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Review

Temperature dependence of thermodynamic properties of Si–Ti binary liquid alloys

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ABSTRACT

This study is an attempt to extract useful thermodynamic information from experimental free energy of mixing of Si–Ti binary liquid alloy at different temperatures. A number of temperature dependent thermodynamic functions are calculated in the frame of a simple approach based on a statistical mechanical model. It is reported that the thermodynamic functions of Si–Ti alloy exhibit strong negative deviation from Raoult's law across the whole concentration range and the impact of temperatures on the liquid alloy is explained. The energetics of mixing in the alloy has been explained through the study of activity, free energy of mixing, concentration fluctuations in the long-wavelength limits, chemical short-range order and diffusion. In addition, it is also observed that the tendency for intermetallic associations, which leads to the formation of SiTi compounds, decreases with the increase in temperature. This study reinforces further that useful thermodynamic information may be obtained from experimental data obtain using FactSage Thermo-Chemical Software and databases for binary liquid alloys.

Contents

1. Introduction

For a clear understanding of the energetics of liquid alloys, it is important to note that the atomic interactions and the related energies [1–3] among the constituent atoms of the alloy is quite dependent on the stability of liquid alloys. Based on this, the interaction energy parameters play a key role in classifying all liquid binary alloys according to the deviations of their thermodynamic and thermophysical properties from the Raoult's law into two main types: short-range ordered (negative deviation) or segregating (positive deviation) alloys [4–10].

Quite a number of models [5–17] have been used by many researchers to understand the alloying behaviour of compound forming alloys. Also, it is a known fact that heterocoordination

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which is the pairing of unlike atoms is an important factor responsible for compound formation. In addition, a good knowledge of the phase diagram of alloys is crucial for proper understanding of the energetics of liquid alloys.

In this study, a simple approach based on a statistical mechanical model [11] which is identical to the quasi-lattice model employed in [12] is used to study liquid Si–Ti alloys at temperatures of 2000 K, 2400 K and 2473 K, respectively. This model has been successfully used in [11,12] to study the alloying behaviour of Au–Zn (a strong interacting system), Cd–Bi (a weak heterocoordinated system), Cd–Mg (a weak heterocoordinated system) and Cd–Ga (a homocoordinated system). Our interest in Si–Ti was motivated by the recently predicted thermodynamic data for liquid Si–Ti alloys obtained using FactSage Thermo-Chemical Software and Databases by Kostov and coworkers [18]. It is quite interesting to investigate the impact of temperature on the intermetallic associates using statistical mechanical model and to elucidate the energetics in the binary liquid Si–Ti alloy for the following noteworthy reasons: Firstly, we observed that thermodynamical study of Si–Ti alloy has not been reported due to none availability of experimental data. Secondly, the FactSage method [19,20] has been employed by some theoreticians to make thermodynamic predictions of binary liquid alloys such as Ti–Al based alloys and thirdly, we attempted to show that useful theoretical thermodynamic information could be extracted from thermodynamic data obtain using FactSage Thermo-Chemical Software and databases for binary liquid alloys and therefore, serves as a basis for comparison with some future critical experimental works.

Furthermore, titanium-based alloys possess characteristics such as high oxidation resistance, low density and high melting point which are of practical interest in aerospace industry and biomedicine [21]. Some Ti-based systems have been studied thermodynamically using FactSage by Kostov et al. [18–20]. The high-melting temperature and good oxidation resistance characteristics of Ti-based intermetallics have motivated the strong interest in their fundamental properties. Today, among the refractory metal/silicon compounds or intermetallics, titanium silicides systems such as $TiSi_2$, TiSi, Ti_5Si_4, Ti_5Si_3 and Ti_3Si have received considerable attention because these materials have been found to possess the lowest electrical resistivity at room temperature, ease of formation and self-alignment capability [22–24]. As a consequence they are preferred when interconnections in silicon integrated electronic devices are required. Moreover, recent studies by [25–27] also suggested that these silicides systems are promising candidates as anode materials in lithium-ion batteries. While, mechanical alloying of Ti/2Si system has been performed by Lee et al. [26] using high-energy milling, in which the phase formation during alloying was analyzed. Remarkably, the thermodynamic assessment and phase equilibria of multi-component systems of Ti such as Ti–Al–N, Ti–Al–Si and Si–Ti–N have also been studied using various method as differential thermal analysis and X-ray diffraction [28,29], which indicate that Si–Ti–N system is attracting much attention due to its higher hardness value and better stability at elevated temperature [29].

