Influence of Enthalpy Changes on the Temperature Dependency of the Viscosity of Pure Liquid Metals

Nobuyuki TAKAHIRA*

R & D Laboratories, Nippon Steel & Sumitomo Metal Corporation, 1 Kimitsu, Kimitsu City, Chiba Prefecture, 299-1141 Japan.

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

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

where \( \eta \) and \( H \) are the viscosity (mPa·s) and liquid–state enthalpy (J/mol) at a given temperature \( T \) (K), \( \eta_0 \) 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 0.986 (mPa·s), \( k \) is the constant coefficient, which is 1/4 (-) for pure metals, and \( R \) 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.

KEY WORD: viscosity; enthalpy; physical property; thermodynamics; molten metal.

1. Introduction

The viscosity of liquid metals is one of important factors in the fields of steelmaking and continuous casting of steel. Both experimental and mathematical studies of the viscosity have been performed for many years. The first attempt to carry out a molecular theoretical study on the viscosity of liquid metals at the melting point was made by Andrade.\(^1\)\(^-\)\(^3\) Afterwards Eyring,\(^4\) Hirai,\(^5\) and Waseda\(^6\) estimated the temperature dependency of the viscosities of pure metals and alloys. Ganesan\(^7\) and Zivkovic\(^8\) reported empirical equations for the viscosities by performing parametric fittings of the temperature and the composition on Al–Cu alloy and based on the Budai-Benko-Kaptay (BBK)\(^9\) equation for the composition of Au–Ag–Cu system, respectively.

Several (semi-)theoretical equations have been derived to describe the excess viscosity of molten alloys. Iida\(^10\) described the excess viscosity using basic physical quantities. Seetharaman\(^11\)\(^-\)\(^12\) developed an equation based on the absolute reaction rate theory adding the Gibbs energy of activation. Kucharski\(^13\) proposed an equation describing the viscosity of multi-component mixtures as functions of composition and temperature using molar volumes and activity coefficients.

As in the case of alloys, equations to estimate the viscosity of molten oxides have also been reported by Urbain,\(^14\)\(^-\)\(^16\) Iida,\(^17\) Mills\(^18\) and Seetharamann\(^9\)\(^,\)\(^20\) recently, Nakamoto\(^21\) constructed a model to estimate the viscosity of aluminosilicate based on thermodynamic quantities of the melt and the bonding state of SiO\(_2\). Kondratiev\(^22\)\(^-\)\(^24\) and Shu\(^25\)\(^-\)\(^27\) have also focused on the bonding states in melts showing that it is possible to express their viscosity using thermodynamic quantities.

In this study, the effect of the enthalpy on the viscosity of pure metals is discussed. The atomic bonds are thought to be cut off and then viscous flow will occur. The state of the bond is thought to be related to the enthalpy. Therefore, this thermodynamic quantity is used to construct the present model to express the temperature-dependent viscosity of pure metals having unity bonding states.

2. Model

2.1. Equation

The bonds between atoms in pure metal melts can be continuously formed and broken. It has been thought that the probability of bonding between atoms in the melts 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 the melts generally decrease with increasing temperature. Therefore, the relationship between viscosity \( \eta \) and bonding probability is given by the following equation:\(^25\)

\[ \eta \propto \exp\left( \frac{A}{T} \right) \]

The present study focuses on the bond strength of atoms in melts of pure metals considering the effect of temperature on the viscosities of the melts. Figure 1 shows a conceptual diagram of the “cutting-off” of the atomic bonding in pure metal melts. When external force is applied on melts, the bonds are thought to be cut off. And then viscous flow will
occur. Therefore, the viscosity depends on the bond strength between the atoms. In this study, the enthalpy of a pure substance is employed to express the bonding states.

Although the possibility of the formation of interatomic bonds has been expressed in Eq. (1), there are no terms 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 Eq. (1) to give:

$$\eta \propto \exp \left( \frac{A - kH/R}{T} \right)$$  \hspace{1cm} (2)

where $k$ is constant (-) and $R$ is the gas constant (J/mol/K).

