Evaluation Model for Viscosity of Fe–Ni–Cr Alloys Using Gibbs Free Energy of Mixing and Geometric Methods

Yanhui LIU, Xuewei LV* and Chenguang BAI

School of Materials Science and Engineering, Chongqing University, Chongqing, 400044 China.

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Purpose of this investigation is to predict the viscosity of liquid Fe–Ni, Fe–Cr, Ni–Cr and Fe–Ni–Cr alloys at 1 873 K. The activation energies of binary alloys were calculated by the mixing Gibbs energies, and the proposed activation energies of pure Fe, Ni and Cr are 72 657, 66 721 and 74 517 J/mol. Geometric models (Kohler, Toop and Chou models) were used to predict the excess activation energies of ternary alloys. The iso-viscosity curves of Fe–Ni–Cr alloy are calculated by three geometric models (Kohler, Toop and Chou models) from sub-binary systems. Ni can decrease the viscosity in the whole range, while Fe has a two-sided effect. Cr can result in the decrease of the viscosity at the Ni-rich corner and Fe-rich corner. The effects of Ni and Cr on viscosities of Fe–Ni–Cr alloys are consistent with the measured results. But when Cr exceeds 20 in mole%, the addition of Cr will cause the rise of the viscosity. The evaluated values by the Chou model are the biggest and have a much more reasonable low viscosity region. Comparison between the evaluated results and experimental values of the Fe–Ni–Cr ternary alloys were investigated. The average errors between the measured results and predicted values by Kohler, Toop and Chou model are below 5%, indicating that evaluated viscosities of Fe–Ni–Cr ternary alloys by three models (Kohler, Toop and Chou) can reproduce the measured results quite well.

KEY WORDS: viscosity; activation energy; mixing Gibbs free energy; geometric models.

1. Introduction

Thermo-physical properties of these liquid metals, such as heat capacity, thermal conductivity, surface tension, density and viscosity are of particular interest because these properties play important roles in heat and mass transport processes. Knowledge of the viscosities of pure liquid metals and respective mixtures is important for practical and theoretical purposes. Furthermore, the viscosity of multicomponent liquid mixtures is an invaluable type of data for the chemical engineer in the design and optimization of industrial processes, particularly for the smelting, casting and welding processes of Fe-based alloys and stainless steels. Therefore, it is very important to obtain a precise and reliable viscosity, especially for high melting point alloys from the industrial point of view. Proposed methods for the measurement of the viscosity include: capillary, oscillating vessel, rotational bob or crucible, oscillating plate, draining vessel, levitation using the damping of surface oscillations and acoustic methods. It is well known that the measurement of the viscosity of molten metals, especially at high temperatures, is difficult because of the reactivity with the crucibles and atmosphere, and also the sensor limitation of the low viscosity. Compilations of the viscosities of pure liquid metals at different temperatures, as well as those of binary liquid mixtures through the whole composition range, can be found in the literature. Nevertheless, the situation changes in the case of multi-component liquid mixtures, and there is only a limited number of viscosity data. Over the last years, a large number of estimation models for viscosity available have been developed and improved. In addition, molecular dynamics provides a way to predict the viscosity of liquid mixtures without making use of experimental data. But the deviations between calculated and experimental values are, in general, greater than those obtained with the other types of models.

Viscosities of molten Fe–Ni alloy were measured by using an oscillating cup viscometer over the entire composition range from liquidus temperatures up to 1 873 K with high precision and excellent reproducibility by Sato et al. However, there are few experimental values available for Fe–Cr and Ni–Cr binary systems, and even less for Fe–Ni–Cr ternary alloys. So no systematic study including experimental measurement and model evaluation has been carried out for Fe–Ni–Cr higher-order metallic system. The aim of this investigation is to predict the viscosities of liquid Fe–Ni, Fe–Cr, Ni–Cr and Fe–Ni–Cr ternary alloys at 1 873 K. Viscosities of the sub-binary alloys were calculated based on the mixing Gibbs energy model proposed by Seetharaman et al. The activation energies of binary alloys are calculated by the mixing Gibbs energies, and viscosities of the binary alloys were evaluated based on the Arrhenius equation, and can reach a good agreement with the experimental values. The polynomial equations were used to describe the variations of excess activation energies.
of three binary systems, and the geometric models (Kohler, Toop and Chou models$^{24-26}$) were used to predict the excess activation energies of ternary alloys. The calculated results of the ternary alloys were compared with the experimental values by considering the applicability of the three geometric models.

