Technical Report

Estimation of Temperature Dependency of Molten Pure Metals Viscosities

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Abstract

The temperature dependency of the viscosity of molten pure metals has been thermodynamically discussed as a function of the change of the liquid-state enthalpy. The following equation has been derived:

$$\eta = C^{1-T_0/T}\, \eta_0^{\,T_0/T} \exp\left(-\frac{k(H-H_0)}{RT}\right)$$

where η and H are the viscosity (mPa·s) and liquid-state enthalpy (J/mol) at a given temperature T (K). η_0 and H_0 are the viscosity (mPa·s) and liquid-state enthalpy (J/mol) at the melting point or at any other temperature T_0 (K), higher than the melting point. C is a proportionality constant with a value of 0.984 (mPa·s), which relates the estimated viscosity and the measured viscosity. K is the constant coefficient with a value of 1/4 (-) for pure metals, which is derived from the closed-packing structure and atom moves caused by melt flow. R is the gas constant (J/mol/K). It has been found that the temperature dependency of various pure metals can be predicted using this equation.

1. Introduction

The viscosities of molten metals are important physical properties in the fields of steelmaking and continuous casting of steel. Both experimental and theoretical studies of viscosities have been performed for many years. The viscosities of molten metals have been estimated for an extended period of time. The first attempt to carry out a molecular theoretical study on the viscosities of molten metals was conducted by Andrade.[1] Afterwards, Eyring et al.,[2, 3] Hirai,[4] and Waseda et al.[5] proposed equations for the temperature dependency of the viscosities of pure metals. Ganesan[6] reported an empirical equation for the viscosities by performing parametric fittings of the temperature and concentration on Al-Cu alloys. Zivkovic[7] reported an empirical equation by performing parametric fittings of the concentration of an Au-Ag-Cu system based on the Budai-Benko-Kaptay (BBK)[8] equation.

Several (semi-)theoretical equations have been derived for the excess viscosities of molten alloys. Iida et al.[9] estimated excess viscosities using heat of mixing and activity coefficient. Seetharaman et al.[10, 11] developed a semi-theoretical equation by adding an excess viscosity term derived from the Gibbs energy of activation based on the absolute reaction rate theory of Eyring et al.[2, 3] Kucharski[12] pro-

posed a semi-theoretical equation by calculating the excess viscosity term from grain size (molar volume) and shear coefficients.

Regarding the viscosities of molten oxides, Urbain[13–15] and Iida et al.[16] have also reported equations that reproduce the viscosities of various types of components relatively well. The former equation has a form similar to the Weymann's empirical equation that has a temperature term and viscosity coefficient of the Arrhenius equation. The equation also has a coefficient for the composition depending on components. The latter is an empirical equation with a network parameter and basicity index. Mills[17] also proposed an equation that focuses on optical basicity. Seetharaman et al.[18, 19] established a semi-theoretical equation by adding an excess viscosity term calculated from the Gibbs energy of activation based on the absolute reaction rate theory as is the case with alloys.

Regarding the viscosities of molten oxides, Nakamoto et al.,[20] Kondratiev et al.,[21–23] and Shu et al.[24–26] proposed equations that focus on the bonding state of molten melts, especially the network structure of SiO_2. These equations suggest that the viscosities may be estimated from the bonding state between the atoms in molten metals and thermodynamic quantities.

When a bond between atoms in molten metals is cut, viscous

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flow occurs. The author considers that the bonding state is related to enthalpy, which is one of the thermodynamic properties, and has been studying to express the temperature dependency of the viscosities of various metals using thermodynamic quantities such as enthalpy and heat capacity.

