Free energy analysis of binary alloys at phase transition

Lisha Damodaran[1], T. P. Suresh[1] and K. M. Udayanandan[2*]

[1]School of Pure and Applied Physics, Kannur University, Kerala- 670 327, INDIA

[2]Nehru Arts and Science College, Kanhangad, Kerala- 671 314, INDIA

[*]*Corresponding author Email*: udayanandan@gmail.com

Abstract: Order-disorder transformation in alloys is a fascinating and extensively studied problem for many years. This transformation has been studied widely using the two state Ising model. But vacancies are not considered in two state Ising model, which may play an important rule in determining the composition of stable configuration. So we used three state Ising model which takes vacancies also at lattice sites. To make a realistic study we have included kinetic energy of the particles in the total Hamiltonian.

Keywords: Ising model, binary alloy, order-disorder transition

1. Introduction

From historic age onwards, human beings used alloys for various purposes. It is very interesting to see that the properties of alloys are entirely different from their constituent metals. The differences occur due to changes happened in the internal and external structure during the process of making alloys. The complex nature shown by alloys is not yet understood completely so far. Alloying one metal with other metal(s) or non-metal(s) enhances its properties. For instance, steel is stronger than iron, its primary element. The physical properties, such as density, reactivity, Young's modulus, electrical and thermal conductivities, of an alloy may not differ greatly from those of its elements, but engineering properties, such as tensile strength and shear strength may be substantially different from those of the constituent materials. Alloys may exhibit marked differences in behavior even when small amount of one element is present. Unlike pure metals, most alloys do not have a single melting point. Instead, they have a melting range in which the material is a mixture of solid and liquid phases [1]. Industrial alloys often undergo complicated fabrication processes, such as solidification and thermo mechanical treatments. Each processing brings in new structural variations to the alloys. We can make bronze, which is an alloy of copper and tin, by removing some of the copper atoms and replacing them with tin atoms; such an alloy is

called a random substitutional solid solution, indicating that the tin atoms substitute for copper atoms in the unit cells of the crystal in a random fashion, thus mixing the metals at the atomic scale to form a "solid solution". On the other hand, if we mix gold atoms to copper to make a copper-gold alloy at the ratio 3:1 then, the cube corners of the unit cell are preferentially occupied by the gold atoms, while those at the face centres are occupied by copper. Such alloys are known as ordered alloys and, it is also known that such alloys, on heating, lose this orderliness and become random substitutional solid solutions at high temperatures. This transformation is known as the order-disorder transformation [2]. In equi atomic compounds, A atoms can substitute on the lattice of B, but atoms B stay on their own lattices which leads to the presence of vacancies to maintain the stoichiometry.

Order-disorder transitions have been an active field of research over decades [3-7]. Bragg-Williams model was the first model for order-disorder transitions in binary alloys in which they used the idea of long range order parameter using two state Ising model [3]. Two state Ising model is used to analyse phase transitions in systems like lattice gas, binary alloys etc., traditionaly. Three state Ising model can also be used to explore phase transition problems [8]. Three state Ising model has a second order phase transition separating a low temperature ordered phase from a high temperature disordered phase. The three state model has been used in connection with problems like magnetism [9], normal liquid mixtures [10], and ternary mixtures [11] as well as other types of three state systems [12, 13]. In this paper we use three state Ising model in which the lattice sites can be occupied by two types of atoms or can be vacant. We obtained the free energy of the system by evaluating partition function in which total Hamiltonian is computed by using the Ising interaction energy along with the kinetic energy of the individual atoms. Bragg-William approximation is used to simplify the Hamiltonian. The equilibrium of the system is determined by minimizing the free energy with respect to the order parameter. By varying the number of vacancies in the alloy, the changes in the stable configuration with different composition is studied. The variation in the minimum of free energy with various mass ratios of elements also is studied.

