COMPUTER OPTIMIZATION OF DENSITY AND VISCOSITY FOR BINARY METALLIC MELTS①

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ABSTRACT By applying algebraic formulae which correlate the density with temperature and chemical composition, computer fitting has been carried out on the the experimental data of densities for binary metallic melts. The relationship between activation energy of viscous flow, temperature and composition has been formularized analogously to that for the integral molar Gibbs energy. The semiemperical model has been successfully applied to calculate the viscosity and kinematic viscosity for various binary metallic melts.

Key words: metallic melts viscosity computer optimization

1 INTRODUCTION

Viscosity in high temperature melts is one of the most important physical properties required for predictions of kinetics and dynamic control in metallurgical processes. The high melting temperatures of these melts make experimental measurements of the physical properties more difficult. The experimental data available in some systems exhibit obvious diversity and can only cover a small range of chemical composition and temperature. The theoretical approach based on micro-structure of the melts at high temperature now seems far from satisfaction. Contrastively, semi-emperical techniques are most frequently used.

The following equation has been commonly used to estimate viscosities for pure liquid substances[1]:

$$\eta = A \cdot e^{E_\eta/RT} \quad (1)$$

where E_η stands for the activation energy of viscous flow. More detailed investigations have indicated that E_η varies with temperature as well as chemical composition for metallurgical melts at high temperature.

Du Sichen *et al*[2] have developed a model to evaluate viscosities for high temperature ionic melts. For unary systems, the viscosity can be estimated by the following equation[3]:

$$\eta_i = \frac{hN}{V_m} e^{\Delta G_i^{\neq}/RT} \quad (2)$$

where h is the Plank's constant; N is the Avagadro's number; V is molar volume.

Eqn. (2) can be rewritten as:

$$\eta_i = \frac{hN\rho_i}{M_i} e^{\Delta G_i^{\neq}/RT} \quad (3)$$

where ρ_i is density of i; M_i is molecular weight of i.

For binary systems, the viscosity can be expressed as:

$$\eta = \frac{hV\rho}{M} e^{\Delta G^{\neq}/RT} \quad (4)$$

where M is molecular weight for the mixture of the system, $M = \Sigma M_i \cdot X_i$; ρ is density of the solution. In Ref. [2], ρ was estimated as a linear summation of the densities of pure components. The activation energy of viscous flow in Ref. [2] was described by expressions analogous to those for the integral molar Gibbs energy in ionic melts[4], so that $\Delta G^{\neq}$ correlated with temperature and chemical composition in these systems.

In present work, the dependence of viscosity on temperature and chemical composition in metallic melts has been investigated and described by expressions analogous to those for integral molar Gibbs energy in metallic systems. The model has been applied

① Supported by National Natural Science Foundation of China Received Mar. 14, 1994; accepted in revised form Jul. 10, 1994

to fit and optimize the experimental data of viscosity in various binary metallic melts. Computer optimized density values were employed in the above evaluations. The combination of the calculations for viscosity and density has provided the optimized kinematic viscosity data for the metallic systems.

2 OPTIMIZATION OF DENSITIES

The density for a pure liquid metal exhibits a linear relationship with temperature:

$$\rho = a + b \cdot T \tag{5}$$

$$\rho = a_m + b(T - T_m) \tag{6}$$

where T_m represents melting temperature; a, b, a_m are constants.

In binary metallic melts, relationship of density with chemical composition can be presented by the following polynomial equation:

$$\rho = \sum_{k=0}^{n} D_k \cdot X^k \tag{7}$$

where $k = 0, 1, 2, \cdots$, X, represents the mole fraction for one component. In general, with the first two or three terms, satisfactory accuracy can be reached. The temperature dependence of D_k may be formulated as:

$$D_k = {}^0D_k + {}^1D_kT + {}^2D_kT\ln T \tag{8}$$

or as the following alternative equation:

$$D_k = {}^0D_k + {}^1D_kT + {}^2D_kT^2 \tag{9}$$

3 MODEL FOR ACTIVATION ENERGY OF VISCOUS FLOW

The activation energy for a pure liquid metal can be expressed as follows:

$$\Delta G_i^{\neq} = a + bT + cT\ln T \tag{10}$$

In order to determine the quantitative relationship of the activation energy with temperature and chemical composition, analogous methodology has been employed.

The integral molar Gibbs energy for ideal solution is described as:

$$G_m = \sum_i X_i\bar{G}_i + RT(\Sigma X_i\ln X_i) \tag{11}$$

By analogy, the following expression has been tested:

$$\Delta G^{\neq} = \sum_i X_i\Delta G_i^{\neq} + RT(\Sigma X_i \cdot \ln X_i) \tag{12}$$

where $\Delta G_i^{\neq}$ represents the activation energy for pure liquid metals. The maximum of the relative deviations between calculated and experimental values can reach 50%. Further, the following analogous expression for the G_m in regular solution has been applied:

$$\Delta G^{\neq} = X_1\Delta G_1^{\neq} + X_2\Delta G_2^{\neq} + RT(X_1\ln X_1 + X_2\ln X_2) + \Delta^E G^{\neq} \tag{13}$$

$$\Delta^E G^{\neq} = X_1X_2L \tag{14}$$

where L depends on temperature for a specific system; $\Delta^E G^{\neq}$ may be defined as excess activation energy. The maximum of the relative deviations between the values calculated using Eqns. (13), (14) and experimental data has been reduced to a level of 20%~30%.