2. Model[27, 28]

2.1 Equation

The bonds between atoms in molten pure metals can be continuously formed and broken. It has been thought that the probability of bonding between atoms in molten metals is a function of the temperature, T, and can be expressed by $\exp(A/T)$, where A is a constant. In addition, the viscosities of molten metals generally decrease with increasing in temperature. The relationship between viscosity η and bonding probability is therefore given by the following equation:[1]

$$\eta \propto \exp\left(\frac{A}{T}\right) \qquad (1)$$

This study focuses on the strength of the bonds between atoms to consider the influence of temperature on the viscosities of molten metals. It is considered that when external force (shear force) acts on a molten metal, the bond is cut and viscous flow occurs as shown in **Fig. 1**, indicating that viscosity depends on the strength of the interatomic bonds. This study uses the enthalpy of a pure substance to express the bonding state. Although the possibility of the formation of interatomic bonds is expressed in Equation (1), the equation has no term to indicate changes in the bonding state as a function of the temperature. Thus, in this model, the enthalpy H (J/mol) is added to Equation (1) to give:

$$\eta \propto \exp\left(\frac{A' - kH/R}{T}\right) \qquad (2)$$

where k is a constant and R is a gas constant (J/mol/K). The viscosity η (mPa·s) in Equation (2) is divided by the constant C (mPa·s) to give the nondimensionalized Equation (3). The details of the constants k and C will be described later.

$$\frac{\eta}{C} = \exp\left(\frac{A' - kH/R}{T}\right)$$

$$RT\ln\left(\frac{\eta}{C}\right) = RA' - kH \qquad (3)$$

Assuming that the temperature is changed from T_0 (reference state) to T_1, the following relation is obtained from Equation (3):

$$RT_1 \ln\left(\frac{\eta_1}{C}\right) - RT_0 \ln\left(\frac{\eta_0}{C}\right) = -\left(kH_1 - kH_0\right)$$

$$\eta_1 = \eta_0^{T_0/T_1} C^{1-T_0/T_1} \exp\left(-\frac{k(H_1 - H_0)}{RT_1}\right) \qquad (4)$$

where η is the viscosity (mPa·s) at temperature T_1 and H is the enthalpy (J/mol) at temperature T_1.

2.2 Constant k

The meaning of the value k is considered as shown below. It is assumed that the atoms in a molten metal are mostly arranged in a close-packing configuration as shown in **Fig. 2**. In this case, the center atom (black circle) is surrounded by a total of 12 atoms: Six at the same height (white circles), three in the front side (dashed line circles), and the other three in the back side (gray circles). When the three dashed atoms move up against the center black atom due to melt flow, the bond between one of the dashed atoms and the center black atom is cut off. On the other hand, the downward movement results in cutting-off of the bonds between two of the dashed atoms and the center black atom. The gray atoms show the same behaviors as the dashed atoms. This means that melt flow changes three bond
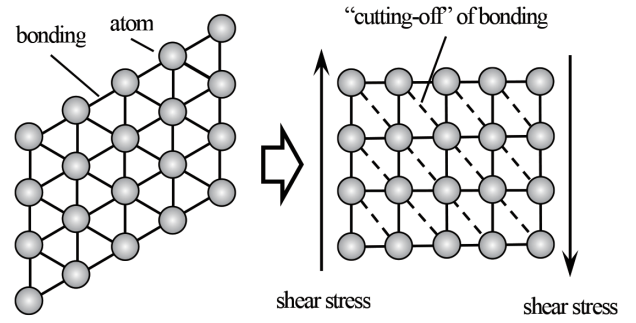

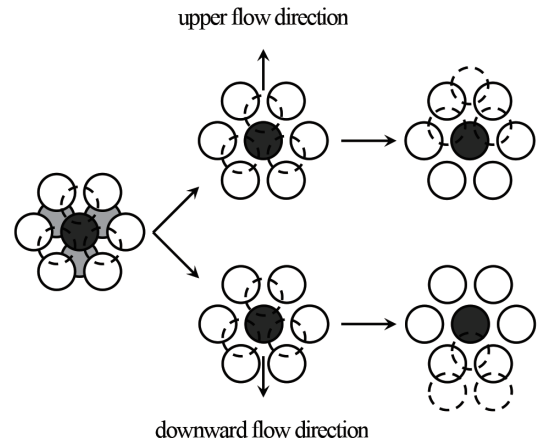**Fig. 1 Conceptual diagram of the "cutting-off" of atomic bonding**

Fig. 2 Close-packing structure and atom moves caused by melt flow

states between the black atom and the surrounding 12 atoms: 1.5 on average for the dashed atoms and 1.5 on average for the gray atoms. Three twelfths $(3/12 = 1/4)$ of the enthalpy per mol are affected, so k is considered to be 1/4.