2. Viscosity Evaluation of the Sub-binary Alloy

The absolute rate theory method of Eyring$^{27}$ provides the expression of the viscosity calculation for a liquid mixture, which has been applied successfully to various metallic as well as ionic systems.

$$\eta = \frac{\rho h N_A}{M} \exp \left( \frac{E_a}{RT} \right) \quad \text{.........(1)}$$

Where $\eta$ is the dynamic viscosity of the alloy, $h$ is Plank’s constant, $N_A$ is Avogadro’s number, $\rho$ is the density of the liquid alloy, $M$ is the molar mass of the alloy, $E_a$ is the activation energy for the flow process, and $T$ is the absolute temperature.

Activation energy is considered to be a function of both temperature and composition of the melt. Theoretically, viscosity of one alloy can be predicted if its activation energy is given out, but it is not easy to obtain the value of activation energy. Seetharaman et al.$^{22}$ proposed the following relationship between the activation energy and the mixing Gibbs energy:

$$E_a = \sum x_i E_{a_i} + \Delta G_{mix} + 3RTx_Ax_B \quad \text{.........(2)}$$

The subscript $i$ stands for component $i$. The first term on the right-hand side of Eq. (2) represents the “linear” variation of the activation energy from the pure components in the absence of interaction between different components. The $E_{a_i}$ is the activation energy of pure component $i$ in liquid state. $\Delta G_{mix}$ represents the mixing Gibbs energy of the alloy in a solution. Where, $x_A$ and $x_B$ are the respective mole fractions.

In the case of high-order metallic systems, the molar mass of the alloy can be calculated by Eq. (3). In a similar way, the density of the melt may be estimated, as a first approximation, by Eq. (4).

$$\rho = \sum x_i \rho_i \quad \text{.........(3)}$$

$$M = \sum M_i x_i \quad \text{.........(4)}$$

2.2. Mixing Gibbs Energies of Binary Alloys

An assessment set of thermodynamic parameters for Fe–Cr and Fe–Ni alloy systems$^{28-30}$ can be used to calculate the mixing Gibbs energies of alloys. Sometimes, there happens some discrepancies between calculations and experimental data of higher order systems, and these troubles can be traced back to the assessments of lower order systems. In order to obtain the accurate values, the revision of activities of the Fe–Cr and Fe–Ni liquid phase proposed by Lee et al.$^{30}$ has been adopted in this study, which can give better agreement with experimental data. Mixing Gibbs energies of binary systems can be calculated by the following equation and these values are as shown in Fig. 1 and listed in Table 2. As for the Ni–Cr system, data concerning its mixing Gibbs energy studied by Novakovic et al.$^{32}$ can reproduce the experimental values fairly well by enabling a more precise classification of the Ni–Cr system in terms of weakly compound-forming alloys. The mixing Gibbs energies of Ni–Cr alloys are also shown in Fig. 1 and listed in Table 2. It should be pointed out that a wide composition range of solid solution exists in Fe–Cr and Ni–Cr systems at 1 873 K, so these alloys are assumed to be super-cooled liquid in order to obtain a smooth line of Gibbs free energy of mixing.

$$\Delta G_{mix} = RT(x_A \ln a_A + x_B \ln a_B) \quad \text{.........(5)}$$

2.3. Evaluation for Viscosities of Binary Alloys at 1 873 K

With the help of mixing Gibbs energy and the activation energies of pure metals proposed in this study, the activation energies of binary alloys at 1 873 K are easy to be

