Microscopic Structure And Thermodynamical Investigation Of Compound Forming Binary Liquid Alloy: Cu – Sn

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Abstract:
The symmetry observed in the properties of mixing of Cu-Sn liquid alloys is discussed on the basis of a simple theory based on the complex formation model. This has been used to evaluate the pair potential and entropy of mixing of Cu-Sn liquid alloys as a function of concentration. The band structure energy has been used to obtain an expression for interionic pair potential ($\Phi_{ij}$) which in turn is used to obtain the hard sphere diameter ($\sigma$) of Cu-Sn liquid alloys. The results suggest that the metallic constituents of the alloys undergo major structural change on alloying. The entropy of mixing of Cu-Sn liquid alloys show anomalous behaviour due to preferential ordering of unlike atoms as nearest neighbour.

Keywords: Thermodynamical Properties; Microscopic properties.

Introduction

In the theory of mixtures the concept of ideal mixtures, though naïve and simple, is an important one. It defines the borderline between, at the one hand, the mixtures with a tendency to clustering or phase separation and at the other hand, the mixture with a tendency to compound formation. The former ones are characterized by preferred coordination with like atoms, the later ones by preferred coordination with unlike atoms. These distinctions are applicable to the solid as well as to the liquid state. They reflect the Chemical short - range order (S.R.O), in contrast to the “topological” S.R.O. which pertains to positions, irrespective of the chemical species.

The study of Cu–Sn alloy is a matter of investigation since past few decades [1-9]. For metals, general rules for alloying have been given by Miedema et al, [10-12]. Whether two metals form alloys or not depend largely on two parameters, a work function and the density of electrons at the boundary of two Wigner – Seitz cells. The work function is closely related to the concept of electronegativity.

The mere distinction is Compound forming and Clustering alloys systems constitutes an over simplification of affairs. The mixing properties may, e.g., depend on composition, temperature and pressure. The classification into compound forming and clustering alloys is closely related to the lattice theories of mixtures. In their most primitive form they boil down to a regular solution model: only interactions with nearest neighbors are taken into account and interaction energy is attributed to each bond between nearest neighbors. If in an obvious notation, $H_{AA}$, $H_{BB}$ and $H_{AB}$ are possible pair interaction enthalpies in a binary system, the quantity $W= \frac{2H_{AB} - H_{AA} - H_{BB}}{2}$, called the interchange energy, determine the general character of the mixing process: $W > 0$ leads to clustering, $W < 0$, compound formation. But the thermodynamics of mixture is not determined by energies alone: also the entropy plays an important role: for $W > 0$, phase segregation may be prevented by the increase of the entropy accompanying the mixing process.

The phenomenon of compound formation in Cu-Sn liquid alloy [12-20, 28-31, 33], Pseudopotential formalism has been incorporated. This has been used to compute interionic pair potential. The computed hard sphere diameter ($\sigma$) has been used to evaluate the entropy of mixing of these alloys as a function of
concentration [14, 27, 32]. The band structure energy has been utilized to obtain an expression for interionic potential \( \Phi_{ij} \) for binary liquid alloys. The expression of form factors has been obtained by using Heine–Abarenkov (HA) [21] model potential theory.

**Theoretical formulation**

Let a binary liquid alloy containing in all \( N_A \) and \( N_B \) of atom A and B be randomly distributed can be written as expression of form factors has been obtained by using Heine–Abarenkov (HA) [21] model potential theory.

The total numbers of scattering points are:

\[
N_i = n_A + n_B + n_m = nN
\]

where \( n_A + n_B + n_m = 1 \) (1)

From atomic conservation principle, we have

\[
\begin{align*}
\Phi = \Phi_{ij} & = \Phi_{ij} = N_A + n_B + n_m = N_A \\
\Phi_{ij} & = \Phi_{ij} = N_A + n_B + n_m = N_B \\
\Phi_{ij} & = \Phi_{ij} = 1 - C - n_m \\
\Phi_{ij} & = \Phi_{ij} = n_A - n_m \\
\Phi_{ij} & = \Phi_{ij} = 1 - (\mu + v - 1) n_m \\
\Phi_{ij} & = \Phi_{ij} = 1 - (\mu + v - 1) n
\end{align*}
\]

where \( \mu \) and \( v \) are small integers; \( C \) is defined as concentration of second species.

