Original Article

Theoretical Assessment on Hetero-coordination of Alloys Silver-Antimony at Molten State

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Abstract

The thermodynamic and structural properties of binary alloy Ag- Sb at temperature 1250K have been reported theoretically using quasi lattice model. The interchange energy has been considered a function of a temperature and thus various thermodynamic quantities are calculated at elevated temperature. The theoretical values of free energy of mixing, heat of mixing, entropy of mixing and chemical activity are reasonable agreement with experimental values in all concentrations of antimony from 0.1 to 0.9. The theoretical analysis tells that the alloy shows both ordering nature in Ag rich end and segregating nature in Sb rich end .The study reveals that the properties of alloy are asymmetric around equi-atomic composition. The Ag_3Sb complexes are most likely to exist in the liquid state and are moderately interacting.

Article Info

1. Introduction

The study of alloying behaviour is an important field in metallurgical science. The alloys may be of binary, ternary, quaternary and so on. Here our concern is only on the binary alloy. The binary alloy is a type of product formed by combination of two elements (at least one metal) in liquid state. Different properties of binary alloys are directly concerned with concentration of constituent elements .The alloys show symmetric or asymmetric behaviour in thermodynamic and structural properties with respect to concentration (Hultgren et al., 1973). Most of the used industrial and commercial materials are solid alloys. So they have deep utilization in solid state. The properties of initial melt play important role in the formation of alloys. Thus determination of different properties of the alloys in the liquid state are important to study the alloying behaviour in metallurgical science as well as knowledge of various properties of alloys at liquid state is important for the production of new materials required for high temperature application. Demand of different and new alloys in metallurgical science is increasing day by day and hence scientists are trying to find different alloys by mixing different elements at different compositions.

Silver is very soft, ductile and malleable metal. The combination of silver with different elements helps to improve hardness and wear-resistance of deposits and higher stability tarnishing antifriction characteristics. There has been growing tendency in calculating the properties of silver–antimony alloys. It has been used as electroplating deposition due to its increased hardness and wear-resistance which, finally aims to the use of smaller plate thickness and consequent saving of expensive materials (Singh et al., 2010).

Different theoreticians are working with various theoretical models to understand the alloying behaviour of compound forming binary alloys. In the present work, one of the Silver alloys Ag-Sb is studied theoretically to determine certain properties at 1250 K assuming Ag_xSb_y (x=3, y=1) complex in melt by using Quasi lattice model. Thermodynamic properties such as free energy of mixing, heat of mixing and entropy of mixing , chemical activity provide the knowledge on the interaction, stability and bonding strength among the constituent atoms whereas information on

the structural ordering of atoms in binary alloys in the liquid state is provided by the quantitative analysis of microscopic functions, the concentration fluctuations in the long wavelength limit (Scc(0)), short-range order parameter ($\alpha 1$) and diffusivity (D_M/D_{id}) (Koirala et al., 2014; Jha et al., 2015; Koirala et al., 2018). Scc(0) represents the nature of ordering of the atoms, $\alpha 1$ quantifies the degree of ordering and diffusion coefficient ratio (D_M/D_{id}) gives the structural behaviour of the alloy.

The organization of this paper is as follows. In Section 2, the expressions required for the calculation are presented. In Section 3, result and general discussion of the alloy Ag-Sb are presented. Finally the conclusions are given in Section 4.

2. Theoretical Formulation

Let a binary alloy contains in all N atoms with N_A and N_B atoms of A and B elements respectively, k_B is Boltzmann constant, T is absolute temperature. Then the model considers the existence of chemical complexes A_xB_y where, A and B are the constituent species of the alloy and x and y are the small integers.

$$x\text{A} + y\text{B} = A_xB_y$$

With this consideration, grand partition function (Guggenheim, 1952) in terms of configurational energy 'E' is expressed as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp[(\mu_A N_A + \mu_B N_B - E)/k_B \text{T}] \quad (1)$$

Where $q_i(T)$ and μ_i are atomic partition function and chemical potential of the ith (i =A, B) species. By using above relation we find following expressions for the determination of different properties. With this consideration the excess free energy of mixing becomes

$$G_M^{XS} = NK_B T \int_0^c \gamma dc \quad (2)$$

Where γ is ratio of the activity coefficient of atom A to B; C is the concentration of atom A

The solution of eq^n. (2) leads to

$$G_M^{XS} = N[\phi \omega + \phi_{AB} \omega_{AB} + \phi_{AA} \omega_{AA} + \phi_{BB} \omega_{BB}] \quad (3)$$

Where ω's are the ordering energies; and Φ = c (1-c) and Φ_{ij}'s (i,j= A,B) are the simple polynomials in c depending on the values of x and y.