On the other hand, silicon finds usage as an important alloying additive to titanium alloys and contributes useful dispersion strengthening and enhances microstructure stability [18]. A recent study by Iwata et al. [30] predicted the thermodynamic properties, as well as activity coefficients and the interaction parameters of the solute elements in infinite dilute Si solutions, from first principles calculations based on density functional theory, while the formation of the Si/Ti interface during the deposition of silicon on titanium polycrystalline substrates has equally been reported by Palacio and Arranz [31], at room temperature using X-ray photoelectron spectroscopy, angle-resolved XPS, ultraviolet photoelectron spectroscopy and ion scattering spectroscopy. In addition, liquid semiconductors have properties which are of both fundamental and practical interest. From a basic viewpoint, many liquid semiconductors such as Ga, Si and Ge are metallic, even though in the solid phase they are semiconductors; the metal-insulator transition on melting suggests a substantial structural change. From a more practical viewpoint, most useful semiconductors are grown from the melt. Therefore, the properties of such liquids, including thermodynamic, electrical conductivity as well as atomic diffusion coefficient are important parameters which often enter into the equations governing crystal growth.

But so far to the best of our knowledge, no systematic theoretical thermodynamic investigation has been performed or reported on liquid Si–Ti alloy up till date. This is why liquid Si–Ti alloy has been chosen for theoretical investigation. Within the statistical mechanical model, expressions for various thermodynamic and microscopic functions such as activity, Gibbs free energy of mixing, concentration–concentration fluctuations in the long wavelength limit, chemical short-range order parameter and diffusion coefficient have been developed to explain the temperature dependence of the thermodynamical properties of Si–Ti binary liquid alloy.

In the next section, theoretical formalism for the model used in our calculations are given. In Section 3, results and discussion on various thermodynamic and microscopic functions as well as diffusion are presented. Section 4 is the conclusion.

2. Theoretical formulation

If a binary alloy contains $N_1(=NC_1)$ atoms of the element 1 and $N_2(=NC_2)$ atoms of the element 2 such that there are $N(=N_1+N_2)$ atoms in the alloy, then the expression for the grand partition function for the alloy can be written as [11]

$$\Xi = \sum \underset{1}{\overset{N_1}{q}}(T) q_2^{N_2}(T) \exp\left(\frac{\mu_1 N_1 + \mu_2 N_2 - E}{k_B T}\right) \tag{1}$$

In Eq. (1) q_i (T) are the partition functions of atoms i (=1 or 2) associated with inner and vibrational degrees of freedom and it is assumed that the partition functions remain unchanged immaterial of whether the atom i is located in the pure state or located in the alloy; μ_1 and μ_2 are the chemical potentials while E is the configuration energy.

If atomic clusters of different sizes are considered then from Eq. (1) an expression for the conditional probability $P_{1/2}$ (i.e. the probability of finding atom 1 as a nearest neighbour of a given atom 2) can be written as [11]

$$P_{1/2} = \frac{1}{1 + ((C_2/C_1)/\sigma)\exp(\omega/zk_B T)} \tag{2}$$

In Eq. (2) σ is defined as

$$\sigma = \frac{(\beta + 2C_1 - 1)\exp(-\omega/zk_B T)}{2C_1} \tag{3}$$

The β in Eq. (3) is defined as [11]

$$\beta = \sqrt{(1 + 4C_1C_2[\exp(2\omega/zk_B T) - 1])} \tag{4}$$

In Eqs. (2)–(4) z is the coordination number while the parameter ω is the ordering energy of the alloy whose value reveals the alloying behaviour of a binary alloy. Hence, when $\omega = 0$ for a given alloy it indicates an ideal behaviour whereas $\omega > 0$ and $\omega < 0$ indicates like-atom pairing (i.e. segregation) and unlike-atom pairing (i.e. ordering), respectively.

