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A pseudopotential approach to the viscosity of liquid Cu-based alloys

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ABSTRACT

A pseudopotential method was applied to calculate the composition dependence of the viscosity in liquid alloys of Cu–Al, Cu–Sn, Cu–Sb, Cu–Pb and Cu–Bi. A new approach is introduced to solve the problem of integration over diverging integrands. In accordance with the experimental findings, the deviations of the viscosities from the additive law were found to be negative for all systems under investigation. A semi-empirical consideration based on fundamental physical quantities combined with the enthalpy of mixing as measure of the interactions between the constituent atoms was included in the discussion.

1. Introduction

Numerous theories are used to explain the composition dependence of the viscosity in liquid alloys. Most of them make use of either semi-empirical parameters fitted to the viscosities of the pure constituents or of experimental thermodynamic quantities in order to explain the deviations from additivity. Particular interest is given to the enthalpy of mixing which is assumed to reflect the interactions between the particle of the liquid and thus to be responsible for the excess viscosity in a binary alloy. According to Moelwyn-Huges [1] exothermic enthalpies of mixing are expected to be associated with positive deviations from the additive law (i.e. with positive excess viscosities) and vice versa:

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

However, the obvious lack of a general correlation between the sign of the enthalpy of mixing and that of the excess viscosity casts doubt on such a simple relationship.

In a previous article [2] the excess viscosities of 53 binary alloy systems have been analyzed in terms of the semi-empirical model proposed by Iida et al. [3]. The theory of Takeuchi and Iida focused on the momentum transfer due to collisions between oscillating atoms [4] and the approach of rigid-sphere fluids extended to multicomponent systems by Tham and Gubbins [5] have also been taken into consideration.

On a very rough scale, the divergencies between these physically different models were assumed to depend on whether the interactions between the particles (via the enthalpies of mixing) are included in the models or not. However, it has also been suggested that alloys of noble metals with polyvalent metals do not generally fit into the picture because of their ambiguous character concerning the atomic interactions. In many of these systems, the enthalpies of mixing adopt negative values on the noble metal side, whereas on the polyvalent metal side positive values may occur. Typical examples are those of Cu–Ge, Cu–Sn, Cu–Sb, Ag–Ge, Ag–Sn and Ag–Sb [6].

The majority of simple empirical models applied in literature have their merits since not much information is needed to arrive at good estimates of the viscosity in a binary system. One of the more elaborate models is that put forward by Rice and Alnatt [7] which broadens the theory of rigid-sphere fluids by including a soft attraction due to a weak long-range potential. In this paper, the formalism worked out by Katajima et al. [8] will be applied to find out whether those alloys based on noble metals can be explained by such a more elaborate theory without the requirement of taking account of the heat of mixing.

The results will be compared with the statistical approach of Iida et al. [3] which is based on simple physical quantities such as diameter, mass, and volume of the constituent atoms and the experimental enthalpies of mixing.

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2. Theory

The notations applied in this paper are those used by Katajima et al. [8] and Bhuiyan et al. [9] for a binary mixture of α and β atoms. The fundamental input parameters are the hard sphere diameters $\sigma_{\alpha\alpha}$ and $\sigma_{\beta\beta}$, the atomic masses m_α and m_β, the number densities n_α and n_β, the respective pair distribution functions $g_{\alpha\beta}(r)$, and the effective pair potentials $u_{\alpha\beta}(r)$.

According to the theory, the total viscosity is made up of a kinetic part, a part due to hard sphere collisions, and one due to soft long-range interactions:

$$\eta = \eta_\mathrm{k} + \eta_\mathrm{v}(\sigma) + \eta_\mathrm{v}(r > \sigma) \tag{2}$$