2.3 Constant C

C is a coefficient that links the exponential term in Equation (2) to the viscosity η and that is obtained from experimental data. The viscosity data of 19 molten metals and semimetals, namely, Fe, Co, Ni, Si, Cu, Au, Ag, Ge, Al, Mg, Sb, Zn, Pb, Cd, Tl, Bi, Sn, In, and Ga, reported by Sato et al.[29-32] were studied to determine the constant C. The viscosities of these metals and semimetals can be expressed by the following Arrhenius equation, which is dependent on the temperature:

$$\eta = B \exp\left(\frac{E}{RT}\right) \qquad (5)$$

where B (mPa·s) and E (J/mol) are constants.

It is well known that the specific heat C_P (J/mol/K) of many types of molten metals does not depend on the temperature, being constant; the enthalpy is expressed by the following equation:

$$H = H_{ref} + C_P T \qquad (6)$$

where H_{ref} is the reference enthalpy (J/mol). When, $A'/k - H_{ref}$ is expressed in Q, Equation (3) gives:

$$\eta = C \exp\left(-\frac{kC_P}{R}\right)\exp\left(-\frac{kQ}{RT}\right) \qquad (7)$$

Comparing Equations (5) and (7), B in Equation (5) corresponds to $C \exp(-kC_P/R)$ in Equation (7).

The heat capacities of molten Fe, Co and Ni reported lately by Fukuyama et al.[33-35] and those of the other metals reported in the
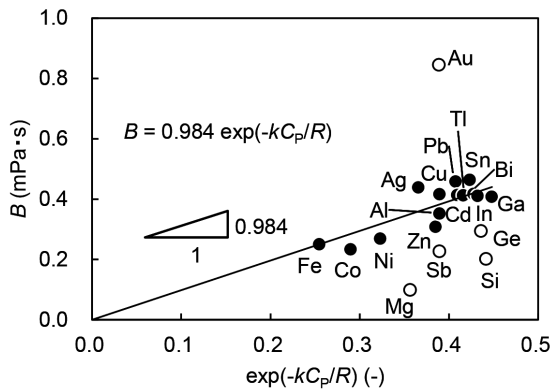
Fig. 3 Relationship between *B* in Eq. (5) and exp(−*kC_P*/*R*) in Eq. (7)

SGTE Unary Database were adopted in this study. Although the heat capacities of molten Au, Pb, Tl, Bi, Sn, In and Ga are slightly dependent on the temperature, the effects are so small that they are neglected in this study.

Figure 3 shows the relationship between *B* in Equation (5) and exp(−*kC_P*/*R*) in Equation (7). Although Si, Au, Ge, Sb, and Mg are the exceptions, the other 14 metals represented by the solid black circles in Fig. 3 clearly show a unique linear relation. The constant *C* is 0.984 (mPa·s) from the slope of the linear relation.

3. Estimation of the Viscosities of Pure Metals at the Melting Points

This section estimates the viscosities at melting points based on the experimental values and experimental temperatures of the viscosities of pure metals. When T_0 in Equation (4) is the experimental temperature, η_0 is the viscosity at the temperature, T_1 is the melting point, and η_1 is the viscosity at the melting point, the viscosity at the melting point can be estimated from each experimental temperature, viscosity, and melting point. As experimental temperatures for pure metals and viscosities at those temperatures, the values measured by Sato et al.[29–32] were used. **Figure 4** shows the estimated viscosities at the melting points. The estimated melting-point viscosity of each metal is constant regardless of the experimental temperatures. Therefore, all the melting-point viscosities estimated from the temperatures and viscosities at those temperatures are constant, which demonstrates that Equation (4) is appropriate.