2. Ising model and binary alloy

In the two state Ising model, a lattice is assumed in which on every site, there can be an atom of two possible different elements, say A and B, and that they can move i.e. exchange their positions on the lattice [14-17]. In three state Ising model, let N_A, N_B are the number of atoms A and B respectively and N_0 be the number of vacancies. The interaction energy given by Ising Hamiltonian is,

$$H_{int} = -\sum_{<ij>} \varepsilon_{ij} \sigma_i \sigma_j \tag{1}$$

where $<ij>$ indicates the interaction between nearest neighbours and σ_i is a variable at lattice site, which can take values ± 1 for spin up or spin down states of a ferromagnetic system, atom *A* or

atom B in the case of a binary alloy. Each atom interacts with its nearest neighbours on the lattice with an exchange interaction energy ε_{ij}. So

$$\sigma_i = +1 \quad \text{for atom A}$$
$$= -1 \quad \text{for atom B}$$
$$= 0 \quad \text{for a vacancy}$$

Here the exchange interaction is assumed as a hard core type and hence

$$\varepsilon_{ij} = \varepsilon_{ij} \quad \text{for nearest neighbour distance } r_0$$
$$= \infty \quad \text{for neighbour distance } < r_0$$
$$= 0 \quad \text{otherwise}$$

where r_0 is the lattice spacing.

3. Hamiltonian for binary alloy

The different types of nearest neighbouring pairs considered in our model are

$$N_{AA} \rightarrow \text{The number of AA pairs}$$
$$N_{BB} \rightarrow \text{The number of BB pairs}$$
$$N_{AB} \rightarrow \text{The number of AB pairs}$$
$$N_{A0} \rightarrow \text{The number of A and vacancy pairs}$$
$$N_{B0} \rightarrow \text{The number of B and vacancy pairs}$$
$$N_{00} \rightarrow \text{The number of vacancy pairs}$$

The Hamiltonian of a binary alloy can be mapped into the Hamiltonian of Ising model [18].
Using Eq. (1) Hamiltonian for the interaction energy is

$$H_{int} = -\varepsilon_{AA} N_{AA} - \varepsilon_{BB} N_{BB} + \varepsilon_{AB} N_{AB} \tag{2}$$

For symmetric pairs (AA, BB) interaction energies are considered as same and is taken as ε_s and between asymmetric pairs (AB), it is taken as ε_a. It is assumed that there is no interaction between vacancies, between vacancy and the atoms A and B. The effect of vacancies comes into the Hamiltonian through the number of pairs of atoms. Hence Eq. (2) is modified as

$$H_{int} = -\varepsilon_s \left(N_{AA} + N_{BB} \right) + \varepsilon_a N_{AB} \tag{3}$$

Let N be the total number of lattice sites, then obviously

$$N = N_A + N_B + N_0 \tag{4}$$

Let γ denotes the co-ordination number of the lattice i. e., the number of nearest neighbours or each lattice site [15]. Since particles are taken to be independent in mean field theory [16,19], the number of N_{AA} pairs can be obtained as follows: since $\gamma N / 2$ is the total number of bonds , the probability

of having an AA pair in the ith configuration is proportional to the product of probabilities of having a site occupied by A and the other by A itself. So

$$\frac{N_{AA}^i}{\gamma N / 2} \approx \left(\frac{N_A}{N}\right)\left(\frac{N_A}{N}\right) \tag{5}$$

Similarly

$$\frac{N_{AA}}{\gamma N / 2} \approx \frac{N_A^2}{N^2}$$

$$\frac{N_{BB}}{\gamma N / 2} \approx \frac{N_B^2}{N^2} \tag{6}$$

$$\frac{N_{00}}{\gamma N / 2} \approx \frac{N_0^2}{N^2}$$

Also we can have,

$$\gamma N_A = 2N_{AA} + N_{AB} + N_{A0}$$

$$\gamma N_B = 2N_{BB} + N_{AB} + N_{B0} \tag{7}$$

$$\gamma N_0 = 2N_{00} + N_{A0} + N_{B0}$$

From these relations we get,

$$N_{AB} = \gamma(N_A + N_B) - (N_{AA} + N_{BB}) + N_{00} - \gamma N / 2 \tag{8}$$

