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Theoretical calculations of the surface tension of $Ag_{(1-x)}$–$Cu_{(x)}$ liquid alloys

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ABSTRACT

The surface tension of silver–copper binary liquid alloys is calculated, in the frame work of Eyring theory. The calculations were made for different compositions (mole fraction, x_{Cu} = 0, 0.2, 0.4, 0.6, 0.8 and 1), in the temperature range 1100–1800 K. The surface tension decreases with temperature increase, at a fixed copper fraction x_{Cu}, and increases with increasing copper content. The calculated results are appropriately compared with existing literature data.

1. Introduction

Thermophysical properties, such as surface tension, of molten alloys play an important role in understanding the thermodynamic state of the liquid and in analyzing and understanding many metallurgical processing operations [1–8]. Its dependence on temperature leads to the Marangoni convection, that plays a central role in casting and welding processes. The silver–copper alloys are widely utilized for joining ceramics [9,10], as well as metallic materials [11,12] using brazing techniques that require reliable values of surface tension and the effects of different high-temperature phenomena accompanying brazing (the melting temperature of the Ag–Cu eutectic is 1052 K) because the surface tension is a property of an alloy which is crucial in describing its wetting behavior on the surfaces of brazed parts. A literature survey on the surface tension of binary Ag–Cu liquid alloys shows a scatter in data [13–17] because liquid metals are difficult to handle due to the high temperatures and their high reactivity because they tend to oxidize which dramatically changes the optical, thermal, and mechanical properties of the surface. Therefore, many attempts have been made to predict the surface tension of liquid metals and alloys, such as computer simulation with Monte Carlo or molecular dynamics methods [18] and models based on Butler's concept [19,20]. The surface tension of several liquid alloys in a wide composition and temperature ranges has been determined experimentally, and has been modeled using the theoretical approach of Butler [21,22]. Note that many models (regular solutions, sub-regular solutions, compound forming models and self aggregating model) are based on Butler's concept, while some probabilistic models [23], (for example, R.N. Singh work and Monte Carlo and molecular dynamics models) are not based on Butler's approach.

This paper represents an attempt to calculate the surface tension of liquid Ag_{x-1}–Cu_x alloys and its composition and temperature dependences in the framework of Eyring theory for pure metals [24], extending its formalism to liquid binary alloys [25]. The calculated results are compared with the available literature data.

2. Theory

In a substitutional alloy, atoms of the solute (the minor component) occupy sites in the lattice of the solvent metal (the element in excess). To maintain the original lattice structure of the host metal, atoms of both components should be of a similar size. The solute atoms must also tolerate the same coordination environment as atoms in the host lattice. An example is sterling silver (used for silver cutlery and jewellery) which contains 92.5% Ag and 7.5% Cu; elemental Ag and Cu both adopt ccp (fcc) lattices and possess approximately similar metallic radius. Silver and copper have, in the liquid phase, different surface tensions, hence it is expected to find a concentration dependence of the surface tension of silver-copper liquid alloys, not being dominated by the bulk properties.

Eq. (1) was, previously, applied for calculating the surface tension of pure liquid metals such as gallium [24], bismuth [26] and mercury [27], in the frame work of Eyring statistical

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Table 1
Parameters needed for the surface tension calculation of pure liquid Ag, Cu and Ag_{x-1}–Cu_x alloys.

Parameter	Ag	Cu
T_m (K)	1235	1357
Density at T_m (g/cm^3)	9.32	8.02
E_s (kJ/mol)	285	338
V_s (cm^3/mol)	11.57	7.92
φ (cm^2/atom)	7.82×10^{-16}	6.1×10^{-16}

thermodynamic theory [28,29]:

$$\gamma = \varphi^{-1}\left(\frac{V_s}{V}\right)^2 kT\left[0.139\frac{E_s}{RT} - 0.053\right] \quad (1)$$

where γ is the surface tension, $\varphi = \sqrt{3}/2(\sqrt{2}V_s/N)^{2/3}$ is the atomic area, V_s and V are the molar volumes at the melting point and at temperature T, respectively, N is Avogadro's number, E_s is the sublimation energy, k is the Boltzmann constant and R is the gas constant. The model for the calculation of the surface tension of pure liquid metals [24,26,27] is extended to be valid for binary liquid alloys [25]. The necessary model equations for calculating the surface tension of a liquid binary alloy are presented as follows:

$$\varphi_{alloy} = x_A\varphi_A + x_B\varphi_B \quad (2)$$

$$V_s^{alloy} = x_A V_s^A + x_B V_s^B \quad (3)$$

$$V^{alloy} = x_A V^A + x_B V^B \quad (4)$$

$$E_{diss}^{alloy} = x_A^2 E_s^A + x_B^2 E_s^B + 2x_A x_B\sqrt{E_s^A E_s^B} \quad (5)$$

where x is the mole fraction, V_s^{alloy} and V^{alloy} are the molar volumes of the liquid alloy at the melting point of pure Ag and Cu, and at temperature T, respectively, and E_{diss}^{alloy} is the dissociation energy of an alloy. Eqs. (2)–(5) are essential assumptions that judge the model's performance. Using these equations, the surface tension of a liquid alloy can be determined both as a function of temperature at constant composition of the enriched liquid metal, and as a function of composition at specific temperature. Parameters needed for calculations are illustrated in Table 1. The experimental literature data on the density and its temperature dependence of pure liquid silver, copper and silver–copper alloys were employed so to have the volumes at any given temperature [30]. Obviously, there is a slight variation in the literature data on the densities of the elements and their temperature coefficients, and therefore, the choice of the reported data may have some influence (up to10%) on the calculated surface tensions.

3. Results and discussion

A theoretical approach for calculating the surface tension of various liquid Ag_{x-1}–Cu_x alloys is applied, in the temperature range 1100–1800 K. The molar volumes V_s^{alloy} and V^{alloy} were calculated using only the molar volumes of Ag and Cu components. These calculations were made by considering the experimentally reported temperature dependence of the density of the Ag_{x-1}–Cu_x liquid alloys at each Cu concentration [30]. The calculated surface tension data for pure liquid silver and copper are fitted as follows:

For Ag, $\gamma(T) = 841 - 0.151(T - T_m)(\text{mJ/m}^2)(1235 - 1550\,\text{K})$
For Cu, $\gamma(T) = 1200 - 0.212(T - T_m)(\text{mJ/m}^2)(1357 - 1798\,\text{K})$.

Fig. 1 shows the calculated temperature dependence of the surface tension of the Ag_{x-1}–Cu_x liquid alloys (1100–1800 K). There are six lines where each line displays the calculated surface tension of the Ag–Cu liquid alloy (x_{Cu} = 0, 0.2, 0.4, 0.6, 0.8 and 1 from bottom to top) as a function of temperature at constant Cu concentration. It is observed that the surface tension decreases linearly with increasing temperature for all Cu compositions that are under investigation, i.e., the temperature dependence of the surface tension is negative. Moreover, the surface tension increases with increasing Cu content. These observations are in accord in behavior and magnitude with the reported experimental data [31] (Fig. 2). As seen, the slopes in Figs. 1 and 2 are negative for all compositions.

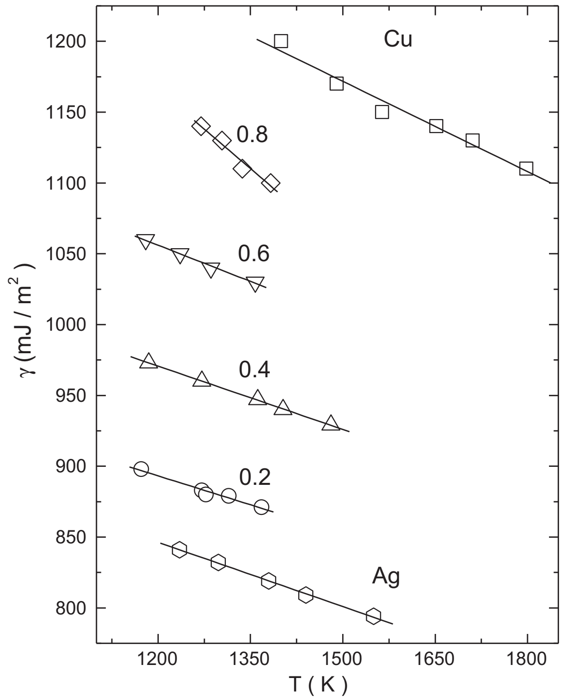

Fig. 1. Calculated temperature dependence of the surface tension of Ag, Cu and Ag_{x-1}–Cu_x liquid alloys at different x_{cu} (0–1) from bottom to top. The solid lines are the linear solid fits of the data.

Figs. 3 and 4 represent a comparison of the calculated and the reported data [13] of the surface tension of Ag–Cu liquid alloys as a function of x_{Cu} at 1381 K and the calculated results of the composition dependence of the surface tension at 1341 K. Both figures reveal that, at constant temperature, the surface tension increases with Cu concentration. However, the inclusion of all available experimental values reflects the limitation of the applied model and the merit of it. To test the approach, Table 2 illustrates the calculated values and various literature data [13–17,31,32] of the surface tension of Ag_{x-1}–Cu_x liquid alloys as a function of x_{Cu} (0–1), at 1373 K. With this comparison, it observed that, in all cases, the surface tension of the alloy increases with an increase in copper content. The calculated values agree remarkably with the experimental mea-

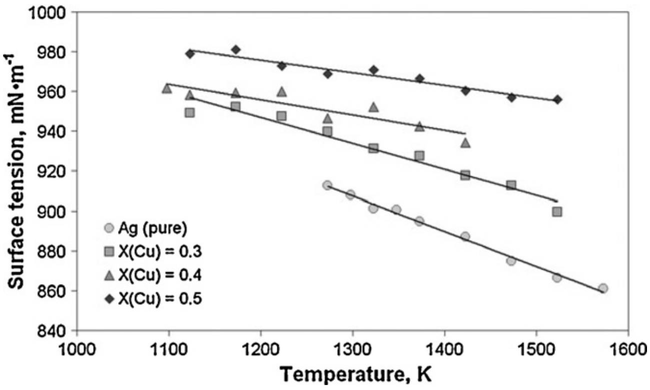

Fig. 2. Experimentally reported [31] surface tension of Ag_{x-1}–Cu_x liquid alloys versus temperature.

Table 2
Calculated and reported experimental composition dependence of the surface tension of Ag_{x-1}–Cu_x liquid alloys at 1373 K.

x_{Cu}	Surface tension (mJ m^{-2})							
	Ref. [31]	Ref. [13]	Ref. [14]	Ref. [15]	Ref. [16]	Ref. [17]	Ref. [32]	Our work
0.0	900	–	–	–	–	–	–	820
0.1	910	–	950	–	–	–	–	–
0.2	–	890	–	–	–	–	900	875
0.3	930	900	965	–	–	–	–	–
0.4	950	–	–	950	–	–	–	950
0.5	970	915	990	–	930	–	–	–
0.6	–	–	–	–	–	–	990	1035
0.7	–	950	1030	1020	990	–	–	–
0.8	–	–	–	–	1060	1080	–	1090
0.9	–	1080	1180	1110	1140	1130	1130	–
1.0	–	1300	1370	–	1270	1190	1320	1200

surements, and with the surface tension calculated from the Butler equation [31]. It should be mentioned that, in Figs. 3 and 4, the composition is presented on a logarithmic scale and show a non-linear manner with concentration. As a matter of fact, it is found to vary linearly if the presentation is given in terms of a linear composition scale. With this illustration one can calculate the surface tension for liquid metals and alloys without searching additional information on the calculated parameters used in the proposed formalism. It should be noted that the material with the lower surface tension (Ag) segregates on the surface, minimizing its total energy. The enrichment or depletion of the surfactant at the alloy's surface is ruled by both entropy and enthalpy acting in opposite directions.

Generally, this formalisms can be successfully applied to all alloy systems that obey Hume-Rothery rule, where the systems characterized by ideal mixing, i.e. characterized by lens type phase diagrams that indicate complete solubility in the liquid and in the solid phase. It can be also applied to weakly segregating alloys whose mixing properties deviate slightly from ideality. Such systems are characterized by the eutectic type phase diagrams, e.g. Ag–Cu, Ag–Bi and Bi–Sn. On the other side, the proposed model is not suitable for strongly interacting compound forming alloys, such as Ni–Al, Au–Sn, and Ag–Hf, whose thermodynamic mixing properties exhibit pronounced negative deviations with respect to Raoult's law and thus, their thermophysical properties deviate positively from ideality. Similarly, the mixing properties of phase separating monotectic systems exhibit large positive deviations with respect to Raoult's law (their thermophysical properties deviate negatively from ideality) and thus, the proposed model is not suitable for such systems.

