculated value using the equation (1)
(1: vatolin et. al, 2: Barfield et al, 3: Samarin, 4: Wen Li-Shin
5: Adachi, Morita et al, 6: Saito and Nakanishi, 7: Frohberg,
8: Schenck et al, 9: Saito et al, 10: Cavalier, 11: Narita and
Onoe, 12: Kawai and Tuji, 13: Lucas, 14: Thile, Φ: calcu-
lated value).

$$\eta \approx \frac{0.47 CMT_m^{\frac{1}{2}} P(T) g(\sigma)}{NM^{\frac{1}{2}} V^{\frac{1}{3}} \sigma}$$

$$= j\{ \frac{P(T) g(\sigma)}{V^{\frac{2}{3}}} \} (MT_m)^{\frac{1}{2}} \qquad (6)$$

where, N is the Avogadro's number

$$j = \frac{0.47c}{N^{\frac{2}{3}}}, \quad \sigma \approx (\frac{V}{N})^{\frac{1}{3}}$$

(Though j is equal to 2×10^{-4} from the equation (6),
experimental values of viscosity for many liquid
metals agree well with the calculated values, when j is
equal to 2.5×10^{-4}).

It is needlness to say that viscosity is the dynamic
physical quantity in non-equilibrium state, therefore,
the thermodynamics deduced from the equilibrium
state cannot, obviously, be applied. However, if the
idea of partial molar quantity of thermodynamics is
allowed to use as an analogy in numerical treatment
for discussing viscosity of liquid binary alloys, the vis-
cosity of A-B binary liquid alloys which consists of
n_A at % of A-atom and n_B at % ·of B-atom may be
expressed in the following form:

$$\eta_{A-B} = \frac{1}{100} (n_A \eta_A^* + n_B \eta_B^*) \qquad (7)$$

where,

$$\eta_A^* \equiv (\frac{\partial \eta_{A-B}}{\partial n_A})_{n_B, T, P}; \quad \eta_B^* \equiv (\frac{\partial \eta_{A-B}}{\partial n_B})_{n_A, T, P}$$

Using the relationship $n_A + n_B = 100$, we have

$$\eta_{A-B} \equiv \eta_A^* + \frac{n_B}{100} (\eta_B^* - \eta_A^*) \qquad (8)$$

Now, let us consider the case that the concentration
of B-atom is extremely dilute. In such case, the state
of A-arom in the dilute solution may be regarded as
almost the same as that in the pure liquid which con-
sists only of A-atom. Then, we obtain

$$\eta_A^* \approx \eta_A \qquad (9)$$

where, η_A is viscosity of pure liquid metals which con-
sists only of A-atoms. Therefore, substituting η_A for
η_A^* in the equation (8) yields the following expression
for the viscosity of dilute binary alloys.

$$\eta_{A-B} = \eta_A + \frac{n_B}{100} (\eta_B^* - \eta_A) \qquad (10)$$

Now, let us consider the physical meanings of the ex-
pression (10). If B* is used to designate the atom in
liquid consists of B-atoms that are completely sur-
rounded by A-atoms and have the interaction with
them, η_B^* in the equation (10) is considered to be the
viscosity of pure liquid which consists only of B*-
atom, and is also given as the intercept at $n_A = 0$ of
the tangent to the curve of η_{A-B} at the infinite dilute
concentration of the component B as shown in **Fig. 3.**

Then, we may apply the above idea to the vis-
cosity of liquid binary alloys. As far as the binary
alloys containing several atomic percentages of solute
can be approximately regarded as dilute solution, the
viscosity of dilute binary alloys, thus, is given from
the equation (10) as follows:

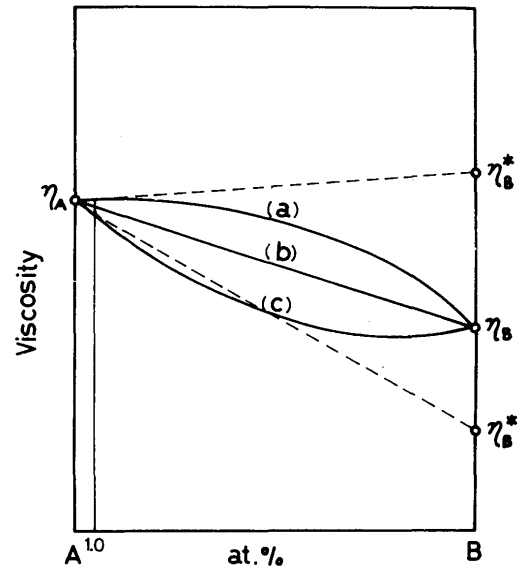$$\eta_{M-X} \approx \eta_M + \frac{n_X}{100} (\eta_X^* - \eta_M) \qquad (11)$$