The expressions for thermodynamic relations employed in our calculations on the basis of Eq. (3) are given as follows [11]

- Free energy of mixing:

$$\frac{G_M}{RT} = C_1 \ln C_1 + C_2 \ln C_2 + C_1 \ln \gamma_1 + C_2 \ln \gamma_2 \tag{5}$$

where $\gamma_1 = [(\beta - 1 + 2C_1)/C_1(1+\beta)]^{z/2}$ and $\gamma_2 = [(\beta + 1 - 2C_1)/C_2(1+\beta)]^{z/2}$

- Concentration–concentration fluctuations:

$$S_{cc}(0) = \frac{C_1 C_2}{[1 + (z/2\beta)(1-\beta)]} \tag{6}$$

- Activities:

$$a_1 = C_1\gamma_1 \tag{7}$$

$$a_2 = C_2\gamma_2 \tag{8}$$

- Short-range order parameter:

$$\alpha_1 = \frac{(S-1)}{[S(z-1)+1]} \tag{9}$$

where $S = (S_{cc}(0)/C_1C_2)$.

3. Results and discussion

3.1. Activity and free energy of mixing

The theoretical model described in the preceding section has been used to study the temperature dependence of the bulk thermodynamic properties of Si–Ti binary liquid alloys at three different temperatures. Using Eq. (5), the Gibbs free energy of mixing, G_M has been computed. The predicted Gibbs free energies of mixing obtained via FactSage Thermo-Chemical Software in [18] were taken as the experimental data since there were no reported direct experimental data at the temperature of investigation due to experimental difficulties [18]. From the phase diagram [18,32], it is evident that Ti and Si are completely miscible in liquid state and can exist as intermetallic compounds in the solid state, SiTi ($\mu = 3$, $\nu = 2$) at nearly all the investigated temperatures, thus suggesting short-ranged order or some form of heterocoordination in the corresponding liquid phase [14]. Obviously, it is not impossible for such associates to exist in some form in the liquid phase close to the melting temperature.

A successful calculation of the thermodynamic quantities defined in the preceding section will require appropriate value of the coordination number z and the ordering energy ω. Thus, we have used $Z = 10$ in all our calculations (in the liquid and amorphous states, the atoms are randomly distributed in a nearly close-packed structure and the coordination number of the nearest neighbours is about 10 [6,11,16,33,34]) and numerically determined appropriate values of the ordering energy parameters for Si–Ti at the three temperature of interest which simultaneously reproduce to a reasonable extent the experimental Gibbs free energy of mixing, G_M and the experimental concentration–concentration fluctuations, $S_{cc}(0)$ (obtained from experimental free energy of mixing). The values of the ordering energy ω obtained for the three different temperatures 2000 K, 2400 K and 2473 K using the above procedure are given in Table 1.

Fig. 1 shows the plot of the calculated values of activities vs. concentration obtained using Eqs. (7) and (8) for the alloys at respective temperatures. Unfortunately, there are no experimental data on activities of the components in the binary alloy of Si–Ti at the three temperatures we investigated, so our calculated activities values could not be compared with experiment.

Table 1
Fitted energy parameters used in all calculations at respective temperatures.

Alloy	T/K	Z	W/k_BT
Si–Ti	2000	10	−9.385
	2400	10	−7.948
	2473	10	−7.450

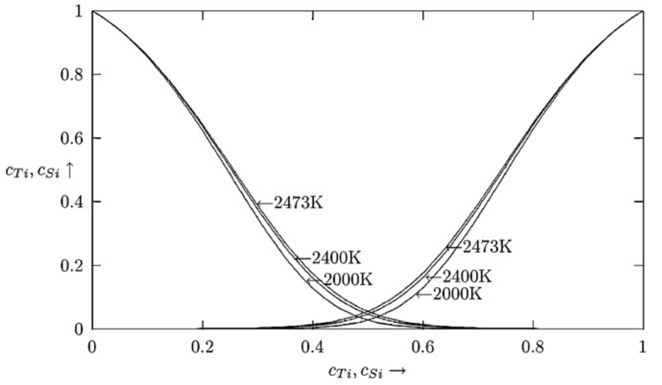

Fig. 1. Concentration dependence of activity of Ti and Si in liquid Si–Ti alloys at 2000 K, 2400 K and 2473 K, respectively. C_{Ti} and C_{Si} are the concentrations of Ti and Si respectively in the alloy.