Volume in which \( N_A \) atoms of A and \( N_B \) atoms of B are randomly distributed can be written as

\[
V = \Omega_{liquid} - n_m V_m
\]

where \( \Omega_{liquid} \) is the atomic volume of the alloy and \( V_m \) is the volume of the complex.

\[
V_m = \mu \Omega_1 + \nu \Omega_2
\]

where \( \Omega_1 \) and \( \Omega_2 \) are the atomic volume of the first and second species respectively.

We may recall that the hard sphere diameters \( \sigma_1 \) and \( \sigma_2 \) occurs as ingredients, the value of \( \sigma_1 \) (i = 1, 2) as a function of concentration, have been determined by minimizing the interionic pair potential \( \phi \) i.e.,

\[
\phi (\sigma_i) = \frac{3}{2} K_B T + \phi_{min}
\]

where \( \frac{3}{2} K_B T \) is mean Kinetic energy and \( \phi_{min} \) is the depth of the first minimum in the interionic pair potential.

Harrison (II) showed that the pairwise potential between the metallic ions can be evaluated from the band structure energy. By generalizing this formalism, one can obtain \( \phi_{ij} \) (i,j = constituent elements) for binary alloys

\[
\phi_{ij} = \frac{Z_i Z_j}{R} \left[ 1 - 2 \pi \int_0^\infty F_{ij}^N \left( \frac{\sin qr}{q} \right) dq \right]
\]

where \( Z_i, Z_j \) are valencies of the constituent element

\[
F_{ij}^N = \text{normalized wave number characteristics}
\]

\[
F_{ij}^N = - (q^2 \Omega / 2 \pi Z_i Z_j) F_{ij} (q)
\]

where \( F_{ij} (q) \) are partial energy wave number characteristics, \( F_{ij} (q) \) in the local approximation can be expressed as

\[
F_{ij} (q) = - \frac{\Omega}{q^2} \left[ \ln \left( \frac{W_{ij}^0 (q) W_{ij} (q)}{W_{ij} (q)} \right) \right]
\]

where \( W_{ij}^0 (q) \) and \( W_{ij}^0 (q) \) are the unscreened form factors of i and j components respectively. \( e^{\pi \Omega} \) is the modified Hartree dielectric function.

The interionic pair potential for Cu-Sn liquid alloys are obtained through equation (11) at different concentration, the unscreened form factor \( W_{ij}^0 (q) \) of the constituent species are obtained using HA model potential as

\[
W_{ij}^0 (q) = -\left( \left( 4 \pi / \Omega q^2 \right) \cos qr_{mn} \right) - \left( 4 \pi A / \Omega q^3 \right) \left( \sin qr_{mn} - qr_{mn} \cos qr_{mn} \right)
\]

Modified Hartree dielectric function, \( e^{\pi \Omega} \) is defined as

\[
e^{\pi \Omega} = 1 - [e^{\pi \Omega}] - 1 - G(q)
\]

where \( e^{\pi \Omega} \) is the usual Hartree dielectric function. \( G(q) \) takes into account of the exchange and correlation effect of the conduction electrons using Vashistha–Singwi [22] expression for \( G(q) \), we have

\[
G(q) = \Omega + 1 + \{ \exp (B(qK_B \Omega)) \}
\]

where \( K_B \) is the Fermi wave vector for compound forming alloys, and may be expressed as

\[
K_B = \left[ \frac{3}{2} \left( (1-C) Z_1 + (Z_2 - Z_{mn}) N \right) N \right] / \left[ \Omega_{liquid} - n_m V_m \right]
\]

In equation (16), and \( A \) and \( B \) are constants given by \( r_s, Wigner – Seitz radius, \) which is expressed as

\[
r_s = \left( \left[ 3 (N \Omega - n_m V_m) / (4 \pi \eta) \right] \right)^{1/3}
\]

The packing density \( \eta \) for compound forming alloys, is expressed as

\[
\eta = \left( \frac{\pi}{6 \Omega_{liquid}} \right) \sum_i X_i Z_i^3
\]

where \( X_i \) = concentration fraction of scattering centers.