Fig. 3. Shematic diagram illustrating partial viscosity in dilute A–B
binary solution. (--- Ideal dilute solution)

where, the subscripts M-X, M and X represent the dilute alloy, the base metal and the alloying elements respectively. Using our present expression (6), further the above equation may be rewritten in the following expression:

$$\eta_{M-X} \approx \eta_M + jn_X \left\{ \frac{P(T)g(\sigma)}{V^{2/3}} (MT_m)^{1/2} \right\}_{X*}$$

$$- \left\{ \frac{P(T)g(\sigma)}{V^{2/3}} (MT_m)^{1/2} \right\}_M$$

$$(12)$$

where, the subscript X^* represents the alloying elements whose atoms are completely surrounded by the base metal atoms.

In the equation (12), of the terms represented by the subscript X^*, $P(T)$, which is a function of boiling point, does not largely depend on it, and $g(\sigma)$ and $V^{2/3}$ may be supposed to be close to the value of base metal rather than that of alloying element by assuming their state described above. On the other hand, the vales of M and T_m would not probably be so different from that of the alloying element, even if the alloying element is placed on that state. (T_m in this paper reters to interatomic bond strength).

Thus, assuming inherent characteristic of alloying element can be expressed by the term $(MT_m)^{1/2}$, the term denoted by the subscript X^* is approximately represented as follows:

$$\left\{ \frac{P(T)g(\sigma)}{V^{2/3}} (MT_m)^{1/2} \right\}_{X*} \approx \left\{ \frac{P(T)g(\sigma)}{V^{2/3}} \right\}_M (MT_m)^{1/2}_X \quad (13)$$

However, as presently it is very difficult to treat strictly the above-mentioned relation from the theoretical point of view, we take this problem into consideration on the basis of experimental results. For an example, viscosities of iron-based dilute binary alloys (1 at %: at 1600°C [9]) which were determined by a number of workers, are plotted as a function of $(MT_m)^{1/2}$ in Fig. 4. Though discrepansies exist between observations of different workers, it is considered from the experimental results shown in Fig. 4 that the relation in the expression (13) can be expected to hold in these iron-based dilute alloy systems. Now, viscosities of molten iron and its alloys have been measured by the oscillational vessel method. This method of measuring viscosity has many practical advantages at elevated temperature, but there are mathematical difficulties in making the calculations, and a precise technique for viscosity measurements of liquid metal and alloys at high temperature has not been well established. Furthermore, the viscosity-standard liquid for liquid metals has not yet established. From these reasons, it is understandable that discrepancies exist between the data which have been reported.
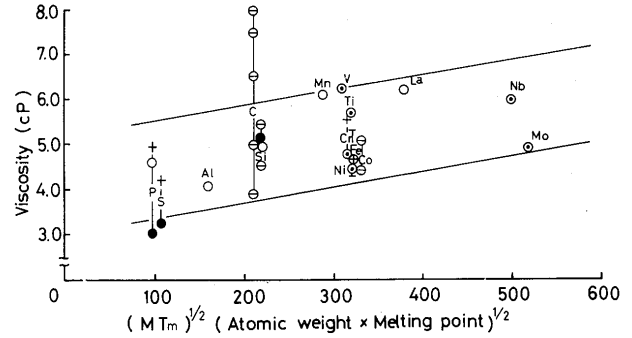

Fig. 4. Change in the viscosity of molten iron due to one atomic percent of various alloying elements at 1600°C.
($\oplus$: calculated value, $\bigcirc$: Romanov and Kochegarov, $\odot$: Narita and Onoe, $\bullet$: Suzuki and Maekawa, $+$: Vostryakov, vatolin and Yesin, $\ominus$: others)

