Study of surface tension and viscosity of Cu–Fe–Si ternary alloy using a thermodynamic approach

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ABSTRACT

The surface tension and viscosity of Cu–Fe–Si ternary alloys were computed at different temperatures using thermodynamic approaches. The thermodynamic data of the alloy were optimized in the framework of the Redlich-Kister (R–K) polynomials and exponential temperature dependent coefficients of the R–K polynomial were obtained. These coefficients were used to compute the excess Gibbs free energy of mixing of the alloy and the partial excess free energy of the components. The partial excess free energy so obtained was used to compute the surface tension of the ternary Cu–Fe–Si alloy system and its binary sub-systems. The enthalpy of mixing was also optimized and it was used to compute the viscosity of the sub-binary and ternary alloys.

1. Introduction

Many researchers [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14] have long been involved in computing the surface tension of binary alloys using the models proposed by Defey et al. [15], Butler [16], Belton et al. [17], Joud et al. [18], and Laty et al. [19] etc. Despite some limitations and requirements of some adjustable parameters, these models provide a reasonable description of the surface tension of binary alloys. Yeum et al. [20] developed a model without using any adjustable parameters in the framework of the Butler equation [11] and applied this model successfully to ten binary alloy systems for the estimation of surface tension. In their model, the chemical potential in the surface phase and bulk phase is considered in the same form and are related by a parameter β, an apparent ratio coordination number, which is taken as 0.75 for a close packed structure. Tanaka et al. [21] revised this model by taking into account the change in binding energy in the surface phase and took the apparent ratio coordination number (β) equal to 0.83 instead 0.75, which gave a better agreement with the experimental values. However, in both of these models, the surface entropy term was neglected, which could affect the estimation of surface tension [22] for several systems.

Similarly, the viscosity of liquid metals and binary liquid alloys has been determined both experimentally and theoretically using different approaches [23, 24, 25, 26, 27, 28, 29, 30, 31]. Budai’s model [32] is used to estimate the viscosity of multicomponent alloys, which is focused on the cohesion energy of the constituents of the liquid alloy and enthalpy of mixing of the alloy [30]. It has been successfully used to explain the viscosity of several systems. Singh and Sommer [33] incorporated Andrade’s equation [34] to describe the viscosity of liquid metals and alloys. The Andrade equation is based on quasi-crystallization theory. Schick et al. [35] suggested an equation for the estimation of the viscosity of Al–Cu binary liquid alloys. This approach is also found to be appropriate to computing the viscosity of some other systems. Other models such as, Moelwyn-Hughes model based on cohesive energy [36], Born-Green model based on kinetic theory [37, 38], Cohen-Sandlers model based on free volume theory [39], Eyring model based on rate theory [40] etc. have also been used to estimate the viscosity of liquid materials.

The development of novel tribomaterials with excellent wear and corrosion resistances are outmost essential for application in under water environments to overcome the pollution caused by the oil hydraulic systems [41, 42, 43]. Austenitic stainless steels are mostly used for this purpose because of their high corrosion resistance; they however, have very poor wear resistance under abrasive and adhesive tribological conditions [44]. This discrepancy can be overcome by using Fe–Cu–Si alloys because the wear rate of Fe3Si–10%Cu is found to be better than austenitic stainless steels [45]. Moreover, the rapid growth in the use of
Table 1. Exponential optimized parameters of coefficient of R-K polynomial for excess free energy (J/mol) of binary alloy.

| System | $A^0$ | $A^1$ | $A^2$ | $A^3$ |
|--------|--------|--------|--------|--------|
| Cu-Si  | -40800 | -81700 | -43000 | -64980 |
|        | exp (-0.000134 T) | exp (-0.000733 T) | exp (-0.000422 T) | exp (-0.000235 T) |
| Cu-Fe  | 36400  | 330    | 22500  | -60940 |
|        | exp (-0.000733 T) | exp (-0.000124 T) | exp (-0.000983 T) | exp (-0.0000235 T) |
| Fe-Si  | -106498 | 26297.5 | -43000 | 22500  |
|        | exp (-0.000235 T) | 26297.5 | exp (-0.000422 T) | exp (-0.000983 T) |

electronic devices has demanded the need for high-energy and long-life lithium ion batteries (LIBs). The elements present in the Cu–Fe–Si/graphite composite together with in situ generated Li$_2$O possess superior anodic behavior and high coulombic efficiency to be used in LIBs [46, 47]. As a result, the Cu–Fe–Si ternary alloy was chosen in present study. Additionally, in the best of the authors knowledge, the database for the surface tension and viscosity of this system is not available till date.