The plots of the concentration dependence of the free energy of mixing at the three different temperature 2000 K, 2400 K and 2473 K are shown in Fig. 2. A comparison of the fits of the calculated values and the experimental data for Si–Ti at respective temperatures shows reasonable agreement despite slight deviations in the concentration range $0 \le c_{\text{Ti}} \le 0.60$. A perusal of this figure shows that their Gibbs free energy of mixing are almost symmetric around the equiatomic composition (i.e. $c_{\text{Ti}} = 0.5$). We as well observe that in these plots the magnitude of G_M/RT decreases with increasing temperature such that the value of G_M/RT at the compound forming composition (i.e. $\left(G_M/RT\right)_{c_c}$, with $C_c = \mu/(\mu+\nu) = 0.6$, using $\mu = 3$ and $\nu = 2$ as obtained from the phase diagram) is highest with value −3.398 at 2000 K and lowest at 2473 K with value −2.766. This implies that Si–Ti alloys at 2000 K exhibit the strongest tendency for compound formation and are most interacting whereas at 2473 K they are least interacting. The value $\left(G_M/RT\right)_{c_c} = -2.925$ obtained at 2400 K reveals that Si–Ti alloys are more interacting at this temperature than at 2473 K where $\left(G_M/RT\right)_{c_c} = -2.766$.

3.2. Concentration fluctuations in the long wavelength limit ($S_{cc}(0)$) and diffusion

It has been reported that the ideal values of S_{cc} (0) (i.e. S_{cc}^{id} (0)) is obtained from the relation: $S_{cc}^{id}(0) = C_1C_2$ and that when $S_{cc}(0) < S_{cc}^{id}(0)$, the existence of chemical ordering leading to complex formation is expected while $S_{cc}(0) > S_{cc}^{id}(0)$ is an indication of segregation [1,9,14]. The same z and ω values used in the calcula-

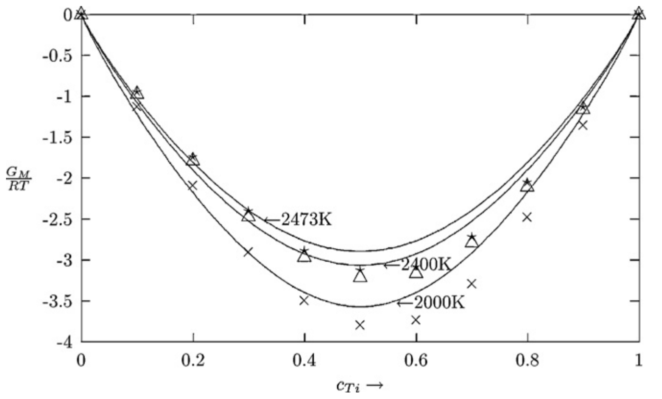

Fig. 2. Concentration dependence of G_M/RT for liquid Si–Ti alloys at 2000 K, 2400 K and 2473 K, respectively. The solid line denotes theoretical values while the times, the triangles and the stars denote experimental values, respectively. c_{Ti} is Ti concentrations in the alloy. The experimental data are from [18].

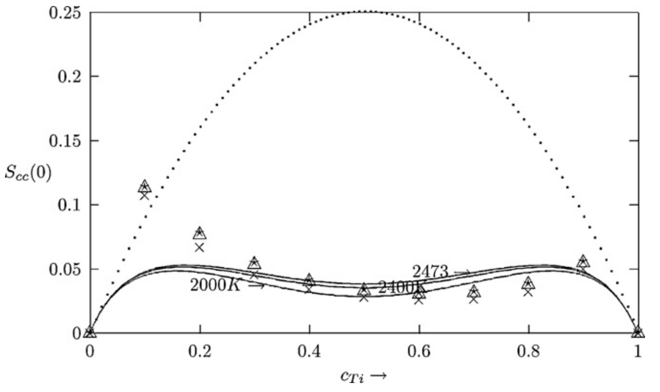

Fig. 3. Concentration fluctuations in the long-wavelength limit ($S_{cc}(0)$ and $S_{cc}^{id}(0)$) vs. concentration for liquid Si–Ti alloy at 2000 K, 2400 K and 2473 K, respectively. The solid lines denote theoretical values while the times, triangles and stars denote experimental values, respectively. The dots stand for the ideal values, $S_{cc}^{id}(0)$. c_{Ti} is the Ti concentration in the alloys.