<table>
<thead>
<tr>
<th>Metal</th>
<th>Viscosity, mPa·s</th>
<th>Density, g/cm³</th>
<th>Molar mass, g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>5.29</td>
<td>6.97</td>
<td>55.85</td>
</tr>
<tr>
<td>Ni</td>
<td>3.82</td>
<td>7.75</td>
<td>58.69</td>
</tr>
<tr>
<td>Cr</td>
<td>5.77</td>
<td>6.28</td>
<td>52.00</td>
</tr>
</tbody>
</table>

Table 1. Data of the viscosity,$^7$ density,$^{31}$ and molar mass used in this study (Note: Viscosity of pure Cr is estimated from the Fe–Cr binary systems).

Fig. 1. Mixing Gibbs free energy of binary A-B systems with $x_A$ at 1 873 K.
obtained, and the values are shown in Table 3. By combining Eqs. (1)–(4), it is not hard to obtain the viscosities of binary alloys. As shown in Fig. 2, the evaluated viscosities of Fe–Ni binary alloy are compared with the measured results proposed by other researchers, showing that the prediction values can reproduce the experimental values quite well. Here another two different evaluation models for the viscosities of Fe–Ni alloys are also studied and plotted in Fig. 2. An expression derived by Iida et al. describes the excess viscosity of liquid binary alloys by using some basic physical properties. Hirai estimated the viscosities of liquid alloys by systematically analyzing the viscosity data for liquid metals from in the literature. By comparing the predicted values by three models and experimental data, it can be found that the ‘Hirai model’ can not reproduce the experimental data at the composition regions near pure iron and pure nickel, while the evaluated values by ‘Iida model’ seems a little higher than the measured results. The predicted results by ‘Seetharaman model’ can reach a good agreement with the average of all the measured values.

Figure 3 shows the comparison between the evaluated viscosities and experimental data of Fe–Cr alloys. Two-side effect can also be observed, which is consistent with the measured results by Kamaeva et al., which are caused by a concentration change in the binding energy between the atoms determined by the geometric and compositional short-range order. Experimental data of Fe–Cr binary alloys measured by Sato et al. and Kobatake et al. were plotted in Fig. 3 and compared with the calculated values by ‘Seetharaman model’, showing that the predicted values can reproduce the experimental data quite well. The predicted viscosities for Ni–Cr alloys are given out as shown.
in Fig. 4, illustrating that Cr has similar effect in Fe–Cr and Ni–Cr alloys.

3. Evaluation for the Viscosity of Ternary Alloy

3.1. Excess Activation Energy Evaluation of Binary Alloy

The excess activation energy can be expressed by the linear relationship as follows:

\[ E_{a_{ex}} = E_a - \sum x_i E_{a_i} \] ................. (6)

Where, \( E_{a_{ex}} \) is the excess activation energy of binary alloy. According to the calculated activation energies and the activation energies of pure metals, the excess activation energies of three sub-binary systems in the Fe–Ni–Cr ternary alloy can be calculated as shown in Fig. 5, which are fit using polynomial equation described by Eq. (7), where \( x_A \) and \( x_B \) are the molar contents of the components, “A” and “B”, respectively, and \( A_k \) are the coefficients related to the sub-binary “A-B” system and their values are listed in Table 4.

\[ E_{a_{ex}} = \sum_{k=0}^{n} A_k (x_A - x_B)^k \] ................. (7)

3.2. Methods to Calculate the Excess Activation Ener -
gies of Ternary Alloys

In order to describe the excess viscosity of ternary alloy from the measured viscosities of sub-binary systems, three possible methods have been considered here. The traditional geometric models can be divided into three types: symmetric (Kohler model), asymmetric (Toop model) and general solution model (Chou model). Geometric models have been used extensively to predict the thermodynamic properties of ternary and multi-component systems from sub-binary systems. Hu et al. first extended geometric models to predict the surface tensions of the Ag–Au–Cu ternary alloy without comparison between calculated and experimental results. Recently, geometrical models were successfully applied to predict the surface tension of the Ni3S2–FeS–Cu2S matte system and the calculated results were in good agreement with the experimental values. Surface tensions of the Sn–Ga–In ternary alloy were calculated from the surface tensions of the Sn–Ga, Ga–In and In–Sn sub-binary systems by using geometric models (the Kohler model, Toop model and Chou model) by Yan et al. with excellent reproducibility.