For A= Ag, B=Sb, x=3 and y=1, the values of Φ_{ij}'s (Bhatia & Singh, 1982) are found to be

$$\Phi_{AB}(c) = \frac{1}{5} c + \frac{2}{3} c^3 - c^4 - \frac{1}{5} c^5 + \frac{1}{3} c^6$$

$$\Phi_{AA}(c) = -\frac{3}{20} c + \frac{2}{3} c^3 - \frac{3}{4} c^4 + \frac{2c^5}{5} - \frac{1}{6} c^6$$

$$\Phi_{BB}(c) = 0$$

The Free energy of mixing for complex forming

$$G_M = G_M^{XS} + Nk_B T[c \ln c + (1-c) \ln(1-c)]$$
$$= RT \left[\Phi \frac{\omega}{k_B T} + \Phi_{AB} \frac{\Delta \omega_{AB}}{k_B T} + \Phi_{AA} \frac{\Delta \omega_{AA}}{k_B T} + \Phi_{BB} \frac{\Delta \omega_{BB}}{k_B T} + c \ln c + (1-c) \ln(1-c) \right] \quad (4)$$

The heat of mixing is found out by using standard thermodynamic relation:

$$\frac{H_M}{RT} = \frac{G_M}{RT} - \left[\frac{1}{R} \frac{dG_M}{dT} \right] c, N, P$$

$$= \Phi \left[\frac{\omega}{k_B T} - \frac{1}{k_B} \frac{d\omega}{dT} \right] + \Phi_{AB} \left[\frac{\Delta \omega_{AB}}{k_B T} - \frac{1}{k_B} \frac{d\Delta \omega_{AB}}{dT} \right] + \Phi_{AA} \left[\frac{\Delta \omega_{AA}}{k_B T} - \frac{1}{k_B} \frac{d\Delta \omega_{AA}}{dT} \right] + \Phi_{BB} \left[\frac{\Delta \omega_{BB}}{k_B T} - \frac{1}{k_B} \frac{d\Delta \omega_{BB}}{dT} \right] \quad (5)$$

The standard thermodynamic relation for entropy of mixing is

$$\frac{S_M}{R} = \frac{H_M}{RT} - \frac{G_M}{RT} \quad (6)$$

The activity of the constituent elements in the alloys is determined from standard thermodynamic relation

$$RT \ln a_i (\text{i = A, B}) = G_M + (1 - c_i) \left[\frac{\partial G_M}{\partial C_i} \right]_{T,P,N} \quad (7)$$

By solving eq^{ns}(4) and (7), the theoretical values activities of each component are given as follows.

$$\ln a_A = \frac{G_M}{RT} + \frac{1-C}{K_B T} \left[(1-2c) \omega + \Phi'_{AB} \Delta \omega_{AB} + \Phi'_{AA} \Delta \omega_{AA} + \Phi'_{BB} \Delta \omega_{BB} + \ln \frac{C}{1-C} \right] \quad (8)$$

$$\ln a_B = \frac{G_M}{RT} + \frac{C}{K_B T} \left[(1-2c) \omega + \Phi'_{AB} \Delta \omega_{AB} + \Phi'_{AA} \Delta \omega_{AA} + \Phi'_{BB} \Delta \omega_{BB} + \ln \left(\frac{C}{1-C} \right) \right] \quad (9)$$

Where, Φ'_{AB}, Φ'_{AA} and Φ'_{BB} are concentration derivatives of Φ_{AB}, Φ_{AA} and Φ_{BB} respectively.

The concentration fluctuation in long wavelength limit (Bhatia & Thornton,1970) for alloy is derived from standard relation

$$S_{cc}(0) = RT \left[\frac{\partial^2 G_M}{\partial c^2} \right]^{-1}_{T,P,N} \quad 10(a)$$

$$= c_2 a_1 \left[\frac{\partial a_1}{\partial c_1} \right]^{-1}_{T,P,} = c_2 a_2 \left[\frac{\partial a_2}{\partial c_2} \right]^{-1}_{T,P,} \quad 10(b)$$

Where c_1 (= c) and c_2 (=1-c) are concentrations and a_1 and a_2 are observed activities of elements A and B respectively.