Therefore, we intended to study and predict the surface tension and viscosity of ternary Cu–Fe–Si alloys at different higher temperatures using a thermodynamic approach in present work. For the equilibrium composition of the ternary Cu–Fe–Si liquid alloys, the mass % of Si must be lower and that of Cu must be higher [48]. The sub-binary Cu–Fe system has no intermediate phase, while Cu–Si has a number of intermediate phases in the higher concentration region of Si [49]. The sub-binary Fe–Si system has intermediate phases in both the lower and higher concentration regions of Si [49]. In this work, the thermodynamic parameter, such as the excess Gibbs energy of mixing has been described by the R–K polynomial [50, 51] assuming the interaction parameter to be exponentially dependent on temperature. When the parameters are assumed to be exponentially dependent on temperature, the possibility of the appearance of high temperature artifact in the thermodynamic properties of the alloys is eliminated [7, 52], which increases the reliability of the estimated data. The thermodynamic parameters computed by using optimized exponential interaction parameters were used in Butler [16], Chou [53, 54], Toop [55] and Kohler [55] models in the framework of the R–K polynomial to calculate the surface tension of the ternary Cu–Fe–Si alloy and its sub-binaries. Similarly, the viscosities of the ternary and sub-binary alloys were computed using the Chou [53, 54], Toop [55], Kohler [55] and Kaptay [56] models.

2. Theoretical modelling

The surface concentration ($x_i^s$) and surface tension ($\sigma$) of binary and multi-component alloys are expressed using Butler’s equation given by [7, 16].

$$\sigma = \sigma_1 + \frac{RT}{A_1} \ln \left( \frac{x_i^s}{x_i} \right) + \frac{G_{i2}^s - G_{i1}^s}{A_1}$$

$$+ \frac{RT}{A_2} \ln \left( \frac{x_i^s}{x_i} \right) + \frac{G_{i3}^s - G_{i2}^s}{A_2}$$

$$+ \frac{RT}{A_3} \ln \left( \frac{x_i^s}{x_i} \right) + \frac{G_{i4}^s - G_{i3}^s}{A_3}$$

(1)

Here, $x_i$ ($i = 1, 2, 3$) are the surface tension of the individual components of the alloy at the temperature of interest $T$, $R$ is the molar gas constant and $x_i^s$ are the surface concentrations of the components in the alloy. The three terms on the R.H.S. of the Eq. (1) becomes equal for three values of $x_i^s$ and these values of $x_i^s$ gives the surface concentration of the alloy. The terms $x_i$ are the bulk concentrations of the components. $G_{i1}^s$ and $G_{i2}^s$ are the partial excess free energy for the surface and bulk phase of the individual components, which are proportional to each other and related as $G_{i1}^s = \beta G_{i2}^s$. The value of $\beta$ depends on the crystal structure and taken 0.82 [7,52]. $A_i$ are the surface area of the monolayer of one mole of pure element $i$. The values of $A_i$ are computed using the relation [7]:

$$A_i = \pi^{1/3} \left( \frac{M_i}{\rho_i} \right)^{2/3}$$

(2)

![Figure 1](image1.png)  

**Figure 1.** Variation of excess Gibbs free energy with concentration ($x_i$) of binary sub-systems of ternary Cu–Fe–Si alloy at 1773 K.

![Figure 2](image2.png)  

**Figure 2.** Variation of the surface tension with concentration ($x_i^s$) of the binary sub-systems of ternary Cu–Fe–Si alloy at 1823 K.

Table 2. Surface tension ($\sigma$) and density ($\rho$) of the pure elements near melting temperature ($T_m$) and their derivatives w.r.t. temperature.

| Element | $T_m$ (K) | $\rho$ (Kg/m³) | $\partial \rho/\partial T$ (Kg/m³K) | $\sigma$ (N/m) | $\partial \sigma/\partial T$ (N/(mK)) |
|---------|------------|----------------|----------------------------------|-------------|----------------------------------|
| Cu      | 1356       | 8000           | -0.8                             | 1.303       | -0.00023                         |
| Fe      | 1809       | 7030           | -0.88                            | 1.872       | -0.00049                         |
| Si      | 1683       | 2530           | -0.35                            | 0.865       | -0.00013                         |
where \( f \) is called the geometric factor and its value is taken to be 1.00 for a simple liquid metal. The terms \( N_A \), \( M_i \) and \( \rho_i \) are the Avogadro’s number, molar mass of element \( i \) and density of the element \( i \). The partial excess Gibbs free energy of individual components (\( G_{xs}^i \)) of multi-component systems are obtained in terms of the integral excess Gibbs free energy (\( G_{xs}^M \)) as \([57, 58, 59]\).