| Table 4. Coefficients of the polynomial for excess activation energies of binary alloys at 1 873 K. |
|-------|---|---|---|---|---|---|---|
| System | \( A_0 \) | \( A_1 \) | \( A_2 \) | \( A_3 \) | \( A_4 \) | \( A_5 \) | \( A_6 \) |
| Fe–Ni  | −32.71 | −31.526.32 | 232.274.11 | −748.344.35 | 1.236.466.71 | −1.035.848 | 346.970.14 |
| Fe–Cr  | −26.01 | −23.548.28 | 216.458.06 | −687.114.24 | 1.106.611.77 | −923.289.20 | 310.872.07 |
| Ni–Cr  | −32.36 | −28.880.05 | 105.019.71 | −150.070.61 | 73.911.50 | 0 | 0 |

Fig. 3. Comparison between the calculated viscosities and experimental values of Fe–Cr binary alloys at 1 873 K.

Fig. 4. Predicted viscosities of Ni–Cr alloys by mixing Gibbs energy at 1 873 K.

Fig. 5. Variation of excess activation energies of three sub-binary A-B alloys with \( x_B \) at 1 873 K.
Here, geometric models are used to predict the activation energy instead of Gibbs free energy. As mentioned above, the melting point of Cr is quite higher than 1873 K, so it is impossible to obtain the iso-viscosity curves of the ternary alloy in the whole range. The liquid projection of Fe–Ni–Cr ternary alloy as a function of temperature by FactSage was shown in Fig. 6. So in this work, the iso-viscosity curves will be cut off by the 1873 K isothermal line in the ternary Fe–Ni–Cr figures.

3.2.1. Kohler Model

In 1960, Kohler\(^{24}\) proposed a symmetric geometric model based on the hypothesis of the similarity of the thermodynamics properties of the three components within the ternary alloy, which can be described as the following equation:

\[
Ea^{ex} = (X_1 + X_2)^2 \left( \frac{Ea_{12}^0}{X_1} \right) + (X_1 + X_3)^2 \left( \frac{Ea_{13}^0}{X_1} \right) + (X_2 + X_3)^2 \left( \frac{Ea_{23}^0}{X_2} \right) \tag{8}
\]

Where, \(Ea^{ex}\) and \(Ea_{ij}^0\) are the excess activation energy of the ternary system and \(A-B\) the binary system, respectively; \(X_i\) is the mole fraction of component \(i\) in the ternary system.

3.2.2. Toop Model

As a classic asymmetric geometric model, the Toop model\(^{25}\) has been widely used and can be described as follows:

\[
Ea^{ex} = \frac{X_2}{X_2 + X_3} Ea_{12}^0 (X_1, 1 - X_1) + \frac{X_1}{X_2 + X_3} Ea_{13}^0 (X_1, 1 - X_1)
+ (X_2 + X_3)^2 Ea_{23}^0 \left( \frac{X_2}{X_2 + X_3}, \frac{X_1}{X_2 + X_3} \right) \tag{9}
\]

In this model, it is of vital importance to determine the asymmetric component \(i\). Qiao et al.\(^{19}\) compared some criteria for judging the symmetry of the ternary system, and pointed out that if the excess thermodynamic properties of the three sub-binary systems are similar to each other, then the ternary system is symmetric. Otherwise, if the deviations of the binary systems A-B and A-C from the ideal solution are similar, but differ markedly from that of the binary system B-C, then the A-B-C ternary system is asymmetric. In the asymmetric system, the common component \(A\) in two sub-binary systems with thermodynamic similarities should be chosen as the thermodynamic asymmetric component. Here, this criterion was extended to our excess activation energy calculation by using geometric models. It is better to pick up “Ni” as the “asymmetric component” for Toop model, since the “Fe–Ni” and “Ni–Cr” two binary systems are much more similar shown in Fig. 5.