Solving eq^{ns} (4) and 10(a), the theoretical value of Scc(0) is found as follows,

$$\text{Scc}(0) = \frac{c(1-c)}{1+c(1-c)\{-2\frac{\omega}{k_B T} + \phi''_{AB}\frac{\Delta\omega_{AB}}{k_B T} + \phi''_{AA}\frac{\Delta\omega_{AA}}{k_B T} + \phi''_{BB}\frac{\Delta\omega_{BB}}{k_B T}\}} \tag{11}$$

Where $\phi''_{i,j} = \frac{\partial^2 \phi_{i,j}}{\partial c^2}$ $(i, j = A, B)$

The Warren-Cowley short order parameter (Warren, 1969; Cowle, 1950) is related with concentration fluctuation in long wavelength limit as

$$\alpha 1 = \frac{S-1}{S(Z-1)+1} , \text{ where } S = \frac{S_{cc(0)}}{S^{id}_{cc(0)}} \tag{12}$$

$$S^{id}_{cc}(0) = c(1-c) \tag{13}$$

The mixing behavior of the alloy forming molten can also be studied at the microscopic level in terms of diffusion coefficient ratio which is related to concentration fluctuation in long wave length limit as,

$$\frac{D_M}{D_{id}} = \frac{S^{id}_{cc(0)}}{S_{cc(o)}} \tag{14}$$

Where D_{id} is the intrinsic diffusion coefficient for an ideal mixture and D_M is chemical or mutual diffusion coefficient.

D_M is given as (Darken & Gurrey, 1953; Singh et al., 2014)

$$D_M = D_{id} C_i \frac{d\ln a_i}{dC_i} \tag{15}$$

3. Results and Discussion

3.1 Thermodynamic properties

Free Energy of Mixing

The energy parameters used for free energy of mixing for Ag-Sb liquid alloy is determined by successive approximation method. The parameters are determined by using Eqn. (4) with experimental value of G_M in the concentration range from 0.1 to 0.9 (Hultgren et al.,1973). The best fit values of the parameters are

$$\frac{\omega}{k_B T} = -3.97, \frac{\Delta\omega_{AB}}{k_B T} = 4.38 , \frac{\Delta\omega_{AA}}{k_B T} = -2.68 \tag{16}$$

Eqn. (4) is used to compute the free energy of mixing (G_M/RT) for Ag-Sb liquid alloy. The plot of free energy of mixing verses concentration of antimony is shown in Fig. 1. The computed and experimental values of G_M/RT are in good agreement. The theoretical value of free energy of mixing is minimum i.e. -1.2RT at C_{Sb} =0.4. The theoretical calculation of free energy of mixing shows that at liquid state, the alloy Ag-Sb is moderately interacting and hence the tendency of compound formation is not so strong.
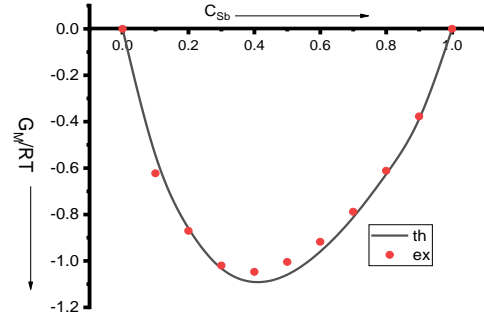

Fig. 1: Free energy of mixing (G_M/RT) vs concentration of antimony (C_{Sb}) in liquid alloy at 1250K
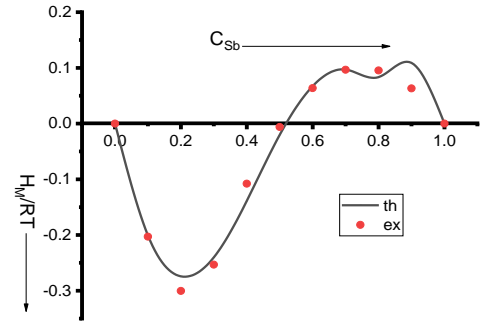

Fig. 2: Heat of mixing (H_M/RT) vs concentration of antimony (C_{Sb}) in liquid alloy at 1250K

