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Review

The viscosity of liquid alloys of polyvalent metals with Cu, Ag and Au: Theoretical treatments based on the enthalpy of mixing

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ABSTRACT

The variation of the viscosity of liquid Cu-, Ag- and Au-based alloys with the composition is discussed with special emphasis on the influence of atomic interactions. The classical rigid-sphere description is extended to the case of interacting particles by adding an extra term based on the enthalpy of mixing. The agreement with the experimental viscosity isotherms is found to be reasonable. The results are compared with semi-empirical considerations based on simple physical quantities such as the diameter of the core atoms, the atomic mass, the atomic volume and the melting temperature of the constituent elements combined with the experimental enthalpy of mixing as basic input quantity. The assessment is not conclusive but the simple semi-empirical approaches appear to be well adapted to give a likewise good interpretation of the excess viscosity in liquid alloys.

Contents

1. Introduction

Numerous efforts have been made to improve the theoretical understanding of the atomic transport in liquid matter. Some of the theories assess the situation as that of a non-interacting rigid-sphere fluid [1–3] while others consider oscillating long-range potentials in order to include weak interactions [4–6]. A few papers are concerned with a short review of the developments in theory [7,8].

One of the most interesting features is the variation of the viscosity with the composition of the alloys. The majority of the currently used viscosity models are of semi-empirical nature focused on thermodynamic quantities such as the enthalpy of mixing [9–14], the free energy of mixing [15,16] or the thermodynamic activity coefficients [17,18]. Another group of models is based on some fundamental properties of the constituent elements or even exclusively on purely semi-empirical factors [19–21]. Many of the semi-empirical approaches apply adjustments which are successful in reproducing the experimental viscosity vs. composition curves but also fail to have a clear physical meaning. Here, those models which apply adjustment parameters varying from one system to the other will not be concerned.

More profound theories, as for instance the small-step theory of Rice and Alnatt [4–7], are expected be free from such empirical ingredients. However, previous pseudopotential-based calculations indicated relevant departures of the theoretical viscosities of the pure elements from the experimental values [22]. After appropriate adjustments the shape of the viscosity isotherms was found to be well reproduced by such an elaborate theory. On the other hand, for a first estimate of the viscosity, the high computational effort needed to evaluate such full theories is probably not justified.

The models based on the rigid-sphere approach [1–3], although easier to handle, are physically unrealistic since they

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disregard the atomic interactions as they are indicated in most of the systems under investigation. This paper will focus on those models which take account of the interactions by considering the enthalpy of mixing as representative input parameter. The most frequently cited relation is that suggested by Moelwyn-Huges [9] which relates the excess viscosity η^{xs} (i.e. the deviation of the viscosity from the linear value, $\eta-\eta_{add}$) at the reference temperature T to the enthalpy of mixing, H^m, according to

$$\eta^{xs} = -\eta_{add}\frac{2H^m}{RT} \tag{1}$$

In this context, exothermic heats of mixing ($H^m<0$) would imply positive excess viscosities and vice versa. As matter of fact, it has been illustrated that even qualitatively there are more than just a few exception to this simple rule [23]. More recent semi-empirical models are concerned a larger number of physical quantities and include such an enthalpy-based interaction term with a different, preferably much smaller weighing factor [10–14].

2. Theory

One of the most convenient models is the semi-empirical approach proposed by Iida and coworkers [10,11] which assigns the excess viscosity of a binary liquid to the superposition of a hard core contribution determined by the diameters (σ_1,σ_2), the masses of the atoms (m_1,m_2), and a soft part represented by the enthalpy of mixing, H^m. In the original three-parameter model the ratio of η^{xs}/η_{add} at a given temperature T reads as

$$\frac{\eta^{xs}}{\eta_{add}} = \alpha\frac{x_1x_2(\sigma_1-\sigma_2)^2}{x_1\sigma_1^2+x_2\sigma_2^2} + \beta\frac{x_1x_2}{2}\left(\frac{m_1^{1/2}-m_1^{1/2}}{x_1m_1^{1/2}+x_2m_1^{1/2}}\right)^2 + \gamma\frac{2H^m}{RT} \tag{2}$$

The compositions of the alloys are given by the respective atomic fractions (x_1,x_2). Here, the second term on the right hand side is a simplified version of the original expression given by Iida et al. [10,11]. The best fit is obtained if the diameters σ_1 and σ_2 are taken as those of the ionic cores. The statistical weights α, β, γ are not to be understood as adjustable to individual systems, they are considered as universal parameters. Based on the assessment of some representative systems Morita et al. [11] arrived at values of $\alpha=-5.0$, $\beta=2.0$ and $\gamma=-0.12$. In this paper, an extended four-parameter version will be adopted.