3.2.3. General Solution Model----Chou Model

Recently, Chou\(^{26}\) proposed a general solution model to predict the thermodynamic properties of a ternary system from the three boundary system. The most attractive characteristic of this new model is bypassing the traditional methods and subsuming symmetric and asymmetric models in a more general approach. Here, the Chou model was also extended to the activation energy prediction of the ternary system from the three boundary systems, as shown in Eq. (10):

\[
\eta^e = \frac{X_1 X_2}{X_{1(12)} X_{2(12)}} \eta_{12}^e + \frac{X_2 X_3}{X_{2(23)} X_{3(23)}} \eta_{23}^e + \frac{X_1 X_3}{X_{1(31)} X_{3(31)}} \eta_{31}^e \tag{10}
\]

Where \(X_{ij(k)}\) is the mole fraction of component \(i\) in the \(i-j\) binary system, which can be calculated from the following equations:

\[
X_{1(12)} = X_1 + \xi_{12} X_2 \\
X_{2(23)} = X_2 + \xi_{23} X_3 \\
X_{3(31)} = X_3 + \xi_{31} X_2
\]

Where \(\xi_{ij}\) is the similarity coefficient, which can be expressed as:

\[
\xi_{12} = \frac{\lambda_1}{\lambda_1 + \lambda_2} \tag{12}
\]

\[
\xi_{23} = \frac{\lambda_2}{\lambda_2 + \lambda_3} \tag{13}
\]

\[
\xi_{31} = \frac{\lambda_1}{\lambda_1 + \lambda_3}
\]

Where \(\lambda\) is the deviation sum of squares, which can be calculated as follows:

\[
\lambda_1 = \int_0^1 (\eta_{12}^e - \eta_{12}^e)^2 dX_1 \\
\lambda_2 = \int_0^1 (\eta_{23}^e - \eta_{23}^e)^2 dX_2 \\
\lambda_3 = \int_0^1 (\eta_{31}^e - \eta_{31}^e)^2 dX_3
\]

It should be pointed out that the similarity coefficients mentioned in the Chou model are considered to study...
the applicability of three models in order to analyze the accuracy of the predicted values. If the third component is similar to the second one, \( \lambda_2 = 0 \), thus \( \xi_{12} = 0 \), and if the third one is similar to the first one, \( \lambda_1 = 0 \), thus \( \xi_{12} = 1 \). Therefore, it can be judged from the similarity coefficient that the third component is more similar to the component one or two. It has been proved\(^{(26, 44-47)}\) that the Chou’s model is a general geometrical model, all traditional geometric models, including the “Kohler model” and “Toop model”, are one of forms of the general geometrical model under the different particular situation.

### 3.3. Evaluation for Activation Energy of Ternary Alloy

The activation energy of ternary alloy can be calculated by Eq. (15) with the excess activation energy and activation energies of pure metals.

\[
E_a = \sum_1^3 x_i E_{a_i} + E_{a''}
\]  

(14)

Similar to the viscosity calculation of binary alloy, the viscosity of ternary alloy can be calculated by combing Eqs. (1), (3), (4), and (15).

### 4. Results and Discussion

#### 4.1. Iso-viscosity Curves of Ternary Alloy

**4.1.1. Iso-viscosity Curves by Kohler Model**

The iso-viscosity curves of the Fe–Ni–Cr ternary alloy predicted by the Kohler model were plotted in Fig. 7. Smooth iso-viscosity curves are observed, showing that there is no remarkable interaction force between the components. Ni can lower the viscosity of the ternary alloy at the whole composition range. Cr can result in the decrease of the viscosity at the Ni-rich corner and Fe-rich corner. But when Cr exceeds 20 in mole%, the addition of Cr will cause the rise of the viscosity. When the Ni is fixed and above 40 in mole%, the addition of Fe can increase the viscosity. Once the Ni is fixed and below 40%, Fe can promote the increase of the viscosity when Fe is below 40%, then the continuing increase of Fe will result in the decrease of the viscosity. Interesting to find that there is a region that the viscosity of the ternary alloy is even lower than that of Ni, and the reason may be attributed into the concentration change in the binding energy between the atoms determined by the geometric and compositional short-range order, which can also be found in the Fe–Cr binary alloys.