Magules model and Redlich formulae[5] seem more sophisticated than the regular solution model in correlating G_m with temperature and composition. By the following expressions of $\Delta^E G^{\neq}$, the experimental data for viscosity in binary metallic melts can be optimized:

$$\Delta^E G^{\neq} = X_1X_2\sum_{k=0}^{n} {}^kL(X_1 - X_2)^k \tag{15}$$

$${}^kL = {}^kL_0 + {}^kL_1T + {}^kL_2T\ln T + \cdots \tag{16}$$

In general, the relative deviations between calculated and measured values can be reduced to a level lower than the measured error by taking $n = 1$ or $n = 2$ in Eqn. (15) and the first three terms in Eqn. (16). In a few systems, the fourth term in Eqn. (16) has to be included.

4 CALCULATION RESULTS

4.1 *Density*

In present study, experimental data of density in various binary metallic melts have been satisfactorily fitted using Eqns. (7), (8). Au-Ag system can be taken as an example. The results of the optimization for the density data measured by Gebhardt[6] gave the following equation:

$$\begin{aligned}\rho = {} & 8.203 + 1.052 \times 10^{-2}T \\ & - 1.363 \times 10^{-3}T\ln T \\ & + (14.457 - 1.351 \times 10^{-2}T \\ & + 1.296 \times 10^{-3}T\ln T)X_{Au} \\ & + (7.691 - 8.244 \times 10^{-3}T \\ & - 8.149 \times 10^{-4}T\ln T)X_{Au}^2\end{aligned} \tag{17}$$

The maximum of the relative deviations

between the calculated and measured data in Au-Ag system is less than 1%. Fig. 1 exhibits a comparison between the calculated and experimental data of density in Au-Ag system at 1 573 K.

4.2 *Viscosity*

As a model, the combination of Eqns. (4), (7), (9), (15) and (16) has been applied for the evaluation of viscosity in various binary metallic melts. Again, taking Au-Ag system as an example, the following equations for $\Delta^E G^{\neq}$ have been obtained by the optimization of the experimental data measured by Gebhardt[7].

$$\Delta^E G^{\neq} = \frac{1}{X_{Au}X_{Ag}} \sum_{k=0}^{2} {}^kL(X_{Au} - X_{Ag})^k \quad (18)$$

Where

$${}^0L = 40\,740 + 5.430\,T + 0.160\,9\,T\ln T - 3.098 \times 10^{10}\,T^{-2} \quad (18\text{-}1)$$

$${}^1L = 16\,220 + 0.247\,1\,T - 0.977\,2\,T\ln T - 1.345 \times 10^{10}\,T^{-2} \quad (18\text{-}2)$$

$${}^2L = -568\,500 + 14.75\,T + 35.02\,T\ln T + 4.217 \times 10^{10}\,T^{-2} \quad (18\text{-}3)$$

The maximum of the relative deviations between the calculated results and measured data[7] has been reduced to 3.8%. Fig. 2 reveals a comparison between calculated viscosity values and measured data in Au-Ag system.

Liquid Pb-Sn system has been considered as two sub-systems, the Sn-poor side and the Sn-rich side. The optimized expressions for $\Delta^E G^{\neq}$ in the sub-systems using the data measured by Fisher *et al*[8] are presented in Eqns. (19-1)～(19-7).

$$\Delta^E G^{\neq} = \frac{1}{X_{Pb}X_{Sn}}[{}^0L + {}^1L(X_{Sn} - X_{Pb}) + {}^2L(X_{Sn} - X_{Pb})^2] \quad (19\text{-}1)$$

For Sn-poor side:

$${}^0L = 139\,600 - 1\,554\,T + 211.5\,T\ln T \quad (19\text{-}2)$$

$${}^1L = 426\,200 - 4\,846\,T + 650.7\,T\ln T \quad (19\text{-}3)$$

$${}^2L = 363\,500 - 4\,026\,T + 540.4\,T\ln T \quad (19\text{-}4)$$

For Sn-rich side:

$${}^0L = 382\,300 + 938.7\,T - 163.8\,T\ln T - 1.457 \times 10^8/T \quad (19\text{-}5)$$

$${}^1L = -2\,023\,000 - 4\,930\,T - 876.9\,T\ln T + 7.768 \times 10^8/T \quad (19\text{-}6)$$

$${}^2L = 3\,147\,000 + 8\,844\,T - 1\,526\,T\ln T - 1.244 \times 10^8/T \quad (19\text{-}7)$$

The maximum of the relative deviations between calculated values and experimental data of viscosity is approximate to 2% for the Sn-poor side and 1% for the Sn-rich side. Fig. 3 illustrates a comparison of the viscosity values calculated using the model with the experimental data[7] for the Sn-poor side, and Fig. 4 presents the same for the Sn-rich side in Pb-Sn system.