If ζ_α^S and ζ_β^S denote the friction coefficients and $g_{\alpha\beta}(\sigma_{\alpha\beta})$ are the respective pair distribution functions at contact, then the kinetic viscosity η_k, the hard core contribution $\eta_\mathrm{v}(\sigma)$ and the soft part $\eta_\mathrm{v}(r>\sigma)$ can be expressed as

$$\eta_\mathrm{k} = \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2} \frac{5k_\mathrm{B}T}{8g_{\alpha\beta}(\sigma_{\alpha\beta})} \frac{1 - 4\pi n_\beta g_{\alpha\beta}(\sigma_{\alpha\beta})\sigma_{\alpha\beta}^3/15}{(4\pi k_\mathrm{B}T/m_\alpha)^{1/2}\sigma_{\alpha\beta}^2 + [\zeta_\alpha^\mathrm{S}/4m_\alpha n_\beta g_{\alpha\beta}(\sigma_{\alpha\beta})]} \tag{3}$$

$$\eta_\mathrm{v}(\sigma) = \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2} \left[\frac{5k_\mathrm{B}T}{36} \frac{m_{\alpha\beta}n_\beta}{m_\alpha n_\beta} \frac{12\pi n_\alpha \sigma_{\alpha\beta}^3/5g_{\alpha\beta}(\sigma_{\alpha\beta}) + (4\pi n_\beta \sigma_{\alpha\beta}^3/5)^2}{(4\pi k_\mathrm{B}T/m_\alpha)^{1/2}\sigma_{\alpha\beta}^2 + [5\zeta_\alpha^\mathrm{S}/4m_\alpha n_\alpha g_{\alpha\beta}(\sigma_{\alpha\beta})]} + \frac{8\pi k_\mathrm{B}T}{15} \frac{n_\alpha n_\beta g_{\alpha\beta}(\sigma_{\alpha\beta})\sigma_{\alpha\beta}^6}{(4\pi k_\mathrm{B}T/m_\alpha)^{1/2}\sigma_{\alpha\beta}^2} \right] \tag{4}$$

$$\eta_\mathrm{v}(r > \sigma) = 4\pi \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2} \frac{m_{\alpha\beta}}{30} \left(\frac{1}{\zeta_\alpha^\mathrm{S}} + \frac{1}{\zeta_\beta^\mathrm{S}} \right) X_{\alpha\beta} \quad (\text{for}\, \alpha \le \beta) \tag{5}$$

The quantity $m_{\alpha\beta}$ is the reduced mass of m_α and m_β, $\sigma_{\alpha\beta}$ denotes the arithmetic mean of σ_α and σ_β. The friction coefficients ζ_α^S and ζ_β^S are solved to satisfy the simultaneous equations:

$$\zeta_\alpha^\mathrm{S} = n_\alpha \zeta_{\alpha\alpha}^\mathrm{S} + n_\beta \zeta_{\alpha\beta}^\mathrm{S} \tag{6}$$

$$\zeta_{\alpha\beta}^\mathrm{S} = \left(\frac{1}{\zeta_\alpha^\mathrm{S}} + \frac{1}{\zeta_\beta^\mathrm{S}} \right) c_{\alpha\beta} \tag{7}$$

The crucial part of the theory is the calculation of the quantities $X_{\alpha\beta}$ and $c_{\alpha\beta}$ which are obtained by an integration over the sum of the first derivative $u'_{\alpha\beta}(r)$ and the second derivative $u''_{\alpha\beta}(r)$ of the effective potential with respect to r:

$$X_{\alpha\beta} = n_\alpha n_\beta \int_{\sigma_{\alpha\beta}}^{\infty} \left[u'_{\alpha\beta}(r) + \frac{4}{r} u'_{\alpha\beta}(r) \right] g_{\alpha\beta}(r) r^4 \,\mathrm{d}r \tag{8}$$

$$c_{\alpha\beta} = \frac{m_{\alpha\beta}}{3} \int_{\sigma_{\alpha\beta}}^{\infty} \left[u''_{\alpha\beta}(r) + \frac{2}{r} u'_{\alpha\beta}(r) \right] g_{\alpha\beta}(r) r^2 \,\mathrm{d}r \tag{9}$$

The most critical point of the evaluation is that due to the weighing factor of r^4 the integrand of $X_{\alpha\beta}$ tends to diverge for large distances, but on the other hand the integration has to be extended to such high values so as to arrive at stable values of physical significance. This problem has been discussed extensively by Bhuiyan et al. [9]. In this paper, a well behaved integration could be achieved if the effective potential is made to decay exponentially from 5 to 10 times the distance of the hard core diameter. More details of the problem and the adopted procedure to arrive at a controlled integration are given in Appendix A.

