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Mixing properties of liquid Al–Au alloys

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Abstract

The thermodynamic and structural properties of liquid Al–Au alloy have been studied in framework of R-K polynomial using temperature-dependent energy interaction parameters at different temperatures. Thermodynamic properties, excess free energy of mixing and activity, and in structural properties, concentration fluctuation in long wave-length limit have been computed at temperatures 1338 K, 1500 K and 1600 K. The properties, such as surface tension and surface concentration of the system have been computed at above mentioned temperatures using Butler model. The system shows transformation from segregating to ordering in nature with increase in concentration of Au.

Keywords

R-K polynomial, Al–Au alloys, Thermodynamic, Structural and Surface properties.

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1 Introduction

The majority of semiconductor packages are assembled via wire bonding, which is typically regarded as the most affordable and efficient connectivity approach. The intermetallic compounds of Al-Au alloys are profoundly used in these metallization processes [1–4]. Hence, the mixing properties of the system has been extensively investigated by several researchers [3,5–18]. The details of the literature related to the chronological investigations of phase structures and thermodynamic properties of the system till 2004 are presented by Li et al. [3]. They accessed the thermodynamic properties of the system using Thermo-Calc (computer-based software) along with other theoretical approaches. They also presented the self-consistent temperature-dependent interaction parameters for excess Gibbs free energy of mixing.

Later, Olajire and Musari used different theoretical models to investigate the thermodynamic and structural properties of the system [10]. Peng et al. [19] experimentally measured the compositional and temperature dependence of density, temperature coefficient of density, molar volumes, self- and inter diffusion and viscosity of Al-Au liquid alloy at 1400 K. They also developed a molecular dynamics (MD) model in order to computed the above mentioned properties using the experimental results [19]. Later Brillo and Kolland [20] experimentally measured the surface tensions of the system and found that the surface tension (σ) decreases linearly with temperature. Further, they found that σ of the system decreased monotonically with increase in Al content at 1400 K. From above literature survey, it can be stated that Al-Au liquid alloy has been extensively studied.

Therefore, an attempt has been made in this work to reassess the thermodynamic properties of the system using optimised coefficients Li et al. [3] of Redlich-Kister (R-K) polynomial [21]. These coefficient are used to compute thermodynamic, structural and surface properties of the system at different temperatures in frame work R-K polynomial. The thermodynamic properties, such as G_M^{xs}, activity (a) and structural properties, such as concentration fluctuation in long wavelength limit ($S_{CC}(0)$) have been computed. The surface properties of have been computed using Butler model [22] with the help of determined values of partial excess Gibbs free energy of individual component of the alloy. The different modeling equations used for the present investigations are presented in the Section 2, the results and discussion are mentioned in the Section 3 and important conclusions of the work are highlighted in the Section 4.

2 Methods and methodology

According to R-K polynomial, the excess free energy of mixing (G_M^{xs}) is expressed as [21, 23]

$$G_M^{xs} = x_{Al}x_{Au}[L_0 + L_1(x_{Al} - x_{Au})] \tag{1}$$

where L_0 and L_1 are coefficients of R-K polynomial, also called interaction energy parameters and are assumed to depend linearly on temperature and x_{Al} and x_{Au} are moalr fraction of constituents of liquid Al–Au alloy.

The energy interaction parameters is linear temperature dependent and the excess free energy of mixing is expressed as

$$G_M^{xs} = x_{Al}x_{Au}[(a_0 + b_0T) + (a_1 + b_1T)(x_{Al} - x_{Au})] \tag{2}$$

The partial excess free energy (G_{Al}^{xs}, G_{Au}^{xs}) of each component of liquid Al–Au alloy can be calculated using the relation [24]

$$\begin{aligned} G_{Al}^{xs} &= G_M^{xs} + x_{Au}\left(\frac{\partial G_M^{xs}}{\partial x_{Al}} - \frac{\partial G_M^{xs}}{\partial x_{Au}}\right) \\ G_{Au}^{xs} &= G_M^{xs} + x_{Al}\left(\frac{\partial G_M^{xs}}{\partial x_{Al}} - \frac{\partial G_M^{xs}}{\partial x_{Au}}\right) \end{aligned} \tag{3}$$