**4.1.2. Iso-viscosity Curve by Toop Model**

Figure 8 shows the iso-viscosity curves of the Fe–Ni–Cr ternary alloy evaluated by the Toop model. Smooth iso-viscosity curves are also observed, showing that there is no remarkable interaction force between the components. Similar influences can be found for Fe, Ni and Cr in Kohler model. But the effect of Cr to decrease the viscosity at the Fe-rich corner is weakened while that at the Ni-rich corner is strengthened. Comparing with the calculated results by the Kohler model, the most apparent point is that the low viscosity region (lower than 3.5 mPa·s) is enlarged, which is not reasonable and may cause a major deviation.
4.1.3. Iso-viscosity by Chou Model

The iso-viscosity curves of the Fe–Ni–Cr ternary alloy evaluated by the Chou model are plotted in Fig. 9. Smooth iso-viscosity curves are also observed, and similar influences can be found for Fe, Ni and Cr. Comparing with the calculated results by the Kohler model and the Toop model, all the iso-viscosity curves shift away from the Fe–Cr line, indicating that the evaluated values by the Chou model are the biggest and have a much more reasonable low viscosity region, which can be thought as the improvement different from other two models.

4.2. Reproducibility of Three Geometric Models

Experimental data of Fe–Ni–Cr ternary alloys measured by Sato et al.\textsuperscript{20,21} were also marked as red dot in Figs. 7–9. The effects of Ni and Cr on viscosities of Fe–Ni–Cr alloys are consistent with the measured results by Sato et al.\textsuperscript{21} The reproducibility is evaluated as the average error defined as Eq. (15), and the average errors between the measured results and predicted values by Kohler, Toop and Chou model are below 5%, indicating that evaluated viscosities of Fe–Ni–Cr ternary alloys by three models reach a good agreement with the experimental data.

\[ \text{Average error} = \frac{1}{N} \sum \frac{\sigma_{\text{Calc}} - \sigma_{\text{Expe}}}{\sigma_{\text{Expe}}} \times 100\% \quad \ldots (15) \]

5. Conclusions

In this work, the viscosities of liquid Fe–Ni–Cr sub-binary alloys and ternary alloys at 1 873 K have been evaluated using mixing Gibbs free energies and geometric models by considering the excess activation energies from the sub-binary systems. The main conclusions are as follows:

1. The activation energies of pure Fe, Ni and Cr at 1 873 K are given their proposed values are 72 657, 66 721 and 74 517 J/mol, respectively. The calculated viscosities of Fe–Ni and Fe–Cr alloys can reproduce the experimental values and the viscosities of Ni–Cr alloys are predicted in this work. Cr has a two-sided effect in Fe–Cr and Ni–Cr alloys.

2. The iso-viscosity curves of Fe–Ni–Cr alloy are calculated by three geometric models (Kohler, Toop and Chou models) from sub-binary systems. Ni can decrease the viscosity in the whole range, while Fe has a two-sided effect. Cr can result in the decrease of the viscosity at the Ni-rich corner and Fe-rich corner. But when Cr exceeds 20 in mole%, the addition of Cr will cause the rise of the viscosity. The evaluated values by the Chou model are the biggest and have a much more reasonable low viscosity region.

3. The average errors between the measured results and predicted values by Kohler, Toop, and Chou model are below 5%, indicating that evaluated viscosities of Fe–Ni–Cr ternary alloys by three models (Kohler, Toop and Chou) reach a good agreement with the experimental data.

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