The construction of the effective potentials was achieved in conventional manner by integrating over the normalized wave number characteristics F^N according to

$$u_{\alpha\beta}(r) = \frac{Z_\alpha Z_\beta}{r} \left[1 - \frac{2}{\pi} \int_0^\infty F_{\alpha\beta}^\mathrm{N} \frac{\sin(qr)}{q} \,\mathrm{d}q \right] \tag{10}$$

The wave number characteristics, in turn, depends on the form factors $w_\alpha(q)$ and $w_\beta(q)$ which result from the model pseudopotential selected to represent the physical system:

$$F_{\alpha\beta}^\mathrm{N} = \frac{q^4}{16\pi^2 n^2 Z_\alpha Z_\beta} w_\alpha(q) w_\beta(q) \left[1 - \frac{1}{\varepsilon(q)} \right] \left[\frac{1}{1 - G(q)} \right] \tag{11}$$

Owing to their optimum transferability to various systems, the pseudopotentials proposed by Bachelet et al. [10] were assumed to be representatives. Z_α and Z_β are the valencies of the constituents, q is the momentum transfer vector, and n denotes the average number density. $\varepsilon(q)$ is the Hartree dielectric screening function and $G(q)$ is the correction factor taking account of exchange-correlation. The values of $G(q)$ used here were taken from the paper Vashista and Singwi [11].

The radial distribution functions $g_{\alpha\beta}(r)$ were identified with those of hard sphere mixtures [12]. The hard sphere diameters were derived from the empirical relation proposed by Protopapas and Parlee [13]:

$$\sigma(T) = 1.126\,\sigma_\mathrm{m} \left[1 - 0.112 \left(\frac{T}{T_\mathrm{m}} \right)^{1/2} \right] \tag{12}$$

σ_m is the hard sphere diameter at the melting point T_m where the packing fraction is assumed to be 0.472. The volumes of the pure elements were taken from the compilation of Crawley [14], those of the alloys were always assumed to be additive. Actual volumes are not always available and their use instead of the ideal ones yielded only minor corrections, therefore the effect of mixing on the volume of the alloys was disregarded throughout the paper.

3. Results and discussion

From the thermodynamic point of view, the binary systems considered in this paper are very different. Some of them are more or less compound forming systems (Cu–Al, Cu–Sn and Cu–Sb), others show a pronounced tendency towards demixing (Cu–Pb and Cu–Bi).

The paper is primarily concerned with the variation of the viscosity with composition at a given reference temperature. Due to the large difference in melting temperature of the elemental constituents the results were not always available at one given temperature, in such cases the viscosities had to be extrapolated to the reference temperature. Thus, in particular case of Cu, the experimental value used for undercooled liquid Cu serves as crude estimate only.

Even if the uncertainty of the experimental data is taken into account, the calculations yielded viscosities very different from the experimental values. The results obtained for the pure elements are listed in Table 1 together with the experimental viscosities. For all elements under consideration, the kinetic contribution turned out to be small compared to the total viscosity ($\eta_\mathrm{k} < 0.12$ mPa s). The viscosity of liquid Cu is primarily determined by the hard core part $\eta_\mathrm{v}(\sigma)$ whereas for some of the polyvalent metals (Al, Sn and Bi) the soft part $\eta_\mathrm{v}(r>\sigma)$ gives the greater contribution. It is worthwhile to note that the values obtained for liquid Sn are different from those quoted in literature [15] ($\eta_\mathrm{k} = 0.019$ mPa s, $\eta_\mathrm{v}(\sigma) = 0.215$ mPa s,