The most convenient model used here is based on the unified equation for the viscosity of pure liquid metals formulated by Kaptay [21]. The only information needed to predict the viscosity is the melting temperature T_m, the atomic mass m, and the molar volume V of the metal under consideration. The extension to the case of multi-component systems involves the volume of mixing V^{xs} and the enthalpy of mixing H^m as additional input parameters [14,21]:

$$\eta = A\frac{\left(\sum_i x_im_i\right)^{1/2}}{\left(\sum_i x_iV_i+V^{xs}\right)^{2/3}}T^{1/2}\exp\left[\frac{B}{T}\left(\sum_i x_iT_{m,i}-\frac{H^m}{qR}\right)\right] \tag{3}$$

Provided all quantities are given in SI units, the average values of the generally valid parameters are quoted to be $A=1.80\times10^{-8}$, $B=2.34$ and $q=25.4$. This approach has been successfully tested on a series of metallic alloy systems. Special attention has to be paid to semi-metals since in these particular cases chemical bonding and coordination of the liquid state are definitely different from the solid state. Strictly, the melting temperature of the semi-metals is assumed to be not representative of the cohesion energy of the hypothetical metallic solid. For Ge, Sb and Bi the corrected melting temperatures proposed by Kaptay [21] were employed.

The main concern of the paper is on the rigid-sphere approach put forward by Enskog [1] that has been extended to the case of a two-component mixture (i,$j=1$,2) by Tham and Gubbins [3]. The basic expression for the hard-sphere viscosity is

$$\eta_E = \frac{1}{2}\sum_{i=1}^{2}n_ikTb_{i0}^1\left(1+\frac{4}{5}\sum_j M_{ij}\rho b_{ij}g_{ij}(\sigma_{ij})\right) + \frac{4}{15}\sum_i\sum_j\left(\frac{2\pi kTm_im_j}{m_i+m_j}\right)^{1/2}n_in_jg_{ij}(\sigma_{ij})\sigma_{ij}^4 \tag{4}$$

The basic input quantities of the theory are the number densities (n_i,n_j), the average mass density ρ, the masses of the atoms (m_i,m_j), and the values of the respective pair distribution functions at contact $g_{ij}(\sigma_{ij})$. The hard sphere diameters (σ_{ii},σ_{jj}) are different from those to be used in Eq. (2), they were considered as temperature dependent being determined by the empirical relation [25]

$$\sigma_{ii} = \sigma_{m,i}\left[1.126-0.126\left(\frac{T}{T_{m,i}}\right)^{1/2}\right] \tag{5}$$

The hard sphere diameters of the pure components at the melting point, σ_{mi}, are determined by the assumption that the packing fractions at the melting point T_m adopt the typical value of $\xi=0.47$. The reduced mass M_{ij} and the quantity b_{ij} are given as

$$M_{ij} = m_i/(m_i+m_j) \tag{6}$$

$$b_{ij} = 2\pi n_j\sigma_{ij}^3/3\rho \tag{7}$$

The magnitude of b_{i0}^1 can be derived from the identity $\sum_j H_{ij}b_{j0}^1 = K_i$ provided H_{ij} and K_i are evaluated with the help of the following relations:

$$K_i = 5n_i\left(1+\frac{4}{5}\sum_j M_{ji}b_{ij}\rho g_{ij}(\sigma_{ij})\right) \tag{8}$$

$$H_{ij} = \sum_l\frac{\sigma_{il}^2n_in_lg_{il}(\sigma_{il})}{(m_i+m_l)^{3/2}}\left(\frac{2\pi kTm_l}{m_i}\right)^{1/2}\left(\frac{40}{3}m_i\delta_{ij}+8m_l\delta_{ij}-\frac{16}{3}m_i\delta_{jl}\right) \tag{9}$$

It has been pointed out that the viscosity obtained for such a rigid-sphere fluid is not exactly correct and needs an adaptation to the case of real systems [24,25]. Different attempts based on different physical backgrounds have been made to calculate the correction factor $f=\eta/\eta_E$ as function of the packing density ξ. A review of the different sets of values is given by Protopapas et al. [26].

Throughout the paper, the enthalpies of mixing were taken from the literature [27], however, at reference temperatures which were in general not the same as those of the viscosity measurements. The volumes of the pure elements (V_1,V_2) at the given reference temperature were deduced from the data compiled by Crawley [28]. The influence of the volume of mixing on the viscosity was considered to be insignificant and the error introduced by disregarding the temperature dependence of the enthalpy of mixing was assumed to be small only.

3. Results and discussion

Five Cu-based systems (Cu–Al, Cu–Bi, Cu–Pb, Cu–Sb and Cu–Sn), four Ag-based systems (Ag–Ge, Ag–In, Ag–Sb and Ag–Sn) and one Au-based system (Au–Sn) were taken into consideration. The calculated viscosity isotherms are shown in Figs. 1–10 together with the experimental results. Experimentally, throughout the series of alloys the excess viscosities adopt negative values, excepting maybe the case of Cu–Al where only a smaller