4. Estimation of Viscosities at a Given Temperature

When the reference temperature T_0 in Equation (4) is regarded as the melting point T_m and the new temperature T_1 is a temperature T higher than the melting point, Equation (4) is rewritten as shown below:

$$\eta = 0.984^{1-T_m/T}\, \eta_m^{\,T_m/T} \exp\left(-\frac{H-H_m}{4RT}\right) \qquad (8)$$

where the melting-point viscosities were obtained by recurring the values measured by Sato et al.[29–32] with the Arrhenius equation and substituting the melting point value in the equation (**Fig. 5**). **Figure 6** shows the viscosities estimated using Equation (8) at temperatures equal to or higher than the melting points for the 14 metals (Fe, Co, Ni, Cu, Ag, Al, Zn, Pb, Cd, Tl, Bi, Sn, In, Ga) along with the experimental values.[29–32] Figure 6 shows that this model successfully reproduces the experimental data of the viscosities of the molten metals well.
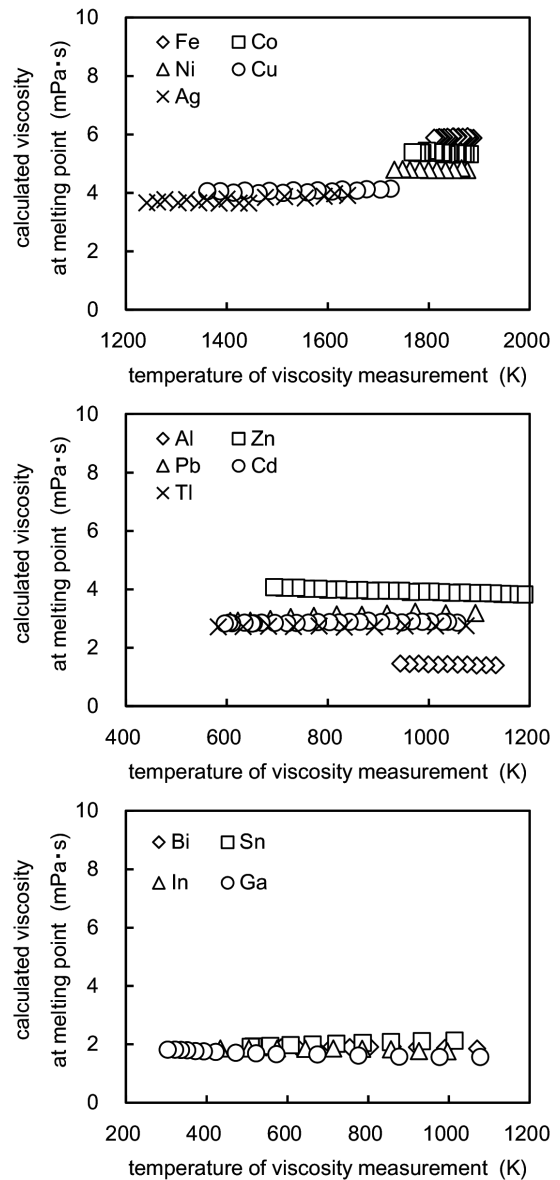

