

Temperature-Dependence of Mixing Properties of Cu-Ti Liquid Alloy

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Abstract

In this study, the temperature-dependence of thermodynamic and surface properties of Cu-Ti binary liquid alloy were studied. In thermodynamic properties, excess Gibbs free energy of mixing, enthalpy of mixing, excess entropy of mixing, and activity of the system were computed at 1873 K. The surface properties were analyzed by computing the surface tension and surface concentration of the system. Thermodynamic properties were computed in the framework of the Redlich-Kister polynomial, and the surface properties were computed using the Butler model. At its melting point, the system exhibited a tendency for the formation of compounds, and as the Cu concentration was increased, the surface tension of the system gradually decreased. The excess Gibbs free energy of mixing, activity and surface tension of the system were also computed at different temperatures, in the range 1873-2173 K. With the increase in temperature of the system, the compound forming tendency of the system gradually decreased.

Keywords: Cu-Ti alloy, R-K polynomial, thermodynamic properties, surface properties.

Introduction

Alloying is one of the greatest gifts of metallurgy to humankind and offers great commercial as well as technological importance (Dogan & Arslan, 2015). As pure constituent metals have less strength than that of the alloy, they are not so useful and significant for applications (Shrivastava et al., 2015). Because of mixing of pure metals at proper proportions and temperatures, the alloy acquires useful properties superior to that of its constituent pure metals like higher tensile strength, lower density, higher corrosion, oxidation and temperature resistance, higher toughness and ductility and more durability (Yadav, Jha, et al., 2018; Yadav, Sharma, et al., 2018). Therefore, alloys are used in wide variety of applications like in buildings, architecture applications, aerospace industries, automobiles, surgical tools, cooking utensils, rigid containers etc. (Yadav, Jha, et al., 2018; Yadav, Sharma, et al., 2018).

To design and develop the high temperature material applicable for technological use, the knowledge regarding characteristic thermodynamic properties like excess Gibbs free energy of mixing which, especially, governs the mixing behavior of the system is mandatory (Dogan & Arslan, 2015; Singh et al., 2011). Although mixing behavior of initial melt of alloy can be studied experimentally but due to many constraints like difficulty in controlling high temperature, time consumption, high economical cost and complexities of well-equipped laboratory setting, theoretical approach can be preferred for the prediction of integral thermodynamic properties of mixing of binary and multicomponent alloys (Chou, 1995; Dogan et al., 2015; Dogan & Arslan, 2019; Yadav et al., 2017). Turchanin et al. (2005) studied the thermodynamic properties of Cu-Ti binary liquid alloy using ideal associated solution model and reported that excess Gibbs free energy of mixing was negative and activity showed negative deviation from ideality at 1873 K over entire concentration range. Kumar et al. (1998) depicted the presence of intermediate phases

such as Cu_2Ti , Cu_3Ti_2 , Cu_4Ti_3 and $CuTi_2$ in the system. But the complete information regarding the thermodynamic and surface properties of the system is not available to date.

Therefore, these properties of Cu-Ti binary liquid alloy at 1873 K were computed using different theoretical approaches. The thermodynamic properties, such as excess Gibbs free energy of mixing, enthalpy of mixing, excess entropy of mixing and activities of monomers were computed using Redlich-Kister (R-K) polynomial (Redlich & Kister, 1948). The surface properties, such as surface tension and surface concentrations of constituent atoms of the system were computed using Butler model (Butler, 1932) with the aid of determined values of partial excess Gibbs free energy of each atom of the system.

The brief outline of the expression used for the computations of abovementioned properties are presented in the Section 2, the results and discussion are presented in the Section 3 and the conclusion is mentioned in the Section 4 of this work.