Substituting in the Hamiltonian

$$H_{int} = -\varepsilon_s \left(N_{AA} + N_{BB}\right) + \varepsilon_a \left(\gamma(N_A + N_B) - (N_{AA} + N_{BB}) + N_{00} - \gamma N / 2\right) \tag{9}$$

To simplify the Hamiltonian, two parameters, relative emptiness 'r ' and asymmetry parameter 'a' are defined [20]

$$r = \frac{N_0}{N}$$
$$a = \frac{N_A - N_B}{N} \tag{10}$$

Substituting we get,

$$H_{int} = -C_1 N a^2 - C_2 N (1-r)^2 \tag{11}$$

where $\quad C_1 = \frac{(\varepsilon_s + \varepsilon_a)\gamma}{4} \quad$ and $\quad C_2 = \frac{(\varepsilon_s - \varepsilon_a)\gamma}{4}.$

Including the kinetic energies of the particles A and B [15, 20], we get the total Hamiltonian as,

$$H = -C_1 N a^2 - C_2 N (1-r)^2 + \frac{N_A p_A^2}{2m_A} + \frac{N_B p_B^2}{2m_B} \tag{12}$$

The canonical partition function

$$Q = \sum_{r=0} g(r,a,N) e^{-\beta H} \tag{13}$$

Where $g(r,a,N)$ is the number of distinct ways in which N_A and N_B indistinguishable atoms can be distributed among N lattice sites with N_0 as the number of vacancies. The summation ensures that the values of N_{AA} and N_{BB} are consistent with the given values of N_A, N_B and N.

$$g(r,a,N) = \frac{N!}{N_A! N_B! N_0!} \tag{14}$$

Using Eq. (10)

$$N_A = \frac{N}{2}(1-r+a)$$
$$N_B = \frac{N}{2}(1-r-a) \tag{15}$$
$$N_0 = Nr$$

Then,

$$g(r,a,N) = \sum \frac{N!}{(Nr)!\left(\frac{N}{2}(1-r+a)\right)!\left(\frac{N}{2}(1-r-a)\right)!} \tag{16}$$

Since the particle numbers are varying, using grand canonical ensemble, partition function is,

$$Z = \sum_{r=0}^{N} g(r,a.N)e^{-\beta H}e^{\beta(\mu N_A + \mu N_B)} = \sum_{r=0} g(r,a.N)z^{(N_A+N_B)}e^{-\beta H} \tag{17}$$

Substituting the value of $g(r,a,N)$

$$Z = \sum \frac{N!e^{-\beta H}z^{N_A+N_B}}{(Nr)!\left(\frac{N}{2}(1-r+a)\right)!\left(\frac{N}{2}(1-r-a)\right)!} \tag{18}$$

where $z = e^{\beta\mu}$ is the fugacity. Integrating and taking logarithms on both sides

$$\ln Z = \ln Z_K + \ln Z_{int} \tag{19}$$

Where $Z_K = \dfrac{1}{\lambda_A^{3N_A}} \dfrac{1}{\lambda_B^{3N_B}} \dfrac{1}{N_A!N_B!}$ and $Z_{int} = \sum \dfrac{N!e^{-\beta H_{int}}z^{N_A+N_B}}{(Nr)!\left(\frac{N}{2}(1-r+a)\right)!\left(\frac{N}{2}(1-r-a)\right)!}$ (20)

$\lambda_A = \dfrac{h}{\sqrt{2\pi m_A kT}}$ and $\lambda_B = \dfrac{h}{\sqrt{2\pi m_B kT}}$ are the thermal wavelength of particle A and B.