Fig. 4 Melting-point viscosities for each metal, calculated from measurements of the viscosity and the corresponding temperature
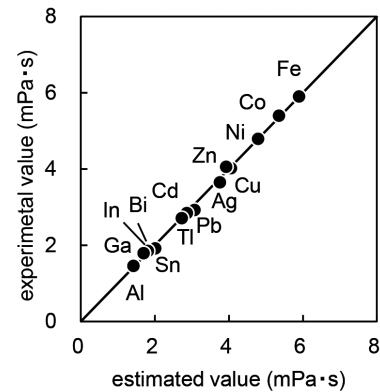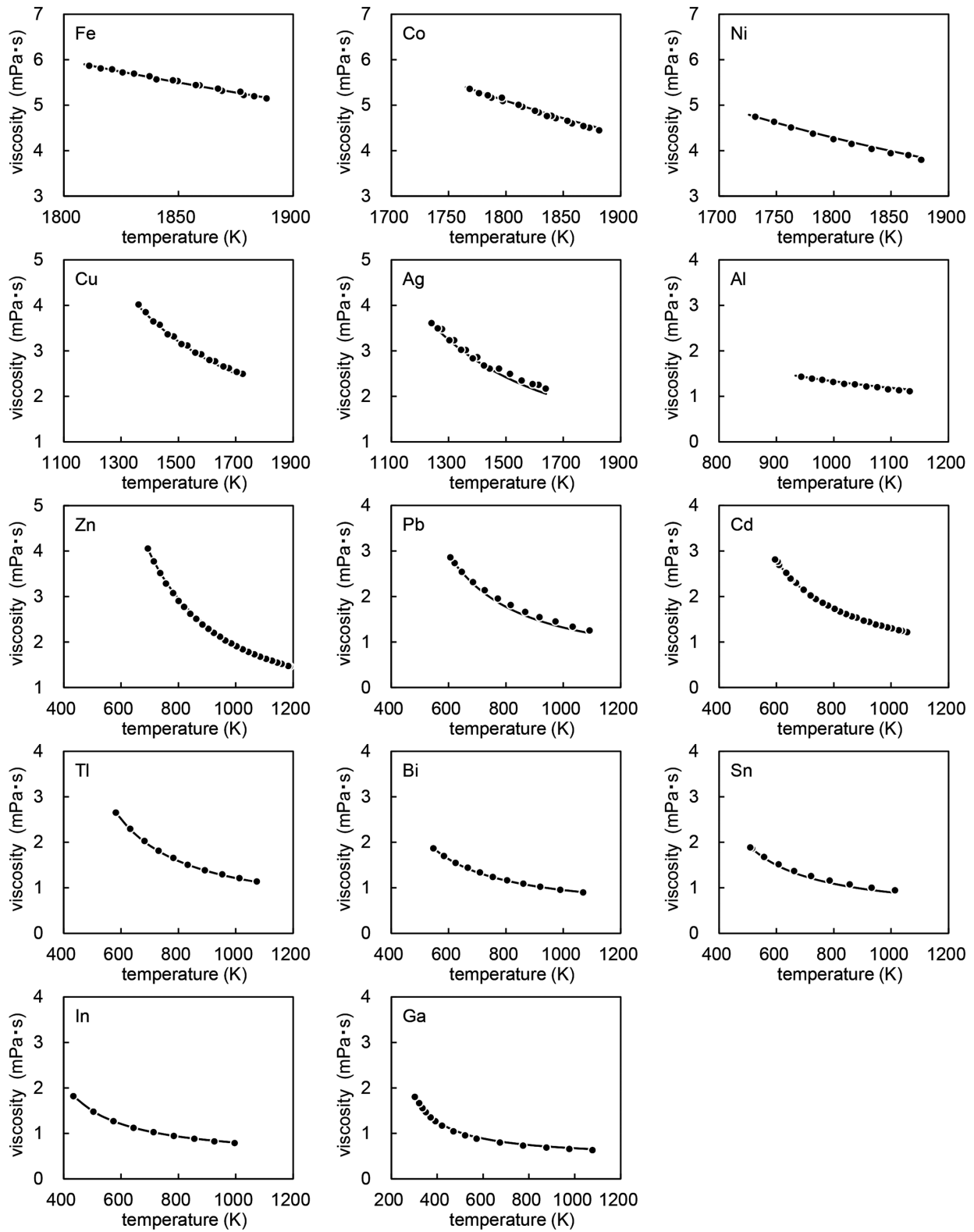

Fig. 5 Relationship between experimental value and estimated value of viscosity at melting point

Fig. 6 Experimental[29–32) (solid circles) and estimated (this model, curve) viscosities

5. Conclusions

The author established the following equation that can estimate the viscosity η (mPa·s) of a pure molten metal at a certain temperature T (K) using changes in the liquid-state enthalpy (H–H_0) when the viscosity η_0 (mPa·s) at the melting point or any other temperature T_0 (K) is known:

$$\eta = 0.984^{1-T_0/T}\, \eta_0^{\,T_0/T}\, \exp\left(-\frac{H-H_0}{4RT}\right) \tag{9}$$

Although this study considered the relatively simple viscosities of pure molten metals, further advancement of studies on the estimation of physical properties of various molten metals that are involved in the steelmaking processes is expected.

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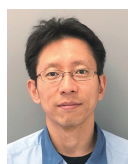
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