Formulations

Thermodynamic Properties

The excess Gibbs free energy of mixing (ΔG_M^{xs}) of binary liquid alloys can be expressed in terms of R-K polynomial as (Azza et al., 2017; Gohivar et al., 2022; Kaptay, 2004; Redlich & Kister, 1948)

$$\Delta G_M^{xs} = x_i x_j \sum_{k=0}^n A_{ij}^k (x_i - x_j)^k \quad (1)$$

where A_{ij}^k are binary interaction parameters which are described in terms of linear functions of temperature and can be expressed as (Yuan et al., 2009)

$$A_{ij}^k = a_k + b_k T \quad (2)$$

where a_k and b_k are semi-empirical parameters associated with enthalpy of mixing (ΔH_M) and excess entropy of mixing (ΔS_M^{Ex}) respectively (Gohivar et al., 2022; Kaptay, 2004).

Standard thermodynamic relation among ΔH_M , ΔG_M^{Ex} and ΔS_M^{Ex} is expressed as (Yadav et al., 2016)

$$\Delta H_M = \Delta G_M^{Ex} + T \Delta S_M^{Ex} \quad (3)$$

By using Equation (2) in Equation(1) and comparing it with Equation (3), ΔH_M and ΔS_M^{Ex} for binary liquid alloy can be expressed as

$$\Delta H_M = x_i x_j \sum_{k=0}^n a_k (x_i - x_j)^k \quad (4)$$

$$\Delta S_M^{Ex} = -x_i x_j \sum_{k=0}^n b_k (x_i - x_j)^k \quad (5)$$

Partial excess Gibbs free energy (ΔG_i^{Ex}) of each component in a liquid alloy can be expressed as (Arslan & Dogan, 2015)

$$\Delta G_i^{Ex} = \Delta G_M^{Ex} + \sum_{j=1}^m (\delta_{ij} - x_j) \frac{\partial \Delta G_M^{Ex}}{\partial x_i} \quad (6)$$

where δ_{ij} is Kronecker delta symbol; $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$ and $m = 2$ for binary system. Thermodynamic activity of i^{th} component of a liquid alloy is calculated by the following expression (Arslan & Dogan, 2015)

$$a_i = x_i \exp \left(\frac{\Delta G_i^{Ex}}{RT} \right) \quad (7)$$

where R is real gas constant (in $\text{J mol}^{-1} \text{K}^{-1}$) and T is absolute temperature (in K).

Surface Properties

The surface tension (σ) of a binary liquid alloy at a temperature can be expressed as (Butler, 1932; Dogan & Arslan, 2019)

$$\sigma = \sigma_1 + \frac{RT}{s_1} \ln \left(\frac{x_1^S}{x_1^b} \right) + \frac{\Delta G_{s,1}^{Ex} - \Delta G_{b,1}^{Ex}}{s_1}$$

$$= \sigma_2 + \frac{RT}{s_2} \ln \left(\frac{x_2^S}{x_2^b} \right) + \frac{\Delta G_{s,2}^{Ex} - \Delta G_{b,2}^{Ex}}{s_2} \quad (8)$$

where x_i^s and x_i^b are the surface concentrations and bulk concentrations of component i respectively. Similarly, $\Delta G_{s,i}^{Ex}$ and $\Delta G_{b,i}^E$ are the partial excess Gibbs free energy for surface phase and bulk phase respectively. $\Delta G_{s,i}^E$ and $\Delta G_{b,i}^E$ are related as $\Delta G_{s,i}^{xs} = \beta \Delta G_{b,i}^{xs}$ (Adhikari et al., 2012), where β is the coordination number that depends on crystal structure. s_i being the surface area of monolayer of one mole of pure element i which can be calculated by using the relation as (Kaptay, 2008)

$$s_i = f N_A^{1/3} \left(\frac{M_i}{\rho_i} \right)^{2/3} \quad (9)$$

where $f (= 1.00)$ (Kaptay, 2008) is the geometrical factor, M_i is the molecular mass, ρ_i is the density and N_A is the Avogadro's number. The temperature dependence of surface tension (σ_i) and density (ρ_i) of pure element in liquid alloy are expressed as (Gale & Totemeier, 2003; Mehta et al., 2021)

$$\sigma_i = \sigma_0 + \frac{\partial \sigma}{\partial T} (T - T_0) \text{ and } \rho_i = \rho_0 + \frac{\partial \rho}{\partial T} (T - T_0) \quad (10)$$

where $\frac{\partial \sigma}{\partial T}$ and $\frac{\partial \rho}{\partial T}$ are the temperature derivative terms of σ_i and ρ_i respectively, and T_0 is the melting temperature of i^{th} pure element.