Substituting from Eq. (15) and maximizing $\dfrac{\ln Z_K}{N}$ with respect to r,

$$\frac{\ln Z_K}{N} = 1 - r + \frac{a}{2}ln\left[\frac{\lambda_A^3(1-r+a)}{\lambda_B^3(1-r-a)}\right] \tag{21}$$

Similarly we get,

$$\frac{\ln Z_{int}}{N} = \beta\left(C_1 a^2 - C_2(1-r)^2\right) - \ln r - \frac{a}{2}\ln\left[\frac{(1-r+a)}{(1-r-a)}\right] \tag{22}$$

So,

$$\frac{\ln Z}{N} = \frac{PV}{k_B T} = \beta\left(C_1 a^2 - C_2(1-r)^2\right) - \ln r - a\ln\left[\frac{(1-r+a)}{(1-r-a)}\right] + 1 - r - \frac{3a}{2}ln\left[\frac{\lambda_A}{\lambda_B}\right] \qquad (23)$$

Landau free energy or grand potential, $\qquad \Phi = -k_B T \ln Z \qquad (24)$

In practice, since the potentials are of hard-core type, there is a maximum number of particles that may be packed into the finite volume *V*. Then the grand free energy density is given by $\phi = \dfrac{\Phi}{V}$ and it is found to be equal to negative of pressure from the principles of thermodynamics [21, 22]. So the thermodynamic potential describing an infinite system at equilibrium with a reservoir of particles at fixed chemical potential is the pressure P (grand canonical ensemble). The Gibbs free energy G and pressure P are each other's Legendre transform. Since each can be obtained from the other by a Legendre transform, G and P contain the same information about the system, and either of them can be used to study the thermodynamic behaviour of the binary alloy [23]. Since the maximum number of particles is *N* and volume of each site is assumed to be unity, *V=N*, we get $\phi = \dfrac{\Phi}{N}$.

$$\phi = -\left(C_1 a^2 - C_2(1-r)^2\right) - \ln r + k_B T\left[a\ln\left[\frac{(1-r+a)}{(1-r-a)}\right] + 1 - r - \frac{3a}{2}ln\left[\frac{\lambda_A}{\lambda_B}\right]\right] \qquad (25)$$

4. Discussions

The plotting of the phase diagram is a crucial part in the study of metallurgy. It shows the equilibrium states of a mixture, so that given a temperature and composition, it is possible to calculate which phases will be formed, and in what quantities. In the case of solid solutions like alloys the free energy of the solution will become dependent on its composition as well as the temperature. So free energy curves can be used to determine the most stable state for a system. Stable state is the phase or phase mixture with the lowest free energy for a given temperature and composition. Here we plot free energy density against the asymmetry parameter (a), at different temperatures. At high temperatures there is a complete solution and the curve has a single minimum. At low temperatures the curve has a maximum and two minima. Upon decreasing the temperature, $\phi(a)$ becomes concave first at the critical temperature T_c. Let a_0 be the value of asymmetry parameter corresponding to the minimum of free energy. For $T < T_c$, in the composition range $-a_0$ to $+a_0$ between the two minima (indicated by the vertical lines), a mixture of two phases is more stable than a single-phase solution, i.e., there is a range of compositions for $a < |a_0|$ where

