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Exponential Temperature-Dependent Parameters for Thermodynamic and Structural Properties of Al-Ti Melt

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ABSTRACT

Thermodynamic and structural properties of Al-Ti melt have been estimated in the framework of Redlich-Kister (R-K) polynomial using linear temperature-dependent (T-dependent) interaction parameters above melting temperatures. These calculations show the existence of the artificial inverted miscibility gaps (artifacts) at temperatures 2000 K, 2500 K, and 2700 K. Therefore, interaction parameters are assumed to vary exponentially with temperature and have been optimised for excess free energy of mixing. The artifacts do not appear in the calculation of these properties of the concerned alloy when these optimized parameters are used.

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1. Introduction

The fabrication of materials for their various applications at high temperatures is one of the major tasks for the researcher in the field of material and metallurgical science. Such high-temperature materials are used as exhaust valves and turbine blades in aerospace and automotive vehicles. Titanium-based alloys are most often preferred as high-temperature materials. Moreover, the AlTi-

based alloys have lightweight as well as high strength. Therefore, complete knowledge of Al-Ti alloys is mandatory and hence several researchers so far have studied the phase diagram of this system [1–9].

The experimental value of enthalpy of Al was used to calculate the enthalpy of Ti using Gibbs-Duhem

relation which were used to compute the enthalpy of mixing of liquid Al-Ti alloy at 2000 K [1]. Kattner et al. [2]. analyzed the phases of stoichiometric compounds, the disordered solution phases and the ordered intermetallic compounds, and optimised the thermodynamic functions of the Al-Ti system. Maeda et al. [3] studied the activity of the system at 2073 K and found that the observed values showed negative deviation from the Raoult's law throughout the entire concentration of Al. Zhang et al. [4] analyzed the Al-Ti system by taking nine phases and calculated excess Gibbs free energy of mixing of disordered solution phases using a generalized bond energy model. Witusiewicz et al. [7] modeled Gibbs free energy of mixing of all phases of the system using computer-based software PARROT optimizer of Thermo-Calc and optimised the thermodynamic parameters of the Al-Ti system. Sudavtsova and Podoprigora [8] used an isoperibolic calorimeter to determine the enthalpy of mixing of the liquid alloy at temperatures $1770 \pm 5\text{K}$ and $1790 \pm 5\text{K}$ and concluded that these values are temperature-dependent. Egry et al. [9] measured the thermo-physical properties of the Al-Ti-based ternary system and compared them with the corresponding values calculated from the optimised parameters of the system of Ref. [7]. Novakovic et al. [10] used quasi-chemical approximation to study the surface, dynamic and structural properties of the liquid Al-Ti alloy at 1973 K and predicted that Al segregates on the surface phase of the solution throughout the entire concentration range. Their result showed that the theoretical value of concentration fluctuations in the long-wavelength limit was found to be greater than the corresponding ideal values at very low concentration of Ti ($x_{Ti} \leq 0.15$) indicating the segregating tendency of the system in the constrained concentration range [11-13]. In this work, R-K polynomial has been used to study the thermodynamic and structural properties of liquid alloy by using the linear temperature interaction parameters. On extrapolating these values at higher temperatures, the artificial inverted miscibility gaps appeared [14-18]. With this regard, the exponential interaction parameters have been optimised and the thermodynamic and structural properties of the system have been recomputed at elevated temperatures, such as 1500 K, 2000 K,

2500 K and 2700 K in order to remove the inverted miscibility gaps.

The necessary mathematical formulation is presented in the Section 2, the results and discussion are presented in the Section 3 and the conclusions are outlined in the Section 4.

2. FORMULATION

The thermodynamic properties like excess free energy of mixing (G_M^{xs}), enthalpy of mixing (H_M), and the activity of components of binary liquid alloy can be determined by using coefficients of R-K polynomial. These coefficients are called the interaction parameters of the system and are considered to be temperature-dependent. The linear temperature-dependent form of the interaction parameters can be given as

$$L_i = a_i + b_i T \quad (1)$$

where a_i and b_i are parameters associated with the enthalpy of mixing and excess entropy of mixing respectively. Likewise, the exponential temperature-dependent terms of the interaction parameters are expressed as [19]

$$L_i = h_i \exp\left(\frac{-T}{\tau_i}\right) \quad (2)$$

where h_i and τ_i are constant parameters which are to be optimised for the preferred alloy. In the framework of R-K polynomial, the excess free energy of mixing (G_M^{xs}) of the liquid alloy is expressed [20]

$$G_M^{xs} = x_{Al} x_{Ti} \sum_{i=0}^3 L_i (x_{Al} - x_{Ti})^i \quad (3)$$

where x_{Al} and x_{Ti} are concentrations of the components Al and Ti of the liquid Al-Ti alloy. Using Equations (2) in Equation (3), one can obtain

$$G_M^{xs} = x_{Al} x_{Ti} \sum_{i=0}^3 h_i \exp\left(-\frac{T}{\tau_i}\right) (x_{Al} - x_{Ti})^i \quad (4)$$