Results and Discussion

Thermodynamic Properties

The integral excess Gibbs free energy of mixing (ΔG_M^{Ex}) of Cu-Ti liquid alloy at 1873 K was calculated using the values of coefficients of R-K polynomial (A_{ij}^k) from Table 1 in Equation (1) and its compositional variation has been shown in Figure (1).

Table 1.

Coefficients of R-K polynomial for ΔG_M^{Ex} of Cu-Ti liquid alloy

Coefficients of R-K polynomial (A_{ij}^k) [Jmol^{-1}]	Reference
$A^0 = -40768 + 7.581T$ $A^1 = 27171 - 9.444T$ $A^2 = 2104 - 1.92T$ $A^3 = -18843 + 7.197T$	Turchanin et al. (2005)

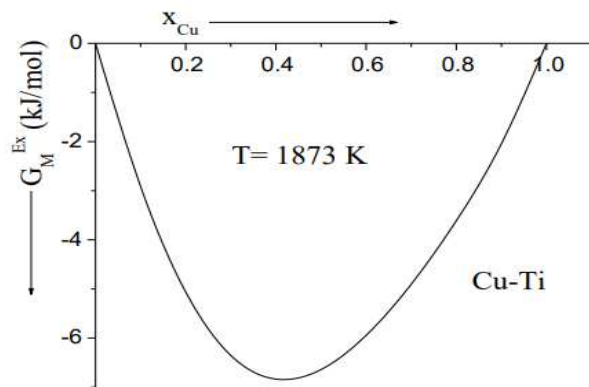


Fig. 1.

Variation of ΔG_M^{Ex} of liquid Cu-Ti alloy at 1873 K as a function of concentration of copper.

The study of ΔG_M^{Ex} of liquid alloy corresponds the idea of mixing or demixing tendency of the monomers of the system. It also gives information about the strength of interaction among the micro-granules of the system (Yadav et al., 2018). The computed values of ΔG_M^{Ex} of liquid Cu-Ti alloy at 1873 K have been found to be negative over the entire concentration range of Cu. Furthermore, G_M^{Ex} of liquid Cu-Ti has negative optimum value of -6.836 kJ/mol at $x_{Cu} = 0.4$ and minimum negative value of -2.042 kJ/mol at $x_{Cu} = 0.9$ at all selected values of x_{Cu} in the range $0 < x_{Cu} < 1$. (Figure 1). This indicates that liquid Cu-Ti has mixing tendency or compound formation tendency at its melting temperature. The system is found to be asymmetric with respect to excess Gibbs free energy of mixing.

The excess Gibbs free energy of mixing (ΔG_M^{Ex}) of the system was also computed in the temperature range 1873-2173 K using Equation (1) and parameters in Table 1. The compositional dependence of ΔG_M^{Ex} at different temperatures is displayed in Figure 2. It can be observed that the computed values of ΔG_M^{Ex} gradually decreases with increase in temperature of the system. These results indicate that the compound forming tendency of the system gradually decreases at higher temperatures. These results are in consistence with the results predicted by other researchers (Gohivar et al., 2022; Mehta et al., 2021).

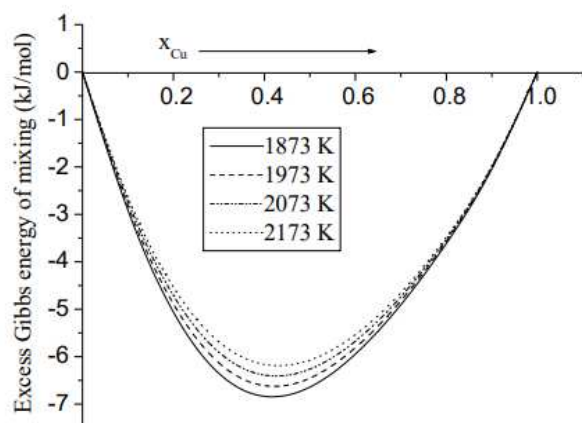


Fig. 2.