$\phi(a)$ is not convex and hence the composition is locally unstable. We can find the value of a_0 for a given alloy graphically. Thus, at very low temperatures, there is mixing at the atomic scale (which is known as ordering), while at high temperatures, the mixing is truly random. We here show that the requirement of convexity of $\phi(a)$ [17] breaks down below a critical temperature T_c.
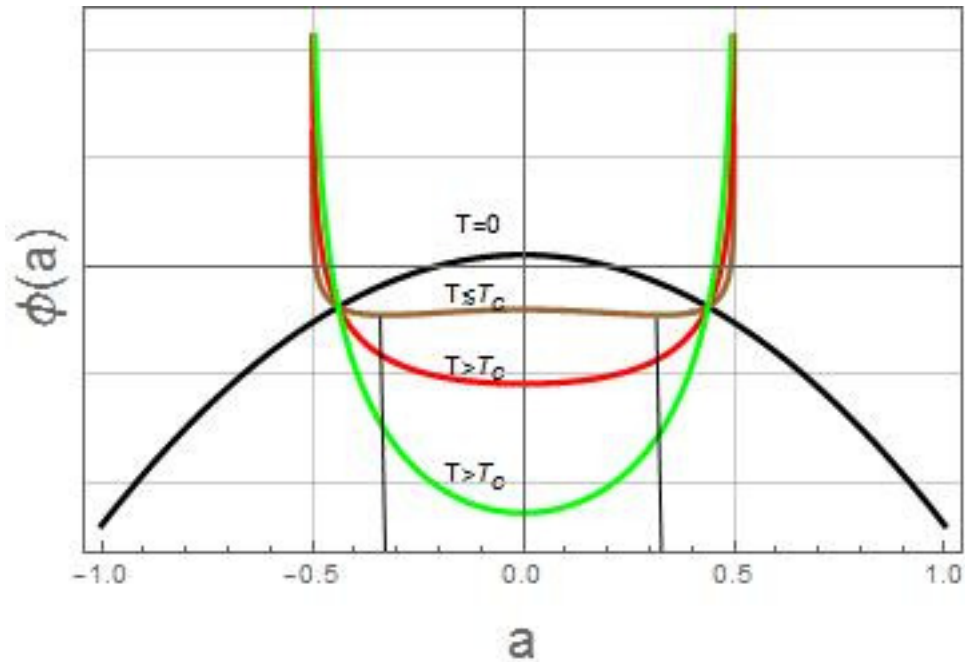

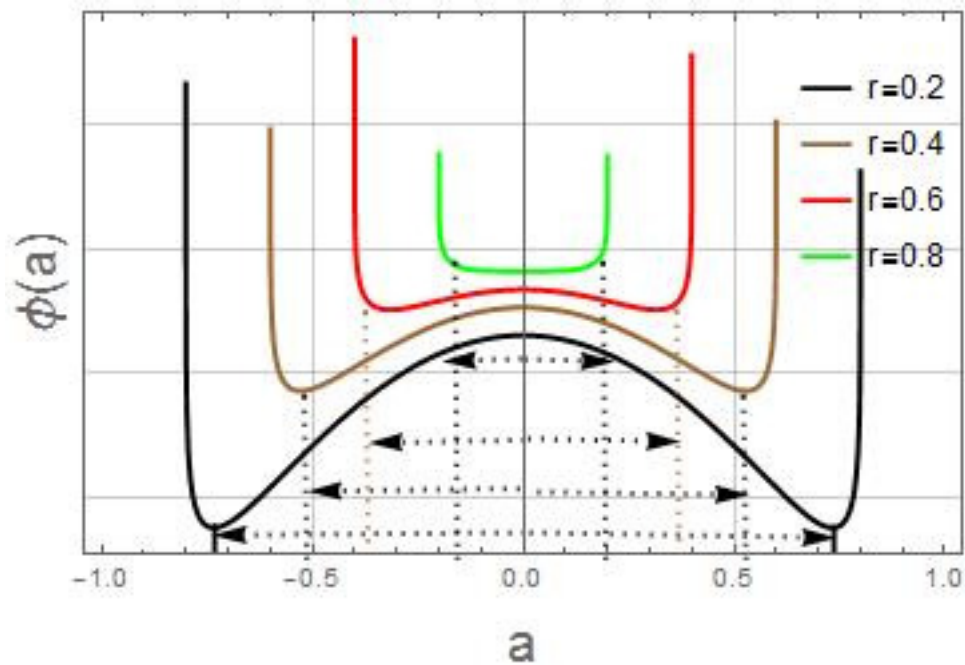Figure 1. Dependence of Free energy on Asymmetry parameter at different temperatures