The hard sphere diameter for compound forming system is determined via equations (11) and (10) using the values of \( r_s, K_B \) and \( \eta \) given by equations (18), (17), and (19) respectively.

**Entropy of mixing for compound forming system**

According to complex formation model we can express entropy of mixing of complex forming liquid alloys [14] as

\[
S_m = S_{gas} + S_{pi} + S_{pi} + S_{comp} \]

where the contribution of pseudomolecules \( A_p, B_p \) has been accounted.

The term \( S_{gas} \) is expressed as,

\[
S_{gas} / K_B = \eta \left[ 2.5 + \ln \left( \Omega_i (m_1^x m_2^y m_3^z K_B T) / (2 \pi h^2) \right) \right]^{1/2}
\]

where \( m_1, m_2, m_3 \) are the masses of constituent atoms and complex respectively. \( \Omega_i (\approx \Omega / N) \) is the scattering volume of the alloy in which free electrons travel, \( K_B \) is the Boltzmann constant, \( T \) is
the required temperature and \( S_c \) is the ideal mixing term.

\[
\frac{S_c}{K_B} = n \left( x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 \right) \quad (22)
\]

The total packing term \( S_\eta \) is given by

\[
\frac{S_\eta}{K_B} = - n (r-1) (r+3) \quad (23)
\]

where \( r = 1 / (1-\eta) \)

\( \eta \) is the packing density given by

\[
\eta = \frac{\pi}{\Omega} \sum X_i \sigma_i^3 \quad (i = 1, 2, 3) \quad (24)
\]

\( \sigma_1 \) and \( \sigma_2 \) are the densities of the constituent atoms 1 and 2 respectively, \( \sigma_3 \) is the diameter of the complex. \( S_\sigma \) arises due to the difference among the diameters of the free atoms and the complex is given by

\[
\frac{S_\sigma}{K_B} = S_\sigma(1,2) + S_\sigma(1,3) + S_\sigma(2,3) \quad (25)
\]

where

\[
S_\sigma(i,j) = X_i X_j (\sigma_i - \sigma_j)^2 \{ U_{ij}^1 + U_{ij}^2 + 3(r-1) U_{ij}^3 \} \quad (26)
\]

\( U_{ij}^1 = \frac{\sigma_i + \sigma_j}{\sigma_3} \) \quad (27 a)

\( U_{ij}^2 = \sigma_i \sigma_j (X_1 \sigma_1^3 + X_2 \sigma_2^3 + X_3 \sigma_3^3) \) \quad (27 b)

\( \sigma_3 = (X_1 \sigma_1^3 + X_2 \sigma_2^3 + X_3 \sigma_3^3) \) \quad (27 c)

\( S_{\text{comp.}} \) is the contribution from the internal degree of freedom of the complexes, which is due to internal modes of vibration. It is approximated by a sum of contributions from each complex \( \Psi_{\text{comp.}} \) may be written as

\[
\frac{S_{\text{comp.}}}{K_B} = n \Psi_{\text{comp.}} \quad (28)
\]

From equation (20), the entropy of mixing of complex forming liquid alloys can be expressed as,

\[
S_m = \Delta S_{\text{gas}} + \Delta S_\eta + S_c + S_{\text{comp.}} \quad (29)
\]

where

\[
\Delta S_i = S_i,\text{alloy} - C_A S_{11} - C_B S_{12} \quad (i= \text{gas}, \eta) \quad (30)
\]

\( S_1 \) and \( S_2 \) are entropies of pure components, whose explicit expression can be obtained by setting either \( C = 0 \) or \( C = 1 \) [33].