The viscosity $\eta$ (mPa·s) in Eq. (2) is divided by the constant $C$ (mPa·s) to give the nondimensionalized Eq. (3):

$$\frac{\eta}{C} \propto \exp \left( \frac{A - kH/R}{T} \right)$$

RTln $\left( \frac{\eta}{C} \right) = RA - kH$  \hspace{1cm} (3)

Assuming that the temperature is changed from $T_0$ (basic state) to $T_1$, the following relation is obtained from Eq. (3):

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

$$\eta_1 = \eta_0 \left( \frac{T_1}{T_0} \right)^{C_1/C_0} \exp \left( -\frac{k(H_1 - H_0)}{RT} \right)$$  \hspace{1cm} (4)

where $\eta_1$ and $H_1$ are the viscosity (mPa·s) and the enthalpy (J/mol) at temperature $T_1$ (K), respectively. If the basic temperature is the melting point, $T_m$, and the new temperature is any other temperature $T$ higher than $T_m$, Eq. (4) can be rewritten as:

$$\eta = \eta_m \left( \frac{T}{T_m} \right)^{C_1/C_0} \exp \left( -\frac{k(H - H_m)}{RT} \right)$$  \hspace{1cm} (5)

The constants $C$ and $K$ are estimated in the following sections.

2.2. Constant $K$

$K$ is thought to express the proportion of cutting-off bonds to total bonds because it is the coefficient of the enthalpy $H$ in Eq. (5). Based on a closed packed solid structure assumed by Speiser et al.,28,29) Tanaka et al.30–32) adopted 12 as a coordination number in various melts to estimate these surface tensions. In this model, it is also assumed that the atoms in melts are mostly arranged in a close-packing configuration and each atom is surrounded by 12 other atoms, as shown in the left side of Fig. 2, although there are also vacancies The center atom (shown in black in Fig. 2) is surrounded by six white atoms that are on the same level. There are also three gray atoms behind the black one and three dashed atoms in front of it. When three dashed atoms move up against the center black atom shown in the upper side of Fig. 2, one bond between the dashed atoms and the black atom are cut off. On the other hand, downward direction flow results in cutting off two bonds between them shown in the lower side of Fig. 2. The gray atoms show the same behaviors as the dashed atoms. They mean that melt flow temporarily cuts off $3 = (2 + 1)/2 \times 2$ bonds on average. These three bonding states are drastically altered whereas the other nine are much less changed. Therefore, the averaged three bonds cutting-off in twelve bonds correspond to $k = 3/12 = 1/4$.

2.3. Constant $C$

$C$ is proportionality constant because it is a coefficient that relates the exponential term in Eq. (2) to the viscosity $\eta$. Constant $C$ is obtained from the experimental data. The viscosity data of nineteen molten metals and semimetals, namely, Fe, Co, Ni, Si, Cu, Au, Ge, Al, Mg, Sb, Zn, Pb, Cd, Tl, Bi, Sn, In and Ga reported by Sato et al.33–36) are focused to determine the constant parameter $C$. The viscosities of these metals and semimetals can be expressed by the following Arrhenius equation, which is dependent on the temperature:

$$\eta = B \exp \left( \frac{E}{RT} \right)$$  \hspace{1cm} (6)

where $B$ is constant (mP·s) and $E$ is the activation energy

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

**Fig. 2.** Close-packing structure and atom moves caused by melt flow.
It is well known that the heat capacities of molten metals do not depend on the temperature, as described below:

$$H = H_{\text{ref}} + C_T T$$ .......................... (7)

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

$$\eta = C_{\text{exp}} \left[ \exp \left( \frac{-kC_P}{R} \right) \right] \frac{kQ}{RT} ................................ (8)$$

Comparing Eqs. (6) and (8), $B$ in Eq. (6) is likely to correspond to $C_{\text{exp}} \left( -kC_P/R \right)$ in Eq. (7).

The heat capacities of molten Fe, Co and Ni measured by Fukuyama et al. and the others reported in the SGTE Unary Database (ver. 5) are 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 can be neglected. The constant heat capacities used in the present study are shown in Table 1.

