Estimation of Viscosity with New Thermodynamic Geometric Model

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ABSTRACT

The viscosity estimation model, base on the combination of Seetharaman's viscosity model and Chou's thermodynamic geometric model, has been deduced. The viscosity of Ag-Au-Cu system has been calculated with the present model. The results are consistent with the experimental data well. The viscosities of Bi-Sn-In and FeO-B_2O_3-SiO_2 system have also been predicted.

1 Introduction

Viscosity of high temperature metallurgical melts is an important property that influences metallurgical processes in many aspects. The knowledge of metallic melts and slag viscosity is essential in understanding of the kinetics of reactions relevant to process metallurgy as well as to process like casting and welding. For examples, the rise of gas bubbles through metallic melts depends on its viscosity; the rate of impurities transfering from metallic melts to slag is affected by the viscosity of both slag and metallic melts. However, the amount of viscosity data is far from satisfaction for the needs of today's technology though a number of experimental measurements have been carried out.

To meet the requirement of viscosity data, modeling of viscosities of complex melts have been received the attention of scientist over the past decades [1-7]. But, the progress is limited because of the lack of basic viscosity data. Seetharaman [5,6] suggested a new method to estimate viscosity of complex melts by using thermodynamic data (Gibbs free energy of mixing). The relatively large amount of thermodynamic data enables viscosity estimation or modeling more convenient and effective.

This paper is going to issue a new model, with the combination of Seetharamn's model with Chou's thermodynamic geometric model, to estimate viscosity of ternary metallic and ionic melts. Some calculations, along with the analysis and discussion, have been carried out.

2 Model of viscosity estimation

The viscosity of metallic and ionic melts can be expressed by the equation[7]

$$\eta = \frac{hN\rho}{M}\exp\left(\frac{\Delta G^*}{RT}\right) \qquad (1)$$

where h is the Plank's constant, N is Avagadro's number, ρ is the density of the melts, M is the molecular weight, and ΔG^* is the Gibbs free energy of activation per mole.

In the case of unary system, the Gibbs free energy of activation can be expressed as

$$\Delta G^* = a + bT + cT\ln(T) + \cdots \qquad (2)$$

In the case of high-order melts, M, p and ΔG^* of the melts can be calculated by the

following equations

$$M = \sum X_i M_i \qquad (3)$$

$$\rho = \sum X_i \rho_i \qquad (4)$$

$$\Delta G^* = \sum X_i \Delta G_i^* + \Delta G_{mix}^* \qquad (5)$$

where X_i, M_i, ρ_i, ΔG_i represent the mole fraction, molecular weight, the density and Gibbs activation energy of component i.

In order to estimate activation energy of multi-component by using Gibbs free energy of mixing, Seetharaman [5,6] suggested the following equations by the correlation between the Gibbs free energy of mixing and the Gibbs activation energy for viscosity. For binary melts, the correlation is

$$\Delta G^* = \sum X_i \Delta G_i^* + \Delta^m G_{mix} + 3RTX_1X_2 \qquad (6)$$

For ternary melts the correlation is (not consider the high order interaction)

$$\Delta G^* = \sum X_i \Delta G_i^* + \Delta^m G_{mix} + 3RT(X_1X_2 + X_2X_3 + X_1X_3) \qquad (7\text{-a})$$

or

$$\Delta G^* = \sum X_i \Delta G_i^* + RT\sum X_i \ln(X_i) + \Delta^E G_{mix} + 3RT(X_1X_2 + X_2X_3 + X_1X_3) \qquad (7\text{-b})$$