Once the values of partial excess free energy of mixing are computed, the values of activity of each component (a_{Al}, a_{Au}) in the liquid alloy is obtained by following expression

$$a_{Al} = x_{Al}\exp\left(\frac{G_{Al}^{xs}}{RT}\right), \ a_{Au} = x_{Au}\exp\left(\frac{G_{Au}^{xs}}{RT}\right) \tag{4}$$

The structural function in long wave-length limit ($S_{CC}(0)$) of binary liquid Al–Au alloy can be expressed in the following form [25]

$$\begin{aligned} S_{CC}(0) &= RT\left(\frac{\partial^2 G_M}{\partial x_{Al}^2}\right)_{T,P,N}^{-1} \\ &= RT\left(\frac{\partial^2 G_M}{\partial x_{Au}^2}\right)_{T,P,N}^{-1} \end{aligned} \tag{5}$$

The analytical expression for $S_{CC}(0)$ of liquid Al–Au alloy [26] is

$$\begin{aligned} S_{CC}(0) &= RT[-2L_0 + (-12x_{Al} + 6)L_1 \\ &+(-48x_{Al}^2 + 48x_{Al} - 10)L_1 + \frac{RT}{x_{Al}(1 - x_{Al})}]^{-1} \end{aligned} \tag{6}$$

The information related to the arrangement of atoms in the nearest neighbourhoods of initial metallic solution can be obtained by computing parameters like concentration fluctuation in the long wave length limit ($S_{CC}(0)$) [25, 26]. The expression for ideal value of $S_{CC}(0)$ is calculated using the relation

$$S_{CC}^{id}(0) = x_{Al}x_{Au} \tag{7}$$

The surface properties of the system have been studied using Butler model [22, 27]. This approximation is based on the assumption of hypothetical monoatomic surface layer being in equilibrium with the bulk phase of the metallic solution. Accordingly, the surface tension (σ) of the solution in terms of molar surface area (λ_1) of constituent atoms is expressed as

$$\begin{aligned} \sigma &= \sigma_{Al} + \frac{1}{\lambda_{Al}}(G_{Al,s}^{xs} - G_{Al,b}^{xs}) + \frac{RT}{\lambda_{Al}}\ln(\frac{x_{Al}^s}{x_{Al}^b}) \\ &= \sigma_{Au} + \frac{1}{\lambda_{Au}}(G_{Au,s}^{xs} - G_{Au,b}^{xs}) + \frac{RT}{\lambda_{Au}}\ln(\frac{x_{Au}^s}{x_{Au}^b}) \end{aligned} \tag{8}$$

where σ_{Al} and σ_{Au} are surface tension of pure components , and G_{Al}^{xs} and G_{Au}^{xs} are the partial excess free energy of component in the surface phase and bulk phase respectively, and x_{Al}^s, x_{Au}^s and x_{Al}^b, x_{Au}^b are the surface and bulk concentrations of Al and Au respectively. Herein, $G_{i,s}^{xs} = \beta G_{i,b}^{xs}$, $i = Al, Au$ with $\beta = 0.8181$ [22] and $\lambda_i$is expressed as

$$\lambda_i = 1.00N_A^{1/3}(\frac{M_i}{\rho_i})^{2/3} \tag{9}$$

where N_A is the Avogadro's number, M_i and ρ_i are the mass and density in the Al–Au alloy respectively. The expression for σ_i and ρ_i can be given as

$$\sigma_i = \sigma_i^0 + \frac{\partial\sigma_i}{\partial T}(T - T_i^0) \tag{10}$$

$$\rho_i = \rho_i^0 + \frac{\partial\rho_i}{\partial T}(T - T_i^0) \tag{11}$$

where T_i^0 is the melting temperature of the ith component and T is the required temperature at which these parameters are to be calculated.

3 Results and Discussion

3.1 Excess free energy of mixing

The energy interaction parameters of R-K polynomial for liquid Al–Au alloy were taken from Ref. [3] are presented in Table 1. The interaction parameters of Table 1 have been used in Equation (1) to compute G_M^{xs} of Al–Au alloy at 1338 K, 1500 K and 1600 K. The computed values are plotted in Figure 1. The negative value of G_M^{xs} of the system decreases with increase in temperature. The minimum value at 1338 K is found to be -19.505 kJ/mol at equi-atomic composition.