Then the observed values by Romanov and Kochegarov[9],[10] and Suzuki and Maekawa[9] are shown in Fig. 5. As shown in Fig. 5, it is obvious that the relation in the expression (13) can be expected to hold approximately in this case. In addition, the above relation is found to hold also for the viscosities of mercury-based dilute binary alloys[2] as shown in Fig. 6. (The viscosities of mercury and its dilute binary alloys have been determined by the capillary method.) From these results, we consider that the equation (13) holds on viscosities of other metal-based dilute binary alloys as well. Consequently, using the equation (13), viscosity of dilute binary alloys can be expressed as follows:
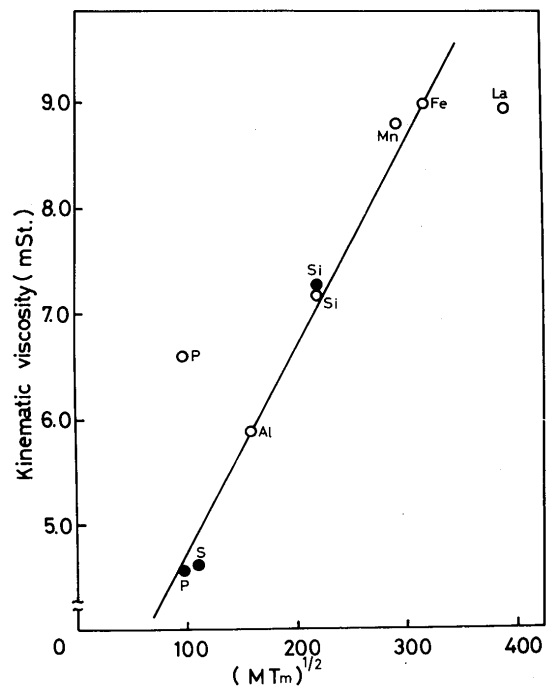

Fig. 5. Change in the kinematic viscosity of molten iron due to one atomic percent of various alloying elements at 1600°C.
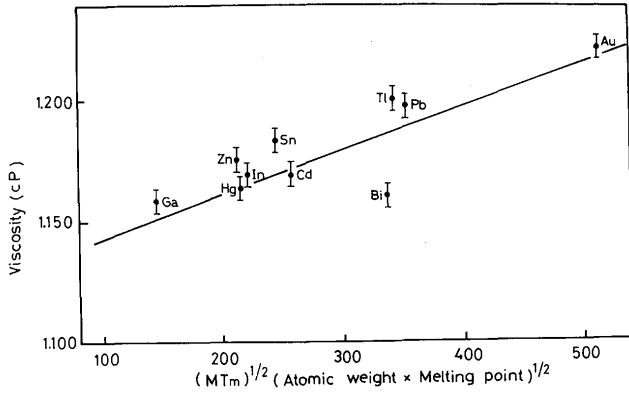($\bigcirc$: Romanov and Kochegarov, $\bullet$: Suzuki and Maekawa)

Fig. 6. Change in the viscosity of mercury with one atomic percent of various alloying metals at 140°C (see Ref. 2).

$$\eta_{M-X} \approx \eta_M + jn_X \left[\frac{P(T)g(\sigma)}{V^{2/3}} \left\{ (MT_m)_X^{1/2} - (MT_m)^{1/2} \right\} \right]$$

(14)

and putting,

$$jn_X \frac{P(T)g(\sigma)}{V^{2/3}} \equiv K$$

we have

$$\eta_{M-X} \approx \eta_M + K \left[(MT_m)_X^{1/2} - (MT_m)_M^{1/2} \right]$$

(15)

Viscosities of molten iron due to one atomic percent of various alloying elements at 1600°C are expressed from Fig. 4 as follows:

$$\eta_{Fe \cdot die} \approx \eta_{Fe} + 3.5 \times 10^{-5} \left\{ (MT_m)_X^{1/2} - 317 \right\}$$

(16)

Accordingly, the expression represented by the equation (15) may be considered to hold not only on the viscosities of iron or mercury-based dilute binary alloys, but on viscosities of other metal-based dilute alloys, and if the value K in the equation (15) is determined from few experimental data for certain base metals, viscosities of those metal-based dilute binary alloys can be evaluated by the use of equation (15).

4. Conclusion

Using the expression for mono-atomic liquid metals which has been derived by one of the authors previously, the viscosity of molten iron at 1600°C was calculated.

A consideration was made on viscosity of dilute binary alloys, and the obtained results may be summerized as follows.

An equation for viscosities of dilute binary alloys could be expressed in the terms of the square root of the product of atomic weight and melting point of alloying elements as a parameter.

Consequently, if the value K in the equation (15) is determined exprimentally or theoretically for certain base metals, viscosities of those metal based dilute binary alloys can be estimated easily by use of the equation (15).

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