For a ternary silicate with two basic oxides, MO and YO, it is considered as a solution of two silicates, $zMO{\cdot}SiO_2$ and $zYO{\cdot}SiO_2$. Therefore the correlation is given as:

$$\Delta G^* = U_{zMO{\cdot}SiO_2}.\Delta G^*_{zMO{\cdot}SiO_2} + U_{zYO{\cdot}SiO_2}.\Delta G^*_{zYO{\cdot}SiO_2} + 3X_{MO}\cdot X_{YO}\cdot(1 - X_{SIo_2})\cdot\Delta^E G_{MIX} \qquad (8)$$

$$U_{zMo{\cdot}SiO_2} = \frac{X_{MO}}{X_{YO} + X_{MO}} \qquad (9\text{-a})$$

$$U_{zYo{\cdot}SiO_2} = \frac{X_{YO}}{X_{YO} + X_{MO}} \qquad (9\text{-b})$$

Combination of equation (1) and (7) or (8) enables us to estimate viscosity of ternary melts by using the Gibbs free energy of mixing and unary viscosities.

To obtain the Gibbs free energy of mixing, it is anticipated that most of the thermodynamic data of ternary and multi-component system will come from a theoretical

calculation rather than direct experimentation because of the difficult of experiment. Chou [8] presented a geometric model to calculation thermodynamic properties of ternary or multi-component system from binary data. From Chou's model, the excess Gibbs free energy of mixing is

$$\Delta G^{E} = \sum_{\substack{i,j=1 \\ i\neq j}}^{m} W_{ij}\Delta G_{ij}^{E} \qquad (10)$$

where ΔG^{E} represents the molar integration thermodynamic property for a multi-component system, ΔG^{E}_{ij} the molar thermodynamic property of an ij binary system, and W_{ij} the probability weight of ij binary.

$$W_{ij} = \frac{x_i x_j}{X_{i(ij)} X_{j(ij)}} \qquad (11)$$

The relationship between composition of components in a multicomponent system (x_i, i= 1-m) and the selected components of i in the ij binary system can be expressed as the following linear relation:

$$X_{i(ij)} = x_i + \sum_{\substack{k=1 \\ k\neq i,j}}^{m} x_k \xi_{i(ij)}^{k} \qquad (12)$$

where $\xi_{i(ij)}^{k}$ is referred to as the similarity coefficient of component k to component i in the ij binary system. It is defined as

$$\xi_{i(ij)}^{k} = \frac{\lambda(ij,ik)}{\lambda(ij,ik) + \lambda(ji,jk)} \qquad (13)$$

where $\lambda(ij,ik)$ is a function related to the excess Gibbs free energy of ij and ik binary systems. $\lambda(ij,ik)$ is defined as

$$\lambda(ij,ik) = \int_{X_i=0}^{X_i=1} (\Delta G_{ij}^{E} - \Delta G_{ik}^{E}) dX_i \qquad (14)$$

Combination of equation (1), (7 or 8) and (10) can calculate the ternary viscosity from unary viscosity and binary thermodynamic data. This viscosity model for ternary melts is:

$$\eta = \frac{hN\rho}{M}\exp((\sum_{i=1}^{3} x_i \Delta G_i + RT\sum_{i=1}^{3} x_i \ln(x_i) + \sum_{\substack{i,j=1 \\ i\neq j}}^{3} W_{ij}\Delta G_{ij}^{E} + 3RT\sum_{\substack{i,j=1 \\ i\neq j}}^{3} x_i x_j)/RT) \quad (15)$$

3 Application of the model

The viscosity of Ag-Au-Cu ternary system was estimated by the present model. The thermodynamic data of binaries and viscosity activation energy of unaries are chosen from literature [11,12] and [5] respectively. The results are shown in Fig.1.

As can be seen from Fig.1, the calculated results are consistent with the data of experimental measurement [10].

The viscosity of In-Sn-Bi and B_2O_3-SiO_2-FeO ternary systems have been calculated with this model, the results are shown in Fig.2 and Fig.3

4 Discussion

As can be seen from Fig.1, calculated viscosity of ternary system by using the model is consistent with the experimental results. Therefore, the large amount of thermodynamic data enables us to estimate or predict much more viscosity data to meet the need of today's technology and research.