The general expression relating the excess free energy of mixing, enthalpy of mixing (H_M) and excess entropy of mixing (S_M^{xs}) is

$$H_M = G_M^{xs} + TS_M^{xs} \quad (5)$$

The excess entropy of mixing can be calculated in terms of (S_M^{xs}) given as

$$S_M^{xs} = \frac{-\partial G_M^{xs}}{\partial T} \quad (6)$$

Using linear parameters and exponential parameters from Equations (1) and (2) in Equations (3), (6) and finally in Equation (5) then respective expressions for enthalpy of mixing (H_M) are

$$H_M = x_{Al}x_{Ti} \sum_{i=0}^3 a_i(x_{Al} - x_{Ti})^i \quad (7a)$$

and

$$H_M = x_{Al}x_{Ti} \sum_{i=0}^3 \left(1 + \frac{T}{\tau_i}\right) h_i \exp\left(\frac{-T}{\tau_i}\right) (x_{Al} - x_{Ti})^i \quad (7b)$$

The partial excess free energy of the components Al and Ti of liquid Al-Ti alloy can be computed using the following relation

$$G_{Al}^{xs} = x_{Ti}^2 \sum_{i=0}^3 L_i [(1 + 2i)x_{Al} - x_{Ti}] (x_{Al} - x_{Ti})^{i-1}$$

and

$$G_{Ti}^{xs} = x_{Al}^2 \sum_{i=0}^3 L_i [x_{Al} - x_{Ti}(1 + 2i)] (x_{Al} - x_{Ti})^{i-1} \quad (8)$$

The activities of the components Al and Ti are calculated using the values from Equations (8) then

$$a_{Al} = x_{Al} \exp\left(\frac{G_{Al}^{xs}}{RT}\right) \quad \text{and} \quad a_{Ti} = x_{Ti} \exp\left(\frac{G_{Ti}^{xs}}{RT}\right) \quad (9)$$

The structural property of the liquid alloy system can be analyzed by computing concentration fluctuations in the long-wavelength $S_{cc}(0)$ limit .

Following Bhatia and Singh, the expression for $S_{cc}(0)$ terms of excess free energy of mixing can be given as [21]

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial x_k^2}\right)^{-1} \quad (10)$$

where $k = \text{Al or Ti}$ and

$$G_M = G_M^{xs} + RT(x_{Al} \ln x_{Al} + x_{Ti} \ln x_{Ti})$$

Using above relation and Equation (3) in Equation (10), then $S_{cc}(0)$ is expressed as

$$S_{cc}(0) = RT[-2L_0 + (-12x_{Al} + 6)L_1 + (-48x_{Al}^2 + 48x_{Al} - 10)L_2 + (-160x_{Al}^3 + 240x_{Al}^2 - 108x_{Al} + 14)L_3 + \frac{RT}{x_{Al}(1-x_{Al})}]^{-1} \quad (11)$$

The ideal value of $S_{cc}(0)$ is calculated using the relation $S_{cc}^{id}(0) = x_{Al}(1 - x_{Al})$