The relationship between $B$ in Eq. (6) and $\exp \left( -kC_P/R \right)$ in Eq. (7) is shown in Fig. 3. Many metals represented by solid circles in Fig. 3 clearly show a unique linear relation, although Si, Au, Ge, Sb and Mg are the exceptions. The deviations of Si, Ge, and Sb from the linear behavior are thought to be explained by the fact that these are semimetals with bonding states that have been thought to be different from those of metals. The reason for the deviation in the case of metallic Au and Mg is still unknown and will be the subject of a future work. Constant $C$ (0.986 mPa·s) is obtained as the slope of the linear relation shown in Fig. 3.

### 3. Estimation of the Viscosities of Pure Metals

#### 3.1. Viscosity at the Melting Point

In this model, the viscosity at a given temperature is estimated from the viscosity at another temperature and the enthalpy change between these two temperatures. In Eq. (4), assuming that $\eta_1$ is the viscosity at the melting point $\eta_m$ and $\eta_0$ is the experimental viscosity determined at each temperature, the $\eta_m$ values of fourteen metals (plotted as solid circles in Fig. 3) are calculated from Eq. (4), as shown in Fig. 4. Figure 4 indicates that the melting-point viscosities of the metals, calculated from various temperatures for which the viscosities were measured, are mostly constant at all the studied temperatures. The average viscosities of the studied metals at the melting point, calculated by this model, are shown in Table 2.

### Table 1. Heat capacities $C_P$ of molten pure substances ($\text{J/mol/K}$).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Si</th>
<th>Cu</th>
<th>Au</th>
<th>Ag</th>
<th>Ge</th>
<th>Al</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45.5</td>
<td>42.4</td>
<td>37.6</td>
<td>27.2</td>
<td>31.4</td>
<td>31.4</td>
<td>33.5</td>
<td>27.6</td>
<td>31.8</td>
<td>34.3</td>
</tr>
<tr>
<td>Sb</td>
<td>31.4</td>
<td>31.4</td>
<td>29.9</td>
<td>29.7</td>
<td>29.2</td>
<td>28.3</td>
<td>28.6</td>
<td>27.9</td>
<td>26.7</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Relationship between $B$ and $\exp \left( -kC_P/R \right)$.

Fig. 4. Melting-point viscosities for each metal, calculated from measurements of the viscosity and the corresponding temperature.
Table 2. Viscosity at the melting point for each metal (mPa·s).

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Ag</th>
<th>Al</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>Tl</th>
<th>Bi</th>
<th>Sn</th>
<th>In</th>
<th>Ga</th>
</tr>
</thead>
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<tr>
<td></td>
<td>5.90</td>
<td>5.35</td>
<td>4.79</td>
<td>4.06</td>
<td>3.76</td>
<td>1.42</td>
<td>3.93</td>
<td>3.07</td>
<td>2.86</td>
<td>2.72</td>
<td>1.89</td>
<td>2.01</td>
<td>1.81</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Fig. 5. Measured\(^{13-16}\) (solid circles) and estimated (this model, curve) viscosities.
3.2. Temperature Dependency of the Viscosity of Pure Metals

From the discussions above, the present model can be described by:

\[ \eta = 0.986^{1-T_m/T} \eta_m \exp \left( -\frac{H_m}{4RT} \right) \text{ (mPa} \cdot \text{s) ... (9) } \]

The measured\(^{33-36}\) and estimated viscosities for various metals are shown in Fig. 5. It can be seen that the present model successfully reproduces the experimental data.

4. Conclusions

A model was derived assuming that the enthalpies of molten metals affect the viscosities of the melts. The center atom in the close-packing arrangement is surrounded by twelve atoms and forms twelve atomic bonds with these atoms. A viscous flow “cuts” three of these twelve bonds. As a result, one fourth of the enthalpy is affected. The equation based on this consideration successfully reproduces the viscosities of various metals, although one viscosity measurement data is required to estimate the viscosities at temperatures above the melting point.

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