\[
G_{xs}^i = G_{xs}^M + \sum_{j=0}^{m} (\delta_{ij} - x_j) \frac{\partial G_{xs}^M}{\partial x_j}
\]

(3)

where \( \delta_{ij} \) is the Kronecker delta function defined as \( \delta_{ij} = 0 \) for \( i \neq j \) and \( \delta_{ij} = 1 \) for \( i = j \). The values of \( m = 2 \) for binary and \( m = 3 \) for ternary liquid alloys. The excess free energy of binary liquid alloys ‘ij’ having bulk concentrations \( x_i \) and \( x_j \) are frequently expressed in terms of the Redlich-Kister (R–K) polynomial as \([57, 58, 59, 60]\).

\[
G_{xs}^M = x_i x_j \sum_{k=0}^{n} A_{ik} x_k
\]

(4)

where \( A_{ik} \) are called coefficients of the R–K polynomial of the binary system ‘ij’ for the excess Gibbs free energy and obey the relation \( A_{ij} = (-1)^k A_{ji}^k \). The excess free energy of mixing of ternary alloy with bulk concentration \( x_1 \), \( x_2 \) and \( x_3 \) is expressed according to the Chou model \([53, 54]\) and is given by the relation

\[
G_{xs}^M = x_1 x_2 \sum_{k=0}^{n} A_{12}^k x_k + x_2 x_3 \sum_{k=0}^{n} A_{23}^k x_k + x_3 x_1 \sum_{k=0}^{n} A_{31}^k x_k + F x_1 x_2 x_3
\]

(5)

| \( \text{Si–Cu} \) | \( A^0 \) | \( 1.66 \times 10^{-4} \ T - 0.416 \) |
| \( A^1 \) | \( 6.98 \times 10^{-5} T^2 - 2.98 \times 10^{-4} T + 0.262 \) |
| \( A^2 \) | \( -2.19 \times 10^{-4} T + 0.036 \) |
| \( A^3 \) | \( -1.81 \times 10^{-7} T^2 + 9.32 \times 10^{-4} T - 1.30 \) |

| \( \text{Cu–Fe} \) | \( A^0 \) | \( 4.85 \times 10^{-4} T + 1.52 \) |
| \( A^1 \) | \( -4.27 \times 10^{-4} T + 1.18 \) |
| \( A^2 \) | \( -6.51 \times 10^{-5} T^2 + 3.14 \times 10^{-4} T - 0.96 \) |
| \( A^3 \) | \( 6.63 \times 10^{-7} T^2 - 3.11 \times 10^{-4} T + 3.77 \) |

| \( \text{Fe–Si} \) | \( A^0 \) | \( 7.54 \times 10^{-4} T - 2.13 \) |
| \( A^1 \) | \( -3.12 \times 10^{-7} T^2 + 1.47 \times 10^{-4} T - 1.46 \) |
| \( A^2 \) | \( -2.67 \times 10^{-7} T^2 + 1.08 \times 10^{-4} T - 1.05 \) |
| \( A^3 \) | \( -1.27 \times 10^{-7} T^2 + 5.90 \times 10^{-4} T - 0.942 \) |

Table 3. Optimized parameters of the coefficients of R–K polynomial for excess surface tension of the binary system.

Figure 3. Variation of surface concentration of monomers of ternary Cu–Fe–Si alloy with concentration from Si-corner at \( x_{Cu} : x_{Fe} = 1:9 \) cross-section (a); \( 3:7 \) cross-section (b); \( 5:5 \) cross-section (c); \( 7:3 \) cross-section (d); \( 9:1 \) cross-section (e).
According to the general solution model (GSM) proposed by Chou [53, 54] and used by many researchers [57, 58, 59, 60], the excess surface tension of the ternary liquid alloy is given by the relation

\[
\sigma'' = \frac{x_i x_j}{X_{i(12)} X_{j(12)}} \sigma''_{12}(X_{i(12)}, X_{j(12)}) + \frac{x_i x_k}{X_{i(13)} X_{k(13)}} \sigma''_{13}(X_{i(13)}, X_{k(13)}) + \frac{x_j x_k}{X_{j(13)} X_{k(13)}} \sigma''_{13}(X_{j(13)}, X_{k(13)})
\]