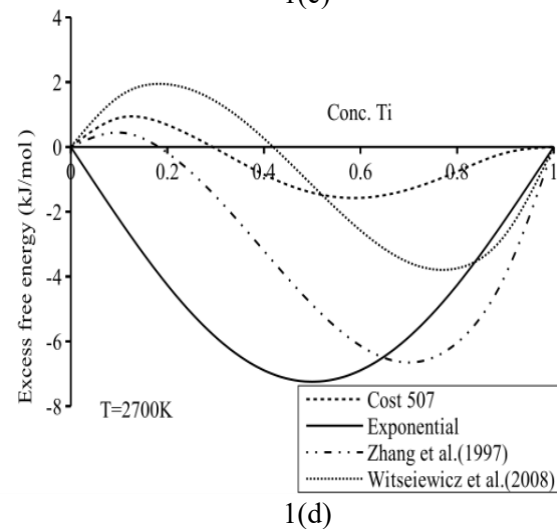
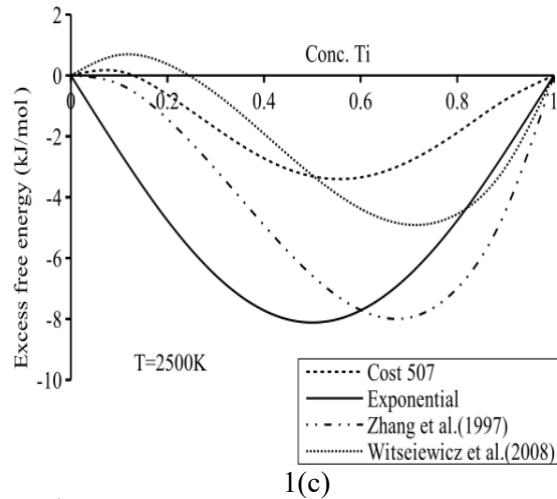
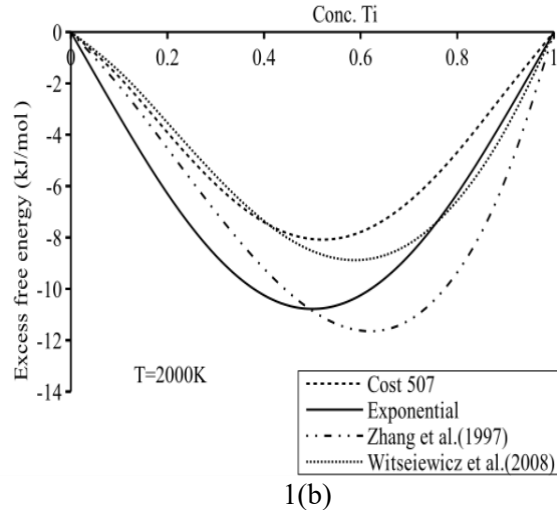
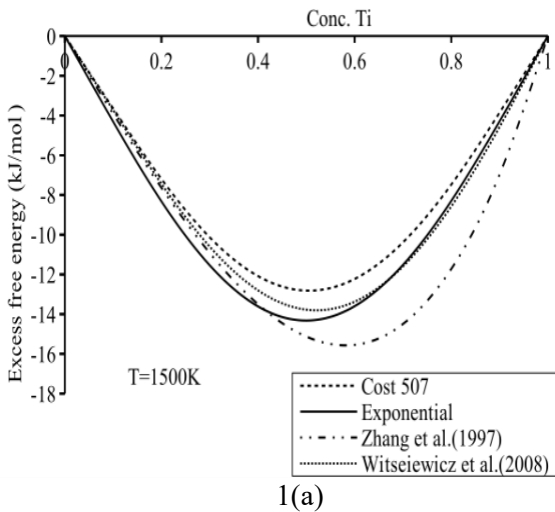
3. Results and Discussion

In present work, we aim to study the thermodynamic and structural properties of the Al-Ti liquid alloy at elevated temperatures. When these properties were calculated using linear temperature-dependent interaction parameters of the R-K polynomial, there appeared unusual trends. Therefore, the interaction parameters of the system were re-optimised assuming the interaction parameters to be exponential temperature-dependent. For the purpose, the linear parameters were taken from the work of Witusiewicz et al. [7] and the exponential parameters were optimised using Equations (1) and (2), and are presented in the Table 1. The excess free energy of mixing (G_M^{xs}) was computed at temperatures 1500 K, 2000 K, 2500 K and 2700 K using Equation (3) with the aid of the exponential parameters and the linear parameters of Zhang et al. [4], Witusiewicz et al. [7] and Cost 507 [5] (Table1). The compositional dependence of the values so obtained are plotted in Figs. 1(a-d).

Table 1. Interaction parameters for the excess free energy of mixing of Al-Ti liquid alloy

Reference	Thermodynamic interaction parameters [J/mol]
Cost 507 [5]	$L_0 = -108250 + 38T$ $L_1 = -6000 + 5T$, $L_3 = 15000$
This work	$L_0 = -134188.7 \exp(-5.677 \times 10^{-4} T)$, $L_1 = -4343504.6 \exp(-7.01 \times 10^{-3} T)$, $L_3 = 41482.8 \exp(-6.85 \times 10^{-4} T)$
Zhang et al. [4]	$L_0 = -111811.4 + 34.199T$, $L_1 = 9746.9 + 7.69T$
Witusiewicz et al. [7]	$L_0 = -118048 + 41.972T$, $L_1 = -23613 + 19.704T$, $L_2 = 34757 - 13.844T$

At temperature 1500 K, all the computed values of G_M^{XS} were found to be in good agreement with each other at lower concentration of Ti whereas the values obtained using the parameters of Zhang et al. differed from the rest at higher concentration of Ti. With the increase in temperatures, the results obtained using the linear parameters showed pronounced wavy natures at lower concentrations of Ti (Figs. 1(b-d)). These types of variations in (G_M^{XS}) is not in accordance with the general trends. It is an indication of the appearance of an artificial inverted miscibility gap. But this artificial inverted miscibility gap has been removed using the exponential parameters.



Figs. 1(a-d): The compositional dependence of the excess free energy of mixing of the liquid Al-Ti alloy at different temperatures.

The enthalpy of mixing (H_M) of the liquid alloy were computed using Equation (7a) and the temperature independent terms of the linear parameters of Table 1.