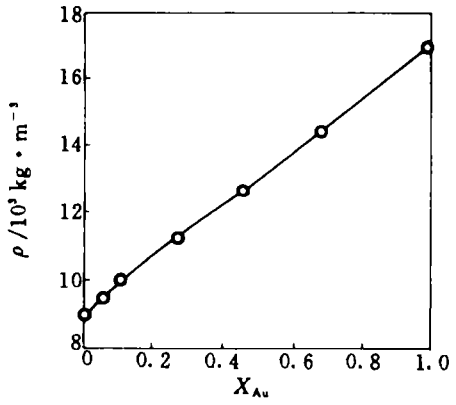

Fig. 1 Variation of density with mole fraction of Au in Au-Ag system(1 573 K)

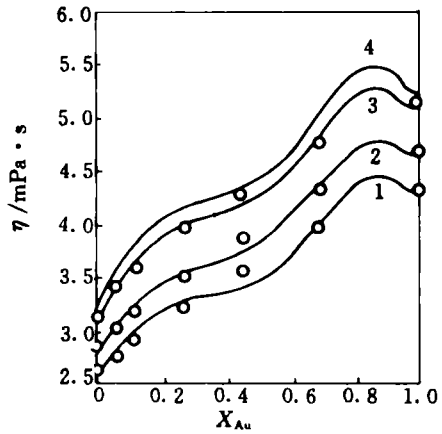

Fig. 2 Variation of viscosity with mole fraction of Au in Au-Ag system

1— T =1 573 K; 2— T =1 473 K; 3— T =1 373 K; 4— T =1 343 K

In present study, the combination of the optimized viscosity and density values in the metallic melts yields the optimized kinematic viscosity data for the same systems which as we know are important parameters for kinetics study in process metallurgy. The variation of the calculated kinematic viscosity with the mole fraction of Au at 1 573 K in Au-Ag system is presented in Fig. 5.

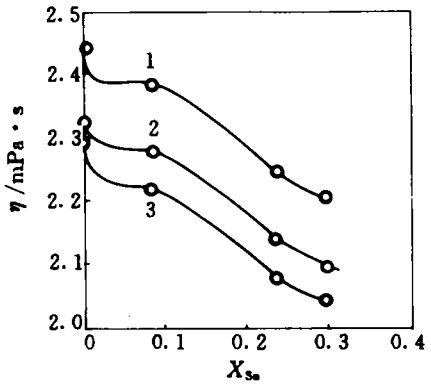

Fig. 3 Variation of viscosity with mole fraction of Sn for Sn-poor side in Pb-Sn system

1— T =623 K; 2— T =653 K; 3— T =673 K

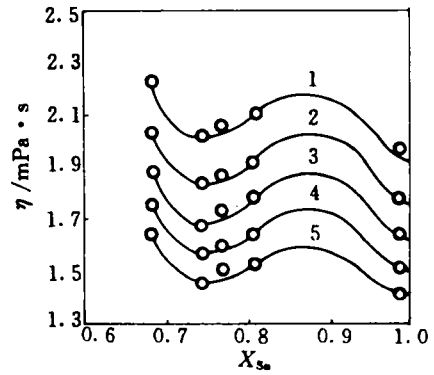

Fig. 4 Variation of viscosity with mole fraction of Sn for Sn-rich side in Pb-Sn system

1— T =513 K; 2— T =553 K; 3— T =593 K; 4— T =623 K; 5— T =673 K

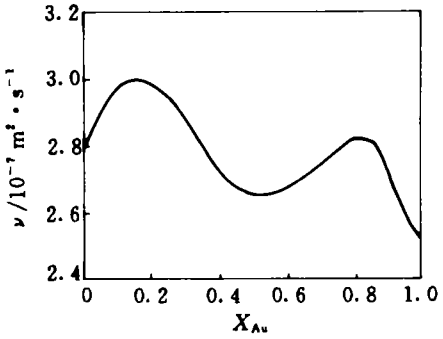

Fig. 5 Variation of kinematic viscosity with X_{Au} in Au-Ag system at 1 573 K

5 CONCLUSIONS

A model correlating activation energy with temperature and composition has been applied to evaluate the viscosity in binary metallic melts. The optimizations of the experimental viscosity data for binary metallic systems have given satisfactory results. The optimized density data was employed in the calculations, indicating an approach for the optimization of kinematic viscosity for high temperature metallic melts.

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