Variation of ΔG_M^{Ex} in the temperature range 1873-2173 K of Cu-Ti liquid alloy.

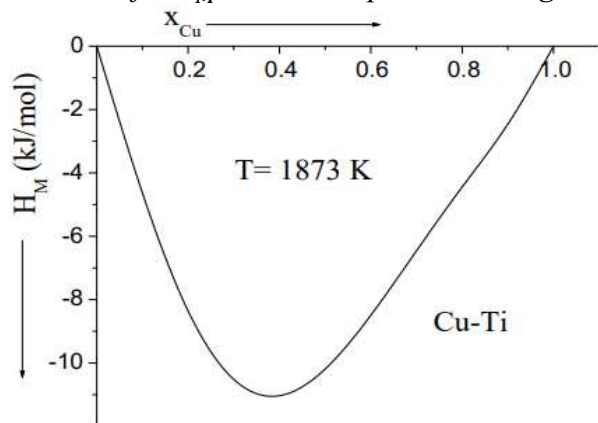


Fig. 3.

Variation of ΔH_M versus concentration of Cu of liquid Cu-Ti alloy at 1873 K.

The knowledge of enthalpy of mixing (ΔH_M) of binary liquid alloys gives the information regarding the strength of bonding between the constituent atoms of the complex. The values of ΔH_M of the system have been calculated using parameters (a_k) from Table 1 in Equation (4). These values have been plotted as a function of concentration of Cu in Figure 3.

The computed values of ΔH_M for the system have found to be negative in the whole concentration range of copper. Furthermore, ΔH_M of the system acquires the maximum negative value of -11.032 kJ/mol corresponding to $x_{Cu} = 0.4$ and minimum value of -2.460 kJ/mol corresponding to $x_{Cu} = 0.9$ in all chosen values of x_{Cu} in the range $0 < x_{Cu} < 1$ (Figure 3). The negative values of ΔH_M indicate the compound formation tendency of the system at its melting temperature, 1873 K. The system is again found to be asymmetric with respect to ΔH_M .

Excess entropy of mixing (ΔS_M^{Ex}) of the alloy at the given condition was computed using the values of b_k from Table 1 in Equation (5) and its variation with concentration has been shown in the Figure 4. The computed values of ΔS_M^{Ex} of the system at 1873 K were found to have negative values corresponding to selected values of x_{Cu} in its entire concentration range. Furthermore, corresponding to $x_{Cu} = 0.4$ and $x_{Cu} = 0.9$ excess entropy of mixing of liquid Cu-Ti at 1873 K were found to acquire negative optimum value of -2.241 kJ/mol and minimum of -0.223 kJ/mol respectively in the range $0 < x_{Cu} < 1$ (Figure 4).