Prediction of thermodynamic properties for ternary and multicomponent system from binary ones is the most attractive and powerful method among all theoretical methods because it is simple and effective and only requires information that is easy to obtain. Before Chou's model, all the models can be classified into two categories, symmetrical and asymmetrical. Both of them have their inherent problem. For a symmetric model, it can not reduce to a binary system if two of the three components are identical. For a asymmetrical model, there will be an undetermined factor about how to distribute three components into three apexes of a triangle. Chou's model breaks the boundary between symmetric and asymmetric models and simplifies various kinds of models to one.

While some binary data is not available, combination of the present model and Miedema's model [9] will enable us to calculate viscosity of ternary or multicomponent system from the fundamental physical properties of constituent elements and unary viscosity. If the viscosities of some ternary points are known, the parameters of estimation model can be modified with

considering the known values.

It has to be pointed, though Chou's model has advantages, it requires that the ternary system is homogeneous and the thermodynamic data of each binary. For a slag system, it is often not homogeneous and the integration Gibbs free energy along binaries is not convenient. Therefore, other method of thermodynamic calculation may be taking into consideration. However, while some ternary data are available, The data of one binary property can be projected by ternary data and the data of the other two binaries

5 Conclusion

The viscosity estimation model, base on the combination of Seetharaman's model and Chou's thermodynamic geometric model, has been deduced. The equation of the model is

$$\eta = \frac{hN\rho}{M}\exp((\sum_{i=1}^{3} x_i \Delta G_i + RT\sum_{i=1}^{3} x_i \ln(x_i) + \sum_{\substack{i,j=1 \\ i\neq j}}^{3} W_{ij}\Delta G_{ij}^{E} + 3RT\sum_{\substack{i,j=1 \\ i\neq j}}^{3} x_i x_j)/RT)$$

The viscosity of Ag-Au-Cu system has been calculated with the present model. The results are consistent with the experimental data. The viscosities of Bi-Sn-In and FeO-B_2O_3-SiO_2 system have also been predicted.

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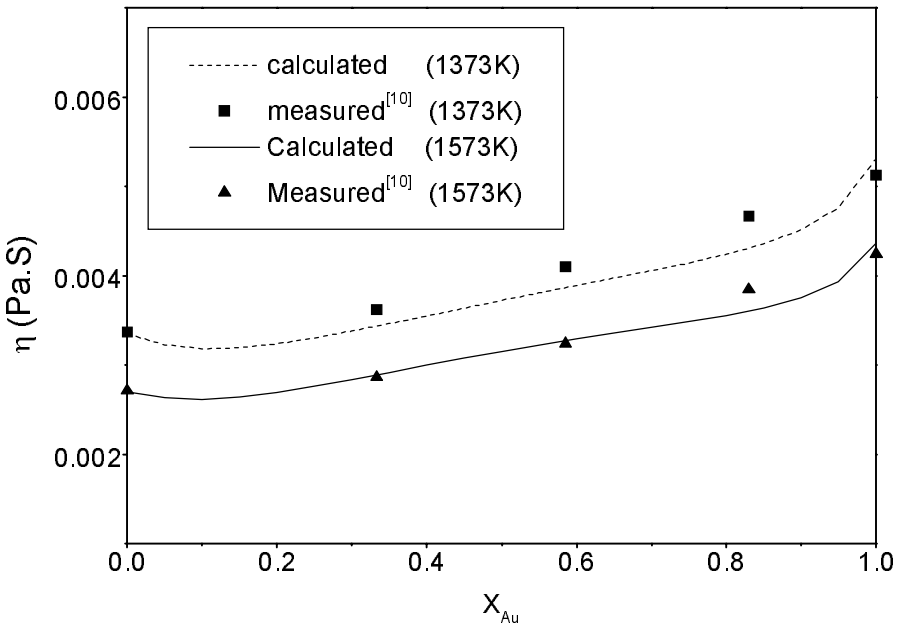

Fig.1 Viscosity of Ag-Au-Cu system (X_{Ag}/X_{Cu} = 0.52/0.48)