Figure 2. Dependence of Free energy on Asymmetry parameter for different r values at Tc

A graph (Fig.2) is drawn by changing the relative emptiness parameter r also. The range of asymmetry parameter shows a variation with r i.e., the occurrence of vacant spaces along with constituents *A* and *B* in the binary alloy changes range of composition where the mixture is locally stable. Today, there are many empirical and semi-empirical models available with which to evaluate the properties of liquid metals and alloys. Experimental and theoretical studies on liquid metals are problematic. The Miedema model [24] developed in the early 1970's is applied to calculate interaction co-efficient using three parameters electronic density, atomic volume and electro negativity. Viscosity plays a critical role in quantitatively understanding the fluid transport process and reaction kinetics in metallurgical process design. However, the parameter of mixed energy in these models is not easily determined, and most predictive models have been poorly applied [25]. From Fig.1, it is clear that if we know the critical temperature for an alloy, we can find C_1 and C_2 by curve fitting from which the interaction energy between constituent elements can be found out. We have studied the variation in free energy by changing the ratio of masses ($l = \sqrt{\dfrac{m_B}{m_A}}$) of the individual atoms.
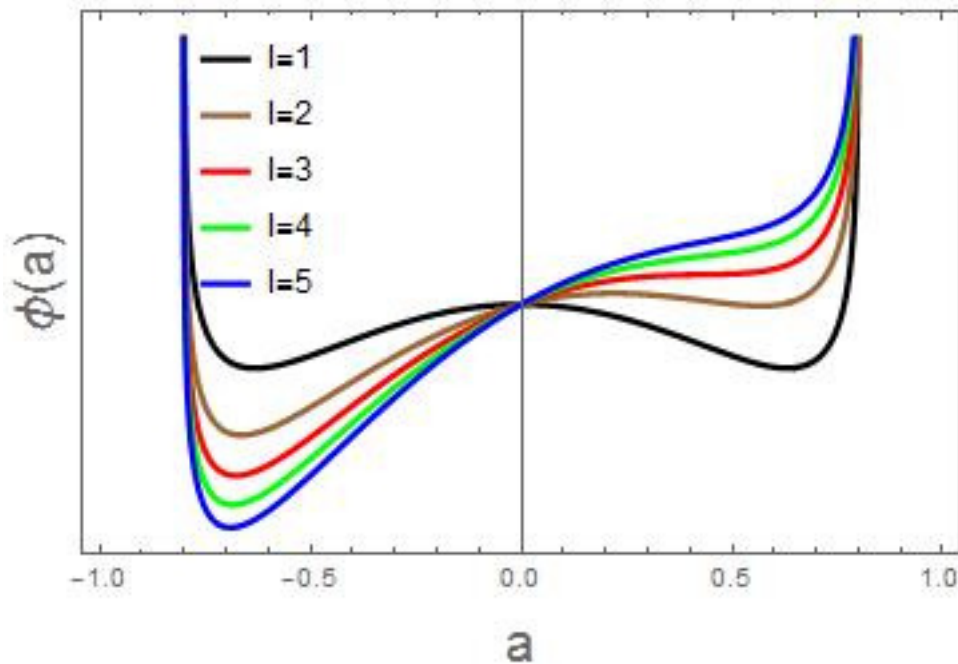

Figure 3: Dependence of Free energy on masses of the components.

It is found that free energy is independent of the masses if the number of atoms *A* and *B* are equal. In all the other cases the minimum of free energy depends on the masses of the component atoms. This analysis help in selecting the components of the alloy to have the most stable configuration.

5. Conclusion

Three state Ising model is used in the free energy analysis of binary alloys. The order-disorder transition nature is clear from the phase diagrams. The interaction energy of the constituent atoms can be found out if we know the critical temperature. The presence of vacancies is found to affect the range of composition of stable configuration. It is also clear that the masses of the atoms have an important role in determining the most stable state of the system.

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