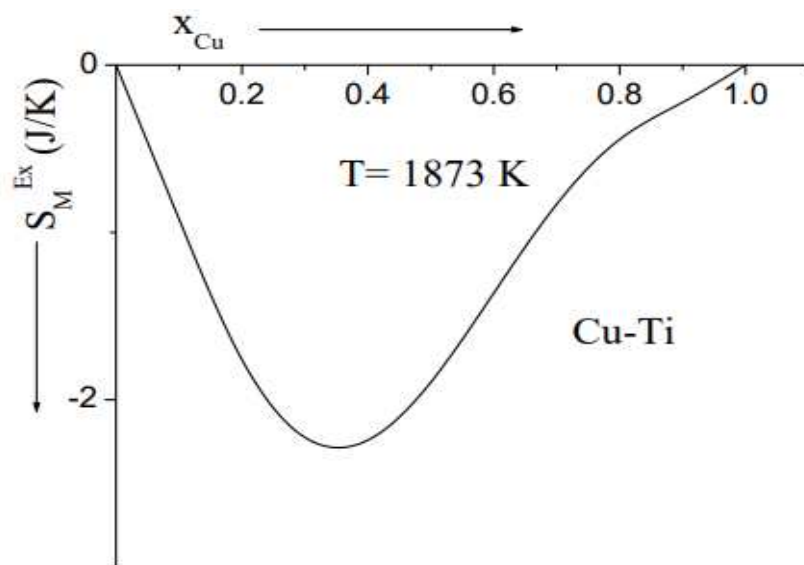
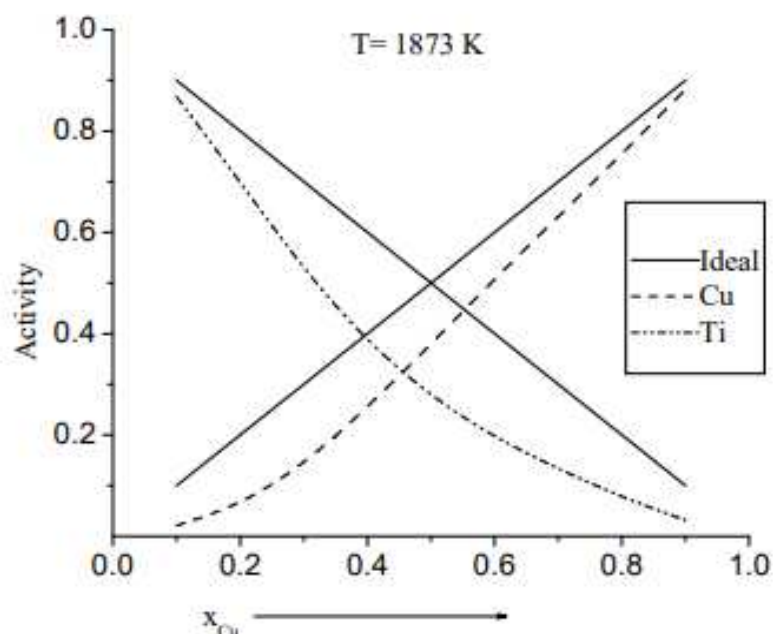


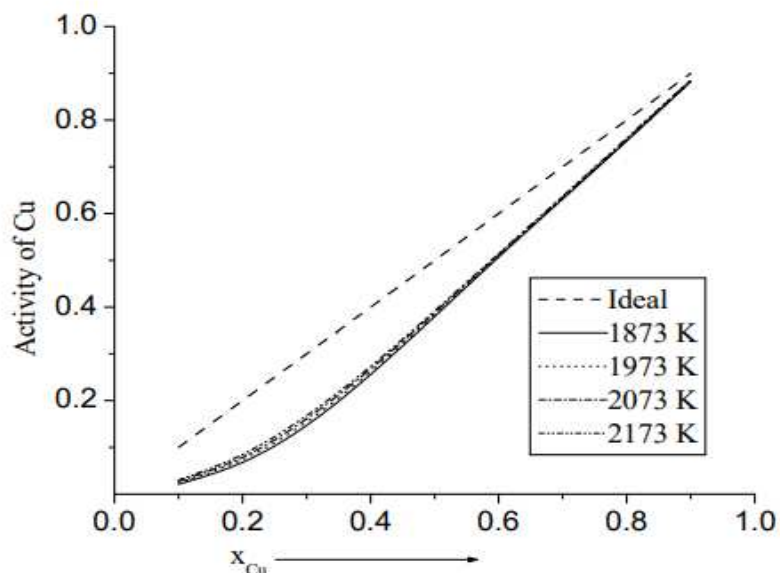
Fig. 4.

Concentration dependence of excess entropy of mixing of liquid Cu-Ti binary system at 1873 K.