(8)

Here, \(x_i\) are the mole fractions of elements \(i\) in the ternary alloy and \(\sigma''_{ij}(X_{i(12)}, X_{j(12)})\) are the excess surface tension of the selected binary system at binary compositions \((X_{i(12)}, X_{j(12)})\) defined by the relations

\[
X_{i(12)} = x_i + \xi_{i2} x_j, \quad X_{j(23)} = x_j + \xi_{j3} x_k, \quad X_{i(13)} = x_i + \xi_{i1} x_k
\]

with the property \(X_{i(12)} + X_{i(13)} = 1\) and \(\xi_i\) are the similarity indexes and are expressed as

\[
\xi_i = \frac{\eta_i}{\eta_1 + \eta_{i1} + \eta_{i11}} = \frac{\eta_i}{\eta_1 + \eta_{i1} + \eta_1}
\]

(10)

The term \(\eta\) is the deviation sum of squares and is computed using the relations [53, 54].

\[
\eta_i = \frac{1}{30} (A_{i1}^2 - A_{i1}^2)^2 + \frac{1}{210} (A_{i2}^2 - A_{i2}^2)^2 + \frac{1}{630} (A_{i3}^2 - A_{i3}^2)^2
\]

\[+ \frac{1}{1386} (A_{i2}^2 - A_{i2}^2)^2 + \frac{1}{105} (A_{i2}^2 - A_{i2}^2)(A_{i2}^2 - A_{i2}^2) \]

\[+ \frac{1}{315} (A_{i2}^2 - A_{i2}^2)(A_{i2}^2 - A_{i2}^2) \]

(11)

\[
\eta_{i1} = \frac{1}{30} (A_{i1}^2 - A_{i1}^2)^2 + \frac{1}{210} (A_{i2}^2 - A_{i2}^2)^2 + \frac{1}{630} (A_{i3}^2 - A_{i3}^2)^2
\]

\[+ \frac{1}{1386} (A_{i3}^2 - A_{i3}^2)^2 + \frac{1}{105} (A_{i3}^2 - A_{i3}^2)(A_{i3}^2 - A_{i3}^2) \]

\[+ \frac{1}{315} (A_{i3}^2 - A_{i3}^2)(A_{i3}^2 - A_{i3}^2) \]

(12)
The Kohler model is a symmetrical geometrical model. The Toop model is an asymmetrical model and a symmetrical element is selected to apply this model. According to this model, the expression for excess surface tension for a symmetrical element having bulk concentration $x_1$ is given by the relation \([55, 62]\).

$$\sigma_{\text{ex}}^{\text{sym}} = \frac{x_2}{(x_2 + x_1)} \sigma_{\text{ideal}}(x_1, 1 - x_1) + \left(\frac{x_2}{x_2 + x_1}\right)\sigma_1 \left(\frac{x_2}{x_2 + x_1}, \frac{x_1}{x_2 + x_1} - \frac{x_1}{x_2 + x_1}\right)$$

(15)

The excess surface tension ($\sigma^{ex}$) of the binary and ternary alloys is the deviation from the value obtained by the additive rule (ideal value) and is expressed by the relation

$$\sigma = \sigma^{ex} + \sigma^{ideal}$$

(16)

where $\sigma_i$ are the surface tensions of the pure constituents of the alloy at the working temperature.

The viscosity of the binary and multicomponent liquid alloys are expressed using the Kaptay equation \([56, 63]\).

$$\eta = \frac{n \eta_i + \eta^0}{(\sum x_i \eta_i)} + \frac{0.155 \pm 0.015}{H_u}$$

(17)

where $n$ is the Planck constant, $\eta_i$ are the molar volume of the individual elements and $\eta^0$ is the excess volume of the mixing of the alloy, which can be neglected. The term $G^*_i$ is called the Gibb’s energy of activation of the viscous flow of $i^{th}$ component and is given as

$$G^*_i = RT \ln \left(\frac{\eta_i \eta_i}{\eta^0} \right)$$

(18)

where $\eta_i$ are the viscosity of the individual pure components of the alloy at the concerned temperature $T$ and evaluated using the relations

$$\eta_i = \eta_0 \exp \left(\frac{E_i}{RT}\right)$$

(19)

where $\eta_0$ and $E$ are constants for the given element. The enthalpy of mixing of the sub-binary alloy is computed using the exponentially optimized parameters of the R–K polynomial for enthalpy using in Eq.