**Result and discussion**

**Interionic Pair Potential:** Interionic pair potential \( \phi_{ij}(r) \) for Cu-Sn liquid alloys has been computed using equations (11) to (13). The value of \( F_{ij}(q) \) and \( K_f \) have been obtained through equations (15) and (17) respectively. The volume of mixing of CuSn liquid alloys is obtained from the work of Veazy et al [25] and tabulated in table 3 along with the hard sphere diameter of the system. The model parameters (table 1) used for the computation have been taken from the work of Ese and Reissland [23]. HA model potential have been used to determine the form factor \( W^0(q) \) which enables us to determine pair potential \( \phi_{ij}(r) \). We have plotted \( \phi_{ij}(r) \) for Cu-Sn system in figure 1, 2 and 3 at different concentrations. The computed results have been discussed with reference to pure state.

The computed values of the pair potential between Cu-Cu atoms (\( \phi_{\text{Cu-Cu}} \)) and Sn-Sn atoms (\( \phi_{\text{Sn-Sn}} \)) in Cu-Sn alloy at (\( C_{\text{Cu 0.5 Sn 0.5}}, C_{\text{Cu 0.75 Sn 0.25}} \)) are depicted in figures (1 and 2) respectively along with the values obtained in the pure state (Cu and Sn).

To understand the nature of potential in a comparative manner, we have presented \( \phi_{\text{Cu-Cu}}, \phi_{\text{Sn-Sn}} \) and \( \phi_{\text{Cu-Sn}} \) at compound forming concentration \( C_{\text{Cu}} = 0.75 \) (figure 3).

![Fig. 1. Variations of interionic potential (\( \phi_{\text{Cu-Cu}} \)) as a function of hard sphere diameter (r) of the system at various concentrations](image)

![Fig. 2. Variation of interionic potential (\( \phi_{\text{Sn-Sn}} \)) as a function of hard sphere diameter (r) of the system at different concentrations](image)
Fig. 3. Variation of interionic potential $\phi_{ij}(r)$ with hard sphere diameter ($r$) of the system at $1400 \text{ K}$

On alloying for Cu-Sn system, the effective interaction between Cu-Cu atoms decreases (figure 3). $\phi_{\text{Cu-Cu}}$ at compound forming concentration ($C_{\text{Cu}} = 0.75$) is greater than that obtained at equiatomic composition; the nearest neighbour distance between Cu-Cu atoms increases if one goes from pure state to Cu-Sn alloy. The nearest neighbour distance remains constant at both concentrations, i.e., $\text{Cu}_{0.5}\text{Sn}_{0.5}$ and $\text{Cu}_{0.75}\text{Sn}_{0.25}$. The effective interaction between Sn-Sn atoms (figure 2) increases in order: pure Sn $<$ $C_{\text{Cu}} 0.5 C_{\text{Sn}} 0.5$ $< C_{\text{Cu}} 0.75 C_{\text{Sn}} 0.25$. The nearest neighbour distance between Sn atom does not change appreciably. $\phi_{\text{Cu-Sn}}$ lies in between $\phi_{\text{Cu-Cu}}$ and $\phi_{\text{Sn-Sn}}$ (figure 3). The depth and position of $\phi_{\text{Cu-Sn}}$ are quite different from $\phi_{\text{Cu-Cu}}$ and $\phi_{\text{Sn-Sn}}$.

**Hard Sphere Diameter:** For Cu-Sn liquid alloys, the results on pair potential throughout the whole range of concentration have been used to determine the hard sphere diameter using equation (10). The value of ‘$r$’ satisfying equation (10) is taken as the hard sphere diameter ($\sigma$) of the system. The computed value of $\sigma$ for Cu-Sn system are tabulated in table 2. The value of $\sigma_1$ (hard sphere diameter of the complex) is fixed by adjusting its value through equation 29, so that a good fitting for $S_{\text{expt.}}$ value is obtained. The value of $\sigma_1$ is 4.3 at $T = 1400 \text{ K}$.