Activity is an important thermodynamic function of liquid alloy and its value gives knowledge about the extent of interaction among the constituent atoms of the stable complexes. At a given condition, its lower value indicates the strong interaction among the atoms in the complex whereas higher value corresponds the weak interaction among the atoms. The partial excess Gibbs free energy (ΔG_i^{Ex}) of individual component of Cu-Ti system was computed using the values of R-K coefficients from Table 1 in Equation (6) which were then used in Equation (7) to estimate the corresponding values of activities. The compositional dependence of the activities of the individual atoms in the liquid alloy are plotted in Figure 5.

**Fig. 5.**

Compositional dependence of activities of Cu and Ti in liquid Cu-Ti at 1873 K.

**Fig. 6 (a).**

Computed values of activity of Cu in the temperature range 1873-2173 K.

Activities of both components in liquid Cu-Ti alloy acquire values less than their respective ideal values in the entire concentration range of x_{Cu} indicating the compound forming tendency of the system. These results predicted by the computations of activities of the monomers of the system are in accordance with those predicted by other thermodynamic functions mentioned above. Apart from this, the activities of both Cu and Ti are consistent with each other corresponding to $x_{Cu} = 0.456$ (Figure 5).

The activities of Cu and Ti of the system were also computed at different temperatures (1873-2173 K) following the procedure as mentioned above. The computed values are plotted in Figures 6 (a,b). The activities of both of the components gradually decreased with increase in temperature of the system beyond 1873 K which is its melting temperature. These values get closure to their respective ideal values indicating the decrease in the stability of the complexes or mixing tendency of the system.

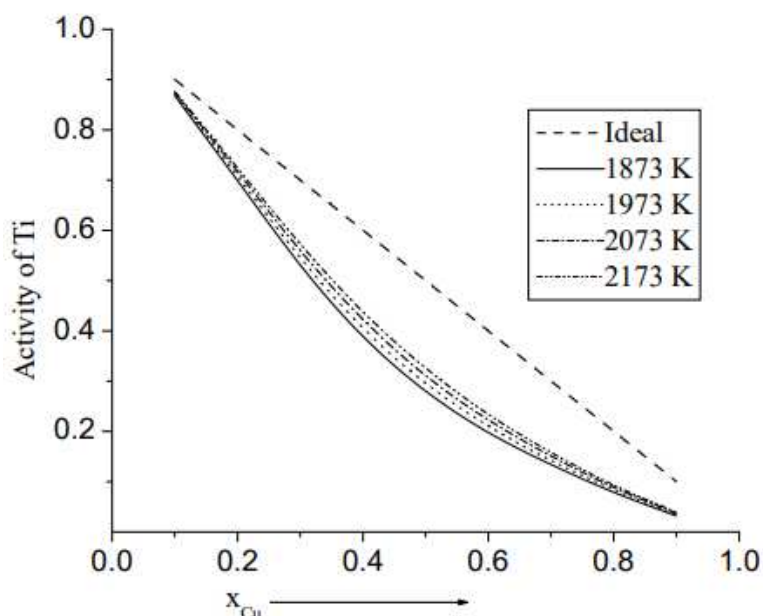


Fig. 6 (b).

Computed values of activity of Cu in the temperature range 1873-2173 K.

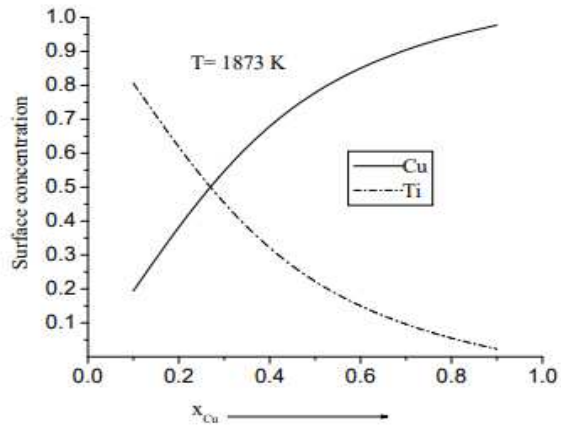
Table 2.