Table 4. Optimized coefficients of R–K polynomials for enthalpy of mixing of the binary alloy.

| Cu–Si | $A^0$ | $A^1$ | $A^2$ |
|-------|------|------|------|
|       | -48000 (1 + 0.000134 T)exp (-0.000134 T) | -81700 (1 + 0.000733 T)exp (-0.000733 T) | -43000 (1 + 0.000422 T)exp (-0.000422 T) |

| Cu–Fe | $A^0$ | $A^1$ | $A^2$ |
|-------|------|------|------|
|       | 36400 (1 + 0.000733 T)exp (-0.000733 T) | 330 (1 + 0.000124 T)exp (-0.000124 T) | 22500 (1 + 0.000983 T)exp (-0.000983 T) |

| Fe–Si | $A^0$ | $A^1$ | $A^2$ |
|-------|------|------|------|
|       | -164980 (1 + 0.000235 T)exp (-0.000235 T) | -60940 (1 + 0.000843 T)exp (-0.000843 T) | 26297.75 |

Table 5. The activation energy (E) and viscosity ($\eta_0$) at very high temperature of the pure elements.

| Element | $\eta_0$ (mPa s) | E (J/mol) | Ref. |
|---------|------------------|----------|------|
| Cu      | 0.3009           | 10900    | [55] |
| Fe      | 0.3699           | 41400    | [55] |
| Si      | 0.107            | 23488    | [55] |
The system of ternary CuFe of binary alloy. Contribution of enthalpy and Ak entropy to the excess free energy \[64\]. The importance of this free energy are expressed in the form of Figure 10. Variation of viscosity of ternary CuFeSi alloy with concentration from Si corner at 1873 K.

\begin{equation}
\text{Figure 9. Variation of viscosity with concentration (x_r) of the binary sub-system of ternary Cu-Fe-Si alloy at 1873 K.}
\end{equation}

\begin{table}[h]
\centering
\caption{Optimized coefficients of R-K polynomials for excess viscosity (mPa s) of binary alloy.}
\begin{tabular}{|c|c|}
\hline
 & Si-Cu \hline
 & $A_0$ 2.297 x 10^{-7} T^2 - 1.164 x 10^{-3} T + 1.559 \hline
 & $A_1$ -4.016 x 10^{-3} T^2 + 1.964 x 10^{-3} T + 2.579 \hline
 & $A_2$ 1.727 x 10^{-3} T^2 - 8.972 x 10^{-3} T + 1.302 \hline
 & $A_3$ 8.684 x 10^{-3} T - 3.783 x 10^{-3} T + 0.3960 \hline
\hline
 & Cu-Fe \hline
 & $A_0$ -1.178 x 10^{-5} T^2 + 5.423 x 10^{-2} T - 65.56 \hline
 & $A_1$ 6.696 x 10^{-4} T^2 - 3.031 x 10^{-3} T + 35.54 \hline
 & $A_2$ -4.021 x 10^{-4} T^2 + 1.797 x 10^{-3} T - 2.064 \hline
 & $A_3$ 2.017 x 10^{-5} T^2 - 8.945 x 10^{-3} T + 10.1577 \hline
\hline
 & Fe-Si \hline
 & $A_0$ -3.818 x 10^{-7} T^2 + 1.771 x 10^{-5} T - 22.08 \hline
 & $A_1$ 6.781 x 10^{-6} T - 3.070 x 10^{-4} T + 35.86 \hline
 & $A_2$ 3.947 x 10^{-6} T - 1.758 x 10^{-4} T + 20.01 \hline
 & $A_3$ -1.098 x 10^{-7} T^2 + 5.029 x 10^{-5} T - 6.028 \hline
\end{tabular}
\end{table}

The enthalpy of mixing of the ternary alloy has been computed using the coefficients of the R-K polynomial in Eq. (5).