$\Psi_{\text{comp.}}$ appearing in equation (28) can be evaluated from the work of Herzberg (1962) [24]. Due to the complexities involved in the determination, we have treated it as a parameter and fixed if as $\Psi_{\text{comp.}} = 18.5 \text{ K_B}$ for CuSn alloys. The computed and experimental (Hultgren et al 1973) values of entropy of mixing for CuSn systems are tabulated in table 3. Variation of entropy of mixing as a function of concentration for CuSn system is depicted in figure 4. Figure 4 shows reasonable agreement between the computed and observed values in the concentration range $0.2 \leq C_{\text{Cu}} \leq 0.6$.

The computed values are positive at all concentrations, being maximum at $C_{\text{Cu}} = 0.8$.

**Table I.** Model parameters for HA forms of potential (in a.u.) below are taken from the work of Ese and Reisland [23].

| System | Cu   | Sn   |
|--------|------|------|
| A0     | 0.604| 1.881|
| R0     | 1.656| 2.185|

**Table II.** Volume, diameter and ratio of diameters ($\alpha$) for Cu - Sn liquid alloys at 1400 K

| $C_{\text{Cu}}$ | Volume $\sigma_{\text{Cu}}$ | $\sigma_{\text{Sn}}$ | $\alpha = \sigma_{\text{Cu}} / \sigma_{\text{Sn}}$ |
|-----------------|----------------------------|---------------------|---------------------------------------------|
| 0.0             | 207.0272                   | ----                | 5.5220                                       |
| 0.1             | 194.8684                   | 3.7025              | 5.5238                                       | 0.67 |
| 0.2             | 182.3520                   | 3.7047              | 5.5260                                       | 0.67 |
| 0.3             | 169.0018                   | 3.7072              | 5.5277                                       | 0.67 |
| 0.4             | 156.6245                   | 3.7100              | 5.5294                                       | 0.67 |
| 0.5             | 143.0870                   | 3.7130              | 5.5320                                       | 0.67 |
| 0.6             | 129.6244                   | 3.7166              | 5.5347                                       | 0.67 |
| 0.7             | 117.2308                   | 3.7209              | 5.5364                                       | 0.67 |
| 0.8             | 107.4845                   | 3.7261              | 5.5383                                       | 0.67 |
| 0.9             | 98.7611 3.7301             | 5.5240              | 0.67                                         |
| 1.0             | 89.4481 3.7401             | ----                | ----                                         |

*Veazy et al (1972), volume at 1375 K
Table III. Entropy of mixing of Cu-Sn compound forming alloys

| Alloy Temp. CuSn | C_{Cu} | Theory | Experiment* |
|-----------------|--------|--------|-------------|
| 1400 K          | 0.1    | 0.279  | 0.45        |
|                 | 0.2    | 0.336  | 0.70        |
|                 | 0.3    | 0.312  | 0.86        |
|                 | 0.4    | 0.343  | 0.94        |
|                 | 0.5    | 0.374  | 0.97        |
|                 | 0.6    | 0.486  | 0.92        |
|                 | 0.7    | 0.691  | 0.81        |
|                 | 0.8    | 0.856  | 0.67        |
|                 | 0.9    | 0.667  | 0.45        |

*Hultgren et al 1973.

Conclusion

In our theoretical model, we have studied entropy of mixing of CuSn liquid alloys as a function of concentration using the Pseudopotential formalism incorporated with the phenomenon of compound formation. The concentration dependent anomaly occurs due to the preferential ordering of unlike atoms as nearest neighbours, forming compound like CuSn in CuSn liquid alloys. Hence the binary mixture can be treated as a ternary mixture of unassociated constituent atoms and the chemical complex. The study reveals that the effective interaction between \( \phi_{Cu-Cu} \) increases on alloying but \( \phi_{Sn-Sn} \) decreases. \( \sigma_{Cu} \) expands on alloying in the whole concentration range of Cu whereas \( \sigma_{Sn} \) expands in the region \( C_{Sn} = 0.1 \) to 0.3, then decreases beyond the range \( S_{M} \) exhibits marked deviation in the concentration range 0.2 < \( C_{Cu} \) < 0.6, this might be due to the great deal of parametrisation of \( \sigma_{3} \) and \( \Psi_{comp}. \)

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