Table 1: Energy interaction parameters of liquid Al–Au alloy

Interaction Parameters (J/mol) [3]
$L_0 = -131996.19 + 36.42T$
$L_1 = 40781.83 - 1.896T$

Table 2: Physical quantities of liquid Al–Fe alloy [28]

Quantities	Element Al	Element Au
M_i (kg)	0.2698154	0.19696665
T_i^0	933 K	1336 K
ρ_i^0(kg/m^3)	2385	17360
$\frac{d\rho_i}{dT}$ (kgm^{-3}T^{-1})	-0.28	-1.5
σ_i(mN/m)	914	1140
$\frac{d\sigma_i}{dT}$ (mN/(mT))	-0.35	-0.52

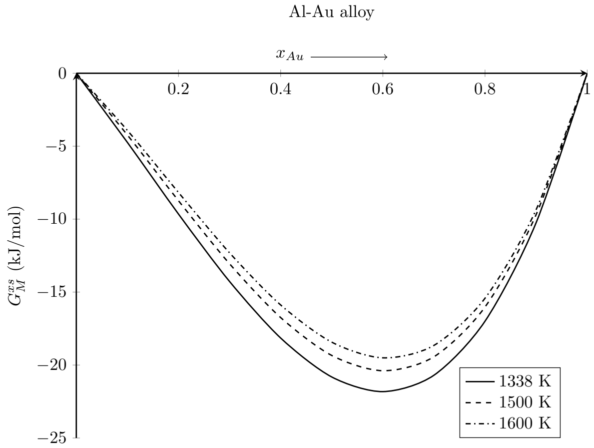

Figure 1: Excess free energy of mixing of liquid Al–Au alloy at different temperatures.

3.2 Activity

The parameters of Table 1 have been used in Equation (3) to calculated the partial excess free energy (G_i^{xs}, i=Au, Al) of each component at above mentioned temperatures. The activity of components Al and Au (a_{Au}, a_{Al}) have been calculated using Equation (4) and these values are plotted in Figure 2. The activity of component Al in the region of high concentration of Al ($x_{Au} < 0.2$) shows positive deviation from Raoult's law and negative deviation at remaining concentrations. This indicates the system shows ordering nature in the region $x_{Au} < 0.2$ and segregating nature at remaining concentrations. Both the components have a very small value of activities in the concentration range $x_i = 0.6$ which indicates strong ordering behaviour of the system (Figure 2).

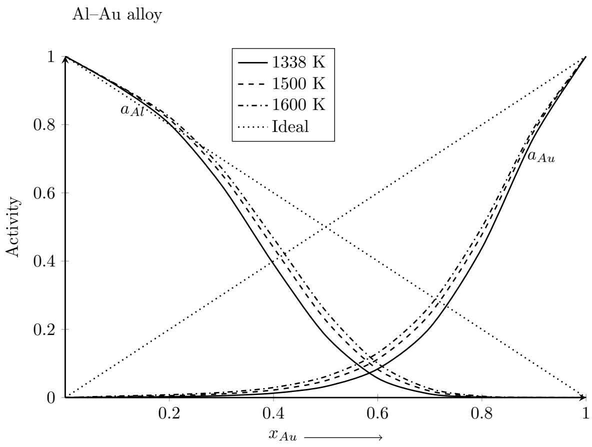

Figure 2: Activity of liquid Al–Au alloy at different temperatures.

3.3 Concentration fluctuation in long wavelength limit ($S_{CC}(0)$)

The structural function ($S_{CC}(0)$) of liquid Al–Au alloy gives an idea about the local arrangement of components Al and Au in the system. The function $S_{CC}(0)$ have been calculated using energy interaction parameters of Table 1 in Equation (6) at above mentioned temperatures, 1338 K, 1500 K and 1600 K. The computed values are plotted in Figure 3. The calculated value of $S_{CC}(0)$ at lower concentrations of Au ($x_{Au} < 0.2$) exceeded ideal values showing segregating nature in those region. However, these values at remaining concentration are less than ideal values indicating the ordering nature. Hence, the system shows transformation from segregating to ordering nature. As the temperature of the system is gradually increased, the computed values of structural function gradually increases (Figure 3).