The temperature dependent linearly optimized parameters for excess free energy are expressed in the form of $A_k^E = a + bT$ in which $a$ represents the contribution of enthalpy and $b$ represents the contribution of the entropy to the excess free energy $[7]$. The linearly temperature dependent function $A_k^E$ can be transformed into the exponential form $A_k^E = h_k \exp(-T/\tau_k)$. In this equation, the term $h_k$ represents the contribution of enthalpy and $h_k/\tau_k$ represents the contribution of the entropy to the excess free energy $[64]$. The importance of this transformation of the linear to the exponential form is to remove the artifact in the alloy at higher temperatures $[64]$.

The use of Eq. (4) for excess Gibbs’s free energy in the standard thermodynamic relations $S_k^E = -(\partial G_k^E / \partial T)$ and $H_k^E = G_k^E + TS_k^E$ gives the expression for enthalpy of mixing:

\begin{equation}
H = x_{A_i} \sum_i^n h_i \left(1 + \frac{T}{\tau_i}\right) \exp\left(-\frac{T}{\tau_i}\right) (x_i - x_i)^k
\end{equation}

In this equation, the term $h_i \left(1 + \frac{T}{\tau_i}\right) \exp\left(-\frac{T}{\tau_i}\right)$ is called the coefficient of the R-K polynomial for enthalpy of mixing of the binary system.

3. Results and discussion

It has been observed from a previous study that when linear temperature dependent interaction parameters optimized from the R-K-polynomial $[50, 51]$ are used to compute the thermodynamic properties of a binary alloy, asymmetric artifacts appear in these properties at high temperatures if $a_i^E < 0$ and $b_i^E > 2R$ in $A_k^E = a_k^E + b_k^E T$, where $a_k^E$ is the enthalpy-like semi-empirical coefficient in Jmol$^{-1}$ and $b_k^E$ is the entropy-like semi-empirical coefficient (with opposite sign) in Jmol$^{-1}$K$^{-1}$ $[7, 52, 65]$. Therefore, instead of using optimized linear temperature dependent interaction parameters in the literature $[66, 67, 68]$ to study the thermodynamic properties of the alloy, these parameters have been used in the R-K polynomials to obtain the exponential temperature dependent parameters for the free energy of mixing of the sub-binary systems Si-Cu, Fe-Si and Cu-Fe of the Cu-Fe-Si ternary alloy. The optimized coefficients of the R-K polynomials for excess free energy of mixing are listed in Table 1. The excess free energies of mixing for the aforementioned sub-binary systems were computed using the linear and exponential optimized parameters at 1773 K and compared in Figure 1.

The excess free energy of mixing computed using the linear parameter is in excellent agreement with that computed by using exponential optimized parameters for each system. The excess free energies of mixing of Si-Cu and Fe-Si binary systems are negative while that for the Cu-Fe system is positive. This result implies that the Si-Cu and Fe-Si sub-binary systems are of ordering nature and that the Cu-Fe sub-binary system is of a segregating nature. Further, the high negative value of the excess free energy of mixing of the Fe-Si system $(-27.2$ kJ/mol) near equiatomic concentration shows that the Fe-Si sub-binary system is a strongly interacting and has strong tendency to form the complex Fe-Si. Some other stable complexes of Fe-Si systems such as Fe5Si3, Fe2Si, FeSi2 and Fe4Si3 have also been reported $[66]$. The Si-Cu system is a weakly interacting system as being the highest negative value of the excess free energy of mixing is $-9.3$ kJ/mol. The Cu-Si binary system has the intermediate complexes Cu9Si11, Cu5Si3, Cu19Si6 and Cu33Si7 $[66]$. The phase diagram of the Cu-Fe system $[66]$ indicates that there is no intermediate phase for Cu-Fe binary system.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Variation of viscosity of ternary Cu-Fe-Si alloy with concentration from Si corner at $x_{Cu} = x_{Fe}$ (a): $1:9 (A), 5:5 (C)$ and $9:1 (E)$ (b): $3:7 (B), 7:3 (D)$.}
\end{figure}
The exponential optimized parameters for the excess Gibbs free energy of mixing were used to compute the partial excess free energy of the individual components of the aforementioned sub-binary alloys. The partial excess Gibbs free energy was then used in the Butler equation to obtain the surface concentrations of the monomers and surface tension of the Si–Cu, Cu–Fe and Fe–Si sub-binary systems at 1773 K, 1873 K, 1973 K and 2073 K. The surface tensions and densities of the pure components required for this purpose were computed at desired temperatures using Eq. (7) with the help of data provided in Table 2. The variation of surface tension with the bulk concentration of a component for the sub-binary system at 1773 K are plotted in Figure 2. The surface tension of the pure Si component is the lowest and that for Fe is the highest among the three components. Therefore, there is a large variation in the surface tension of the Fe–Si system w.r.t. the concentration and varies non-linearly with the increase in the concentration of Fe. Similarly, the surface tension of the Cu–Fe system decreases with an increase in the concentration of Cu and that of the Si–Cu system decreases with an increase in the concentration of Si. The values of surface tensions so obtained for the binary sub-systems were also compared with the values computed from data presented in the literatures [4, 11, 71] (Figure 2).