The temperature-dependent (H_M) was computed using Equation (7b) and the exponential parameters of Table 1. The compositional dependence of H_M so computed values is compared in Fig. (2).

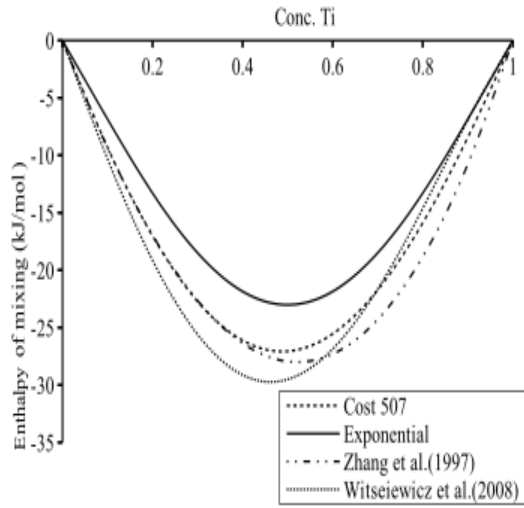
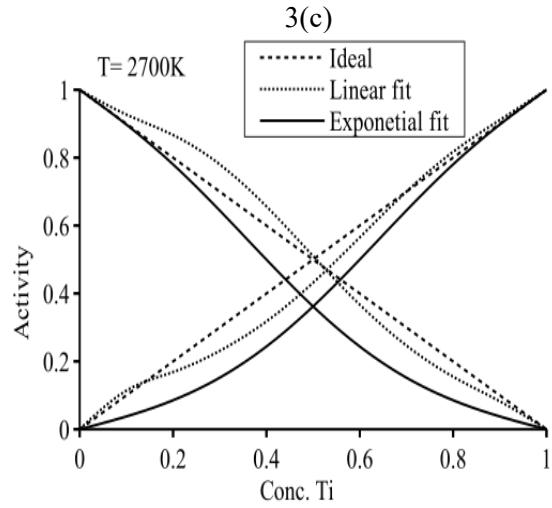
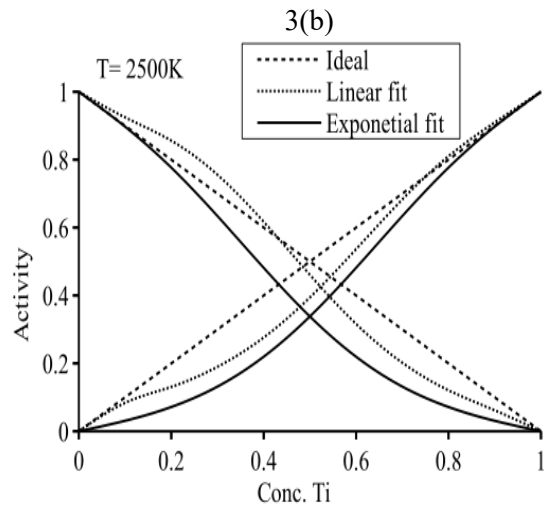
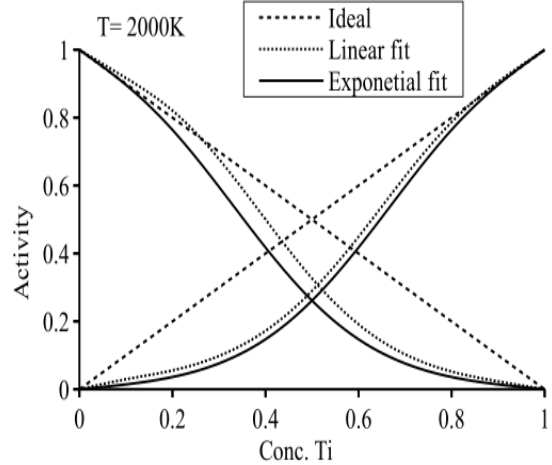
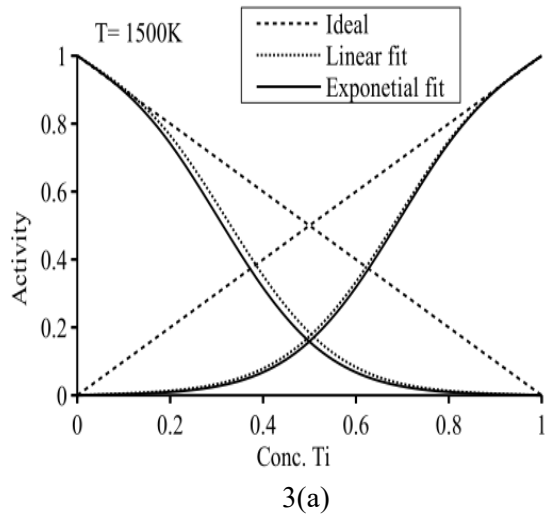