tion of the free energy of mixing and activity were employed in the calculations of $S_{cc}(0)$ using Eq. (6) while the experimental values of $S_{cc}(0)$ were obtained from the experimental free energy of mixing using [1,9,14]:

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial c_1^2}\right)^{-1}_{T,P,N}$$

The results obtained from the above computations are plotted in Fig. 3. As we can see from the figure, $S_{cc}(0) < S_{cc}^{id}(0)$ throughout the entire range of concentration. This indicates strong negative deviation from the ideal mixture behaviour which is in agreement with Kostov et al. [18] on thermodynamic prediction of Si–Ti binary system and, also confirms the presence of chemical ordering, a preference for unlike atoms to pair with nearest neighbours and a tendency of complex formation in the alloys. The effect of temperature on $S_{cc}(0)$ for Si–Ti alloys as can be seen in Fig. 3 follows the same trend as that of temperature on the free energy of mixing. Thus, we observe that at compound forming concentration, C_c the deviation of the calculated $S_{cc}(0)$ from the computed $S_{cc}^{id}(0)$ is highest at temperature 2000 K (the deviation = 0.208) and lowest at temperature 2473 K (the deviation = 0.199). This again confirm that Si–Ti alloys at 2000 K exhibit the strongest tendency for compound formation and are most interacting whereas at 2473 K they are least interacting. The deviation value of 0.202 obtained at 2400 K reveals that Si–Ti alloys are more interacting at this temperature than at 2473 K where the deviation is 0.199.

3.3. Short-range order parameter (α_1)

In order to shed light on the nature of local arrangements of atoms in the mixture the Warren–Cowley chemical short-range order parameter (α_1) is computed using the expression given in Eq. (9)[4,9,16]. It is to be noted that $\alpha_1 > 0$ refers to like atoms pairing, $\alpha_1 = 0$ indicates a random distribution, and $\alpha_1 < 0$ corresponds to unlike atoms pairing as nearest neighbours. The computed values of α_1 at the different temperatures are shown in Fig. 4. The negative values of α_1 throughout the whole concentration range and temperatures suggest the presence of chemical order. This further indicates that Si–Ti binary liquid alloy is an ordered alloy. In addition, the plot of α_1 vs. c_{Ti} becomes shallow with the increase of temperature as can be observed from Fig. 4, indicating a lower degree of association or compound formation with increase in temperature.

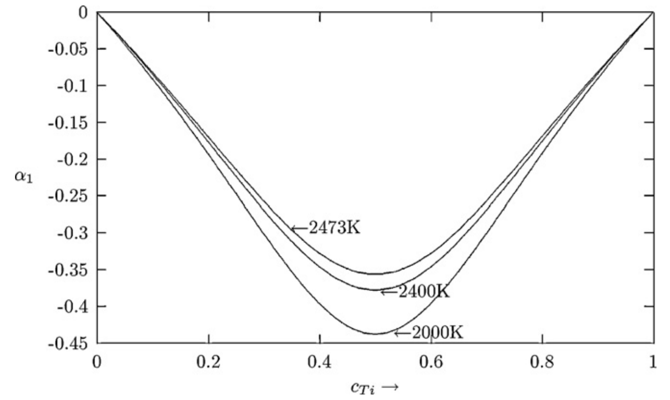

Fig. 4. Calculated Warren–Cowley short range order parameter, α_1 using Eq. (9) vs. concentration for liquid Si–Ti alloys at 2000 K, 2400 K and 2473 K, respectively. C_{Ti} and C_{Si} are the concentrations of Ti and Si respectively in the alloy.