Heat of Mixing

For the theoretical determination of heat of mixing temperature derivatives of interaction parameters are done. The observed values of H_M (Hultgren et al., 1973) are used by successive approximation method. The best fit values of parameters are

$$\frac{1}{k_B}\frac{d\omega}{dT} = 2.28, \frac{1}{k_B}\frac{d\Delta\omega_{AB}}{dT} = -7.89, \frac{1}{k_B}\frac{d\Delta\omega_{AA}}{dT} = -4.32 \tag{17}$$

Eqn. (5) is used to compute the heat of mixing (H_M/RT) for Ag-Sb alloy. The plot of heat of mixing verses concentration of antimony is shown in Fig. 2. It is found from the analysis that the heat of mixing is negative in antimony rich region whereas it is positive in the silver rich region. The observed S-shaped nature of heat of mixing verses concentration curve is well explained by the theory. The computed and experimental values of H_M/RT are in reasonable agreement with some discrepancies.

Entropy of Mixing

Using equation (6) along with equations (4) and (5), the entropy of mixing (S_M) is computed. For theoretical calculation same energy parameters eq^n (17) are used.

The plot of entropy of mixing(S_M/R) verses concentration of antimony is shown in Fig. 3 for the both theoretical and observed values. From figure, it is

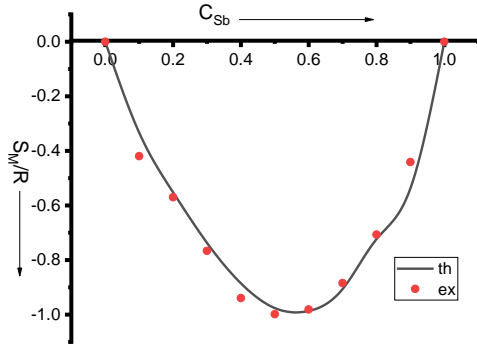observed that theoretical values are in good agreement with observed values.

Fig. 3: Entropy of mixing(S_M/R) vs concentration of antimony(C_{Sb}) in liquid alloy at 1250K
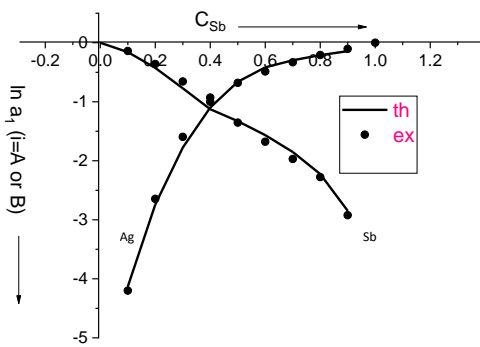

Fig. 4: Chemical activity vs concentration of antimony (C_{Sb}) in liquid alloy at 1250K

Chemical activity

The deviation from ideal behavior of alloys can be explained by chemical activitities. The eq^{ns} (8) and (9) are used for theoretical calculation of chemical activity of constituent elements of alloy Ag-Sb. Fig. 4 shows the observed and theoretical values of chemical activity of the alloy.There is good aggrement between experimental and thheoretical values of activity of Ag and Sb in Ag-Sb alloys at 1250K at all concentrations of Sb.

3.2 Structural properties

Concentration fluctuation in long wave length limit

One of the important function for the study of nature of atomic order of the binary liquid is considered as the Concentration fluctuations in the long-wavelength limit($Scc(0)$) because it removes difficulties in diffraction experiment(Bhatia & Thornton, 1970). For given concentration if $Scc(0) > S^{id}cc(0)$, the alloy is expected to have tendency of segregating while if $Scc(0) < S^{id}cc(0)$, the expected nature is complex formation .The experimental and theoretical values of Scc(0) at different concentrations of element antimony are obtained from eq^{ns} (10) and (11) respectively. The

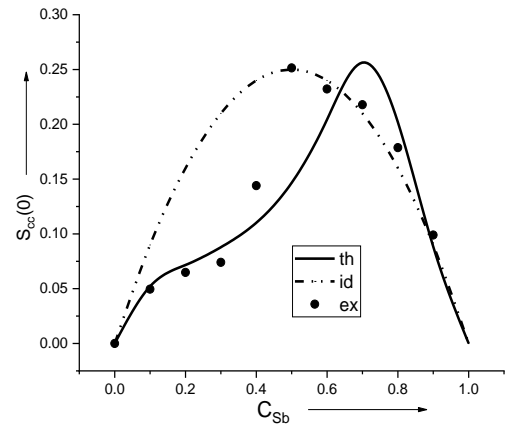plot of experimental and theoretical along with ideal values of Scc(0) verses concentration is shown in Fig.5.