The surface tensions of the sub-binary systems were used to compute the excess surface tension (deviation from the surface tension obtained by the additive rule) of the respective system. The excess surface tensions of the sub-binary systems were then used in the R–K polynomial to obtain the optimized coefficients. The temperature dependent optimized coefficients of the R–K polynomial for the excess surface tension of the sub-binary alloys are listed in Table 3. The surface tension of the Cu–Fe–Si ternary alloy at different temperatures was computed using the Chou, Kohler and Toop models [53, 54, 55] using the optimized parameters given in Table 3. The Butler equation was used to compute the surface concentration of the monomers and the surface tension of the Cu–Fe–Si ternary alloy at all three corners at five different cross-sections (x_Fe : x_Si = 1 : 9 (A), 5 : 5 (C) and 9 : 1 (E)). The variation in the surface concentrations of the monomers of the ternary alloy with the bulk concentration from the Si corner at the aforementioned five different cross-sections are shown in Figure 3a-e. The surface concentration of the monomers increases or decreases non-linearly with the increase or decrease in the bulk concentration of the corresponding component. The surface concentration of Si component is higher than the other components, even at a relatively lower value of bulk concentration (Figure 3a). The surface concentration of Cu is greater than that of Fe at their equal bulk concentration, as shown in Figure 3c. These results show that the components with lower value of surface tension in the pure state segregate more...
in the surface of the alloy (i.e., higher surface concentration). This result agrees with the physical law, which states the requirement of minimizing the energy of the system. The variations in the surface concentration of the monomers of the ternary alloy with temperature at the compositions, \( Si_{25}Cu_{50}Fe_{25} \), are shown in Figure 4. The surface concentration of Si and Cu decreased and the surface concentration of Fe increased with increase in the temperature. This shows that the surface concentration shifts towards the ideal value with increasing temperature. At composition \( Si_{25}Cu_{50}Fe_{25} \) the surface concentrations of Si and Cu are 0.49 and 0.39, respectively and that of Fe is 0.12 at 1773 K, while the respective ideal values (bulk concentrations) of their surface concentrations are 0.50, 0.25 and 0.25.

The variation in the surface tension of the Cu–Fe–Si ternary alloy with concentration from all three corners at five different cross-sections \( x_1/x_2 = 1:9, 3:7, 5:5, 7:3, 9:1 \) computed at 1773 K using the aforementioned models are shown in Figures 5, 6, and 7. The surface tension computed using the four different models is in good agreement with each other. The surface tension of the ternary alloy decreased non-linearly when viewed from the Si corner (Figure 5a,b). This is due to the lowest value of the surface tension of the pure Si component among the three components. The surface tension of the liquid Cu lies in between the surface tension of Si and Fe. Therefore, the surface tension of the ternary alloy either increases or decreases or remains constant depending on the concentration of Fe and Si in the alloy when viewed from Cu corners (Figure 6a,b). The surface tension of the ternary alloy increases non-linearly when observed from the Fe corner (Figure 7a,b) at all cross-sections owing to the highest value of surface tension of Fe among the three constituents of the alloy. The variation of the surface tension of the ternary alloy with temperature is shown in Figure 8 at concentrations \( Si_{25}Cu_{50}Fe_{25}, Si_{10}Cu_{35}Fe_{50}, Si_{25}Cu_{45}Fe_{30}, Si_{35}Cu_{45}Fe_{20} \) and \( Si_{45}Cu_{45}Fe_{10} \). It is observed that the surface tension of the alloy decreases linearly with increasing in the temperature at all concentrations.