3.4. $S_{cc}(0)$ and diffusion

To further substantiate our findings, the relation between $S_{cc}(0)$ and diffusion coefficient, D, is examined. This parameter is likely to play an important role due to its possible application in many technological and corrosion phenomena [16,35]. The interdiffusion coefficient (D_M) of any binary alloy is related to the activity (a_i) and self-diffusion coefficient (D_{id}) of pure components through Darken's thermodynamic equation [36] as:

$$D_M = D_{id}\frac{d\ln a_1}{dc_1} \tag{10}$$

with

$$D_{id} = c_1 D_2 + c_2 D_1 \tag{11}$$

The expression relating diffusion D_M and $S_{cc}(0)$ is given by

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{12}$$

From Eq. (12) it is obvious that in the case of ideal mixing, $S_{cc}(0) \to S_{cc}^{id}(0)$, and hence, $D_M D_{id}^{-1} \to 1$. The presence of chemical order is indicated by $D_M D_{id}^{-1} > 1$ as $S_{cc}(0) < S_{cc}^{id}(0)$. Similarly, $D_M D_{id}^{-1} < 1$ suggests the tendency for homocoordination; leading to phase segregation. Fig. 5 shows the plots of the ratio D_M/D_{id} (computed using Eqs. (6) and (12)) against concentration at the three temperatures. A look at the figure shows that the ratio D_M/D_{id} is greater than 1 throughout the whole concentration range. This indicates the presence of chemical order in Si–Ti alloys at investigated

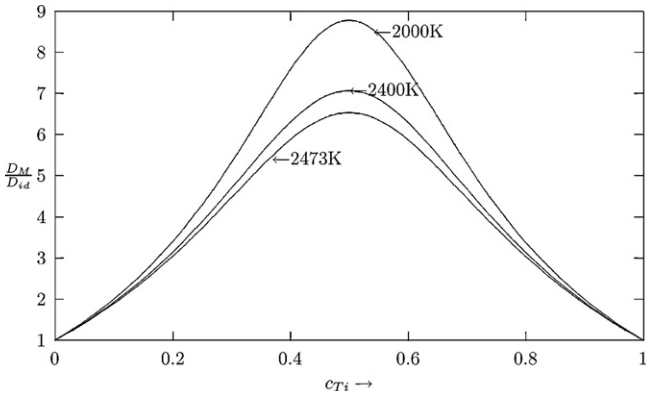

Fig. 5. Concentration dependence of diffusion coefficient, D_M/D_{id} using Eqs. (6) and (12) for liquid Si–Ti alloys at 2000 K, 2400 K and 2473 K, respectively. C_{Ti} and C_{Si} are the concentrations of Ti and Si respectively in the alloy.

temperatures. It is also noticed that D_M/D_{id} exhibits maximum peak at around the equiatomic composition $c_{\mathrm{Ti}} = 0.5$. It suffices to say that as temperature increases, the magnitude of the peaks are reduced and thus, the degree of chemical order in liquid alloy increases as temperature is lowered. It is interesting to observe that this temperature effect on diffusion is in agreement with our earlier observations on the effect of temperature on free energy of mixing and concentration–concentration fluctuations.

4. Conclusion

The descriptions of the Gibbs free energies of mixing of all phases of the Si–Ti system at temperatures of 2000 K, 2400 K and 2473 K obtained by Kostov and coworkers [18] employing FactSage software has been used to investigate the thermodynamic properties of Si–Ti binary liquid alloys.

From the results presented it is clear that Si–Ti alloys exhibit strong negative deviation from the Raoultian behaviour. The study of concentration fluctuations in the long wavelength limit, chemical short-range order parameter and diffusion coefficient clearly demonstrate that Si–Ti is strongly heterocoordinated. We also observed that the tendency for intermetallic associations, which leads to the formation of SiTi compounds, decreases with the increase in temperature. In addition, this study has shown that experimental data obtain from FactSage Thermo-Chemical Software and Databases could be used to extract useful theoretical thermodynamic information from binary liquid alloys and could as well serve as a basis for comparison with some future critical experimental results.

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