Fig. 5: Concentration fluctuation in long wavelength limit($S_{cc}(0)$) vs concentration of antimony (C_{Sb}) in liquid alloy at 1250K
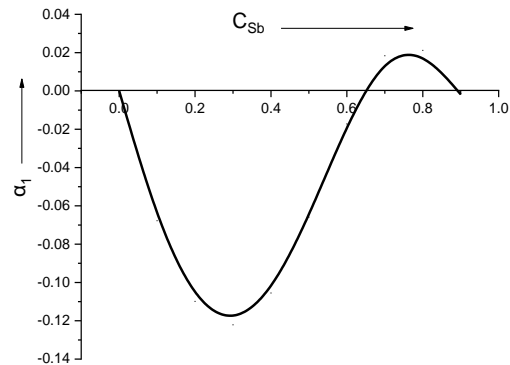

Fig. 6: Waren-Cowley short range order parameter vs concentration of antimony (C_{Sb}) in liquid alloy at 1250K

Warren- Cowley short range order parameter

The Warren-Cowley short-range orderparameter (α_1) is one of the useful parameter to quantify thedegree of chemical order in the alloy melt. It provides information of the local arrangement of the atoms in the molten alloys. For the equi-atomic composition, the Warren-Cowley short range orderparameter is found to be $-1 \leq \alpha_1 \leq 1$. Negative values of α_1 indicate ordering nature in the melt, which is complete if $\alpha_1 = -1$. On the other hand, positive values of α_1 indicate segregating nature, which is completeonly if $\alpha_1 = 1$. But $\alpha_1 = 0$, indicates the random distribution of the atoms in the mixture. The Scc(0) and α_1 have been computed as a function of concentration of Sb using Eqns. (12) and (13) respectively. The plot of theoretical value of α_1 verses concentration of Sb is shown in Fig. 6.

The Fig. 6 also shows that α_1 is between concentrations 0 to 0.62 of Sb which is the indication of unlike atoms pairing between constituent atoms.

3.3 Diffusivity

In terms of diffusion coefficient ratio, mixing behavior of liquid alloys can also be explained at the microscopic level. The relationship between Scc(0) and the diffusivity is expressed by the ratio of the mutual and self-diffusion coefficients (D_M/D_{id}) which indicates the mixing behavior of the alloys, i.e., the tendency for heterocoordination ($D_M/D_{id} > 1$) or homocoordination nature of atoms ($D_M/D_{id} < 1$) or ideal mixing ($D_M/D_{id} = 1$).
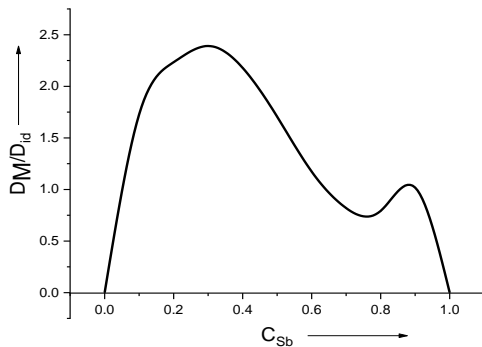

Fig. 7: Diffusion coefficient ratio vs concentration of antimony (C_{Sb}) in liquid alloy at 1250K

The calculated values of Scc(0) are used in eqⁿ. (15) to determine the ratio of the mutual and intrinsic-diffusion coefficients(D_M/D_{id}). Fig. 7 shows the plot of D_M/D_{id} against the concentration of antimony. In the figure, the value of D_M/D_{id} is found to be less than 1 in the range of concentration, which is indicative of the phase separarion in the mixture. A maximum value of $D_M/Di_d = 2.39$ for concentration of Sb = 0.3 confirms tendency for chemical ordering, observed by the Scc(0) and chemical short range orded parameter.

4. Conclusions

The thermodynamic properties of Ag-Sb alloy at melting temperature 1250K are examined on the basis of Quasi- lattice model. The model successively explains concentration dependent nature of the alloys by assuming Ag$_3$Sb complex in melt. From analysis it is justified that the alloy is moderately interacting in nature and hence it doesn't have strong tendency of compound formation. The energy parameters depend on temperature.

Conflicts of Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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