Input parameters for surface tension (Gale&Totemeier, 2003)

Element	T_0 (K)	ρ_0 (kgm^{-3})	$\frac{\partial \rho}{\partial T}$ ($\text{kgm}^{-3}\text{K}^{-1}$)	σ_0 (Nm^{-1})	$\frac{\partial \sigma}{\partial T}$ ($\text{Nm}^{-1}\text{K}^{-1}$)
Cu	1356	8000	0.80	1.303	-0.00023
Ti	1958	4130	0.23	1.65	-0.00026

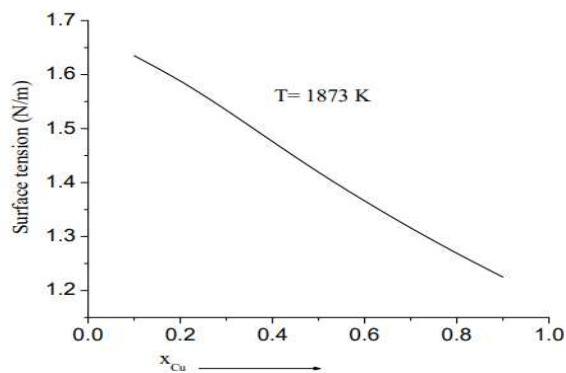
Surface properties

The knowledge of surface properties gives information related to various physical properties of liquid alloy. As stated earlier, the surface properties of the liquid alloy have been computed using Butler model (Butler, 1932). The above determined values of ΔG_i^{Ex} were used for this purpose. Surface tension as well as surface area of monolayer of individual components of Cu-Ti at the temperature of interest were computed using respective physical parameters from Table 2 in Equations (9) and (10). These values were then used in Equation (8) to estimate the surface concentrations ($x_i^S, i = \text{Cu, Ti}$) of components of the liquid alloy. Compositional variation of surface concentrations of Cu and Ti are plotted in Figure (7).

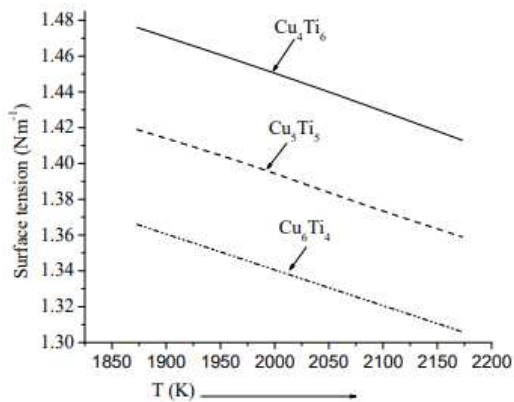
**Fig. 7.**

Compositional dependence of x_{Cu}^S and x_{Ti}^S of liquid Cu-Ti at 1873 K.

The perusal of Figure 7 corresponds that the computed values of x_{Cu}^S increases whereas x_{Ti}^S decreases with the increase of x_{Cu} over the entire concentration range of copper. It is also found that at $x_{Cu} = 0.265$, surface concentrations of both Cu and Ti are the same (Figure 7).

**Fig. 8.**

Variation of σ with the concentration of copper in liquid Cu-Ti at 1873 K.

**Fig. 9:** Temperature-dependence of σ of Cu-Ti liquid alloy.

The surface tension (σ) of the alloy at 1873 K was computed using Equation (8) and above determined input parameters. The values so computed are plotted against the bulk concentration of Cu in Figure 8. It can be observed that the computed values of σ gradually decreased with increase in bulk concentration of Cu. The surface tension of the system was also computed at different temperatures mentioned above following the similar procedure. The computed values are plotted in Figure 9. It can be observed that the computed values of σ were found to decrease at elevated temperatures.

Conclusion

The important conclusions of the work are highlighted below:

- i. Cu-Ti binary system exhibits mixing behaviour in its liquid state at 1873 K.
- ii. The mixing behaviour of the system gradually decreases with increase in its temperature.
- iii. Increase of copper concentration in liquid Cu-Ti at 1873 K reduces the surface tension of the alloy.
- iv. Increase of temperature causes the surface tension of the alloy to reduce linearly.

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