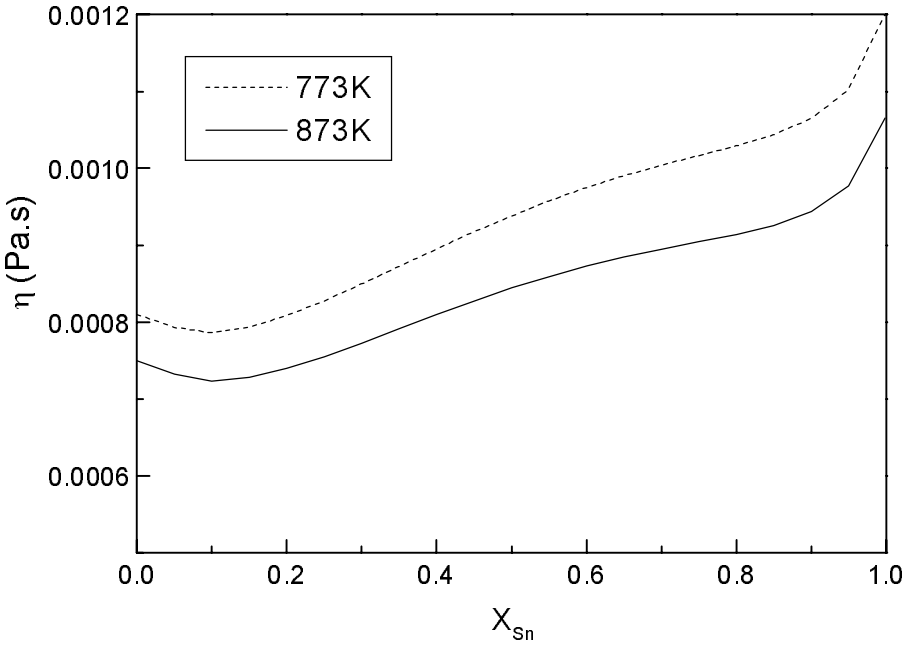

Fig.2 Viscosity Of Bi-Sn-In system (X_{Bi}/X_{In}=1)

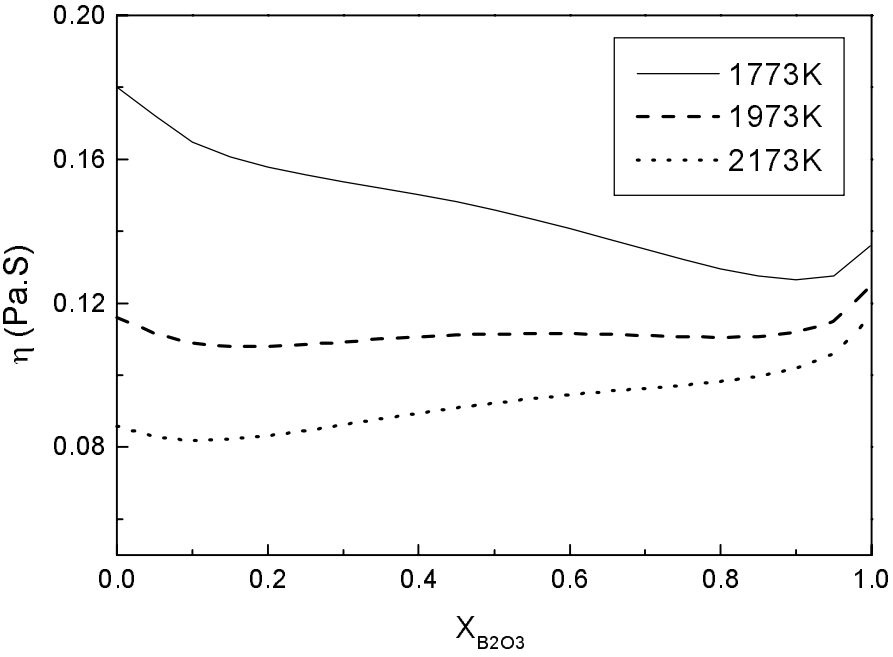

Fig.3 Viscosity Of FeO-B_2O_2-SiO_2 system (X_{FeO}/X_{SiO2}=1)