The enthalpy of mixing of sub-binary alloys was computed at 1773 K, 1873 K, 1973 K and 2073 K using the optimized coefficients of the R–K polynomial for the enthalpy of mixing listed in Table 4. These optimized parameters were used in the Chou equation to compute the enthalpy of mixing of the Fe–Cu–Si ternary alloy at different concentrations and temperatures. The viscosity of the pure components at a desired temperature was computed using the data given in Table 5. The enthalpy of mixing, activation energy and viscosity of the individual components were used in Eq. (17) to compute the viscosity of the Fe–Si binary subsystem at 1873 K using the Kaptay model [56], the Kozlov-Romanov-Petrov (KRP) equation [69] and the Moelwyn-Hughes (MH) equation [36]. The details of the equations of KPR and MH can be found in the reference [32]. The computed value of the viscosity for the Fe–Si system at 1873 K using the Kaptay model is in an excellent agreement with that of the experimental value [70]. However, those computed using the KPR and MH equations greatly deviate from the experimental value (Figure 9). In this regard, the Kaptay model was considered for further computation of the viscosities of the Si-Cu and Cu-Fe sub-systems. The viscosity of the Si-Cu alloy appeared almost constant at all compositions. This is due to the comparable values of the viscosities of the pure Si and Cu components at 1873 K. The viscosity of the Cu-Fe alloy decreased non-linearly with the increase in the concentration of Cu and the viscosity of the Fe-Si liquid alloy increased non-linearly with the increase in the content of Fe in the alloy.

Further, the viscosity of the binary alloys computed using the Kaptay model was used to obtain the excess viscosities of the sub-binary systems Cu–Fe, Fe–Si and Si–Cu. The excess viscosities of the sub-binary systems were then used to optimize the coefficients of the R–K polynomial for excess viscosity, which are listed in Table 6. The viscosity of the ternary alloy using the Chou, Kohler and Toop models at different temperatures and concentrations was computed using the optimized parameters as given in Table 6.

The viscosity of the ternary alloy computed using the Chou, Toop, Kohler and Kaptay models are in good agreement with each other at all compositions, as shown in Figures 10, 11, and 12. The viscosity of the ternary alloy remains almost constant when viewed from the Si corner in the Cu-rich region (line E in Figure 10a). The viscosity of the graph decreases with the concentration of Si and the rate of decrease of the viscosity increases with the Fe content in the alloy (Figure 10a,b). The variation in the viscosity of the alloy from the Cu corner (Figure 11a,b) follows the same pattern as that from the Si corner. The viscosity of the ternary alloy increases non-linearly at all cross-sections when observed from the Fe corner shown in Figure 12a,b. Figure 13 shows the variation in the viscosity of the alloy with temperature at five different compositions \( Si_{25}Cu_{50}Fe_{25}, Si_{10}Cu_{35}Fe_{50}, Si_{25}Cu_{45}Fe_{30}, Si_{35}Cu_{45}Fe_{20} \) and \( Si_{45}Cu_{45}Fe_{10} \). It is observed that the viscosity decreases non-linearly with the rise in the temperature at Fe rich region. The viscosity decreases linearly with the temperature when the concentration of Cu and Si are higher.

4. Conclusion

From the above study the following conclusions can be drawn:

1. The Cu–Fe binary system is segregating and the Fe–Si and Si–Cu binary systems are ordering in nature. The Fe–Si system of binary alloy is strongly interacting and the Cu–Si system is weakly interacting.
2. The elements having the lower value of surface tension segregate more on the surface. The surface segregation of Si is much greater than the other components in Cu–Fe–Si alloy at equal bulk concentrations.
3. The surface concentration of the components tends to change towards the ideal value with the rise of temperature.
4. The surface tension of the Cu–Fe–Si alloy increases non-linearly with the rise in the concentration of Fe at all cross-sections and decreases non-linearly with increase of concentration of Si.
5. The surface tension decreases linearly with the rise of temperature for all alloy compositions.
6. The viscosity of the Cu–Fe–Si alloy increases non-linearly with the Fe contents of the alloy at all cross-sections and decreases non-linearly with the concentration of Si in Fe rich cross-sections.
7. The viscosity of the Cu–Fe–Si ternary alloy decreases non-linearly with the increase in temperature at higher of concentration of Fe in the ternary alloy. At lower concentration of Fe in the alloy, the viscosity decreases linearly with the rise of temperatures.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Author contribution statement

U. Mehta: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
S.K. Yadav: Conceived and designed the experiments; Performed the experiments; Wrote the paper.
I. Koirala: Conceived and designed the experiments.
R.P. Koirala, G. K. Shrestha: Contributed reagents, materials, analysis tools or data.
D. Adhikari: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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