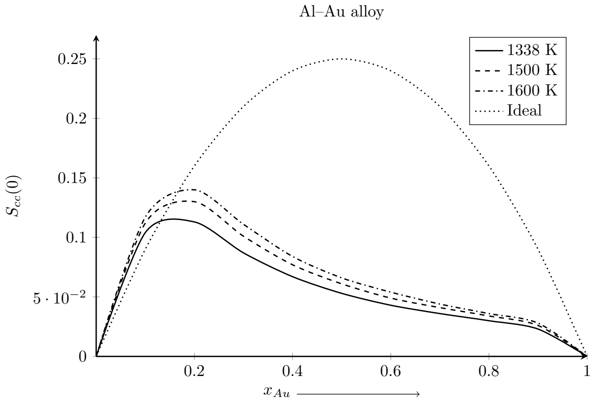

Figure 3: $S_{CC}(0)$ of liquid Al–Au alloy at different temperatures.

3.4 Surface tension (σ)

Surface tension (σ) of liquid Al–Au alloy has been calculated at above mentioned temperatures using physical parameters of Table 2 and Equations (8,9,10,11). The calculated values of (σ) are plotted in Figure 4 as a function of concentration of Au. The surface concentrations x^s_{Al} and x^s_{Au} of the alloy have been optimised during the computations of (σ) and are plotted in Figure 5.

It can be observed that the surface tension (σ) of the system at its melting temperature (1338 K) gradually increased with increase in the bulk concentration of Au. As mentioned earlier, σ was also computed at different temperatures. With increase in the temperature, the values of σ gradually decreased with increase in the content of Au (Figure 4) and these results are similar to those obtained by [19], [20].

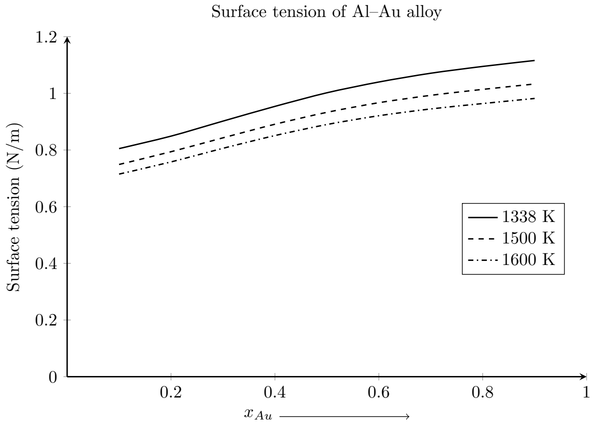

Figure 4: Surface tension of liquid Al–Au alloy at different temperatures.

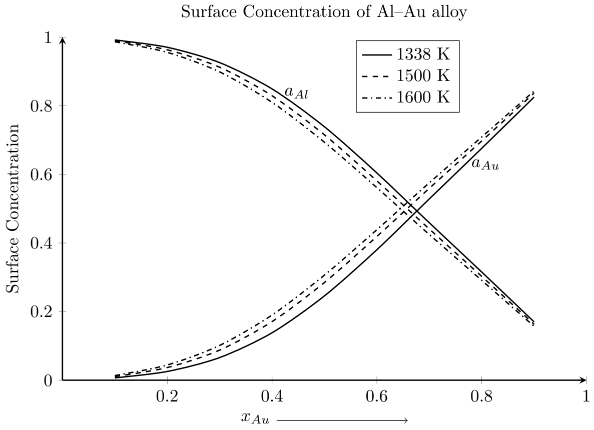

Figure 5: Surface concentration of liquid Al–Au alloy at different temperatures.

The surface concentrations of Au and Al (x^s_{Au} and x^s_{Al}) have the same value at/about x_{Au} = 0.7. With increase in x_{Au}, x^s_{Au} gradually increases whereas x^s_{Al} gradually decreases. At higher temperatures, the computed values of x^s_{Al} gradually decreases whereas those of x^s_{Au} gradually increases (Figure 5). These results indicate that there is exchange of atoms between the surface and bulk phases of the liquid alloy in order to maintain equilibrium [29].

4 Conclusion

Present theoretical investigations show that the liquid Al–Au is found to be the most interacting at its melting temperature. The system shows tranformation from segregating to ordering nature. With increase in temperature, its mixing tendency gradually decreases.

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