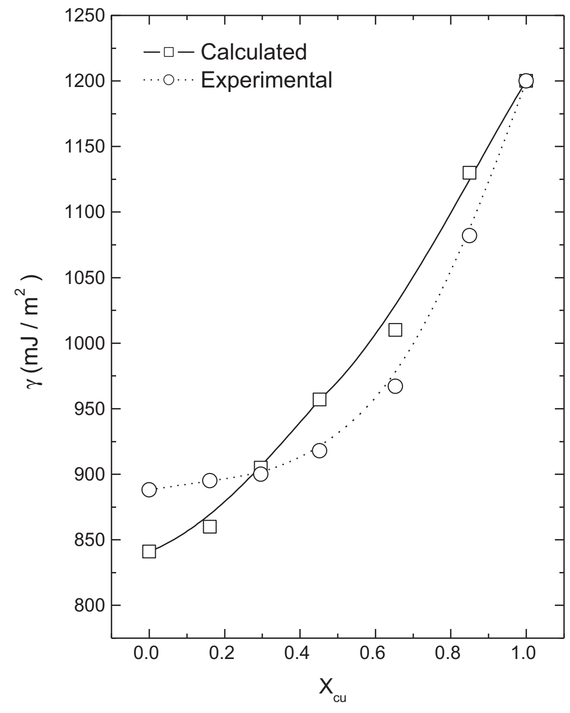

Fig. 3. Calculated and experimental [13] composition dependence of the surface tension of Ag_{x-1}–Cu_x liquid alloys at 1381 K.

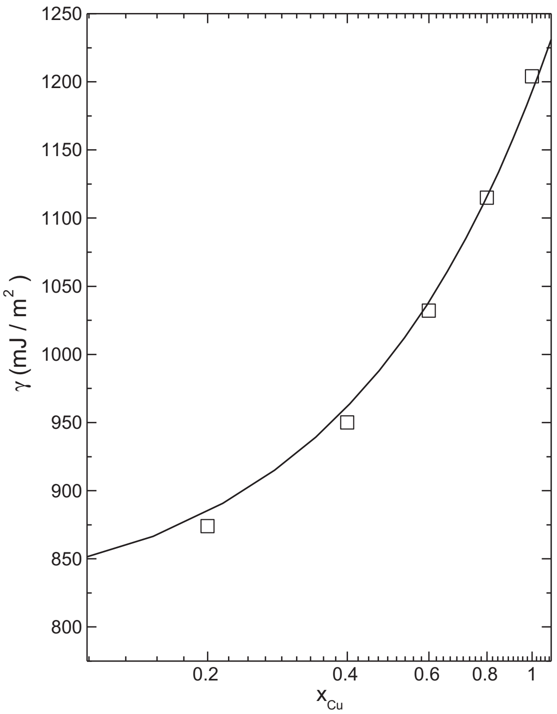

Fig. 4. Calculated surface tension of Ag_{x-1}–Cu_x liquid alloys as a function of x_{Cu} at $T = 1341$ K.

4. Conclusion

The surface tension of molten Ag, Cu and Ag–Cu alloys was calculated by a simple method over a temperature range and composition. The results obtained are in good agreement with other reported measurements on pure liquid elements and their alloys as well as with calculated surface tension values [17]. As reported, the phase diagram of Ag–Cu system shows the existence of a simple eutectic indicating a tendency towards phase separation. For all examined compositions, the surface tension for pure liquid silver, copper and Ag–Cu alloys is a linear function of temperature, and it increases with increasing concentration of Cu. Our data agree very well with the data of other authors. These calculations may be considered of major significance in the field of surface science of liquid binary alloys. The calculated data for the surface tension of these alloys in the liquid state show a clear deviation from an ideal mixing behavior. This does not mean, that the surface tension of the mixture cannot simply be derived without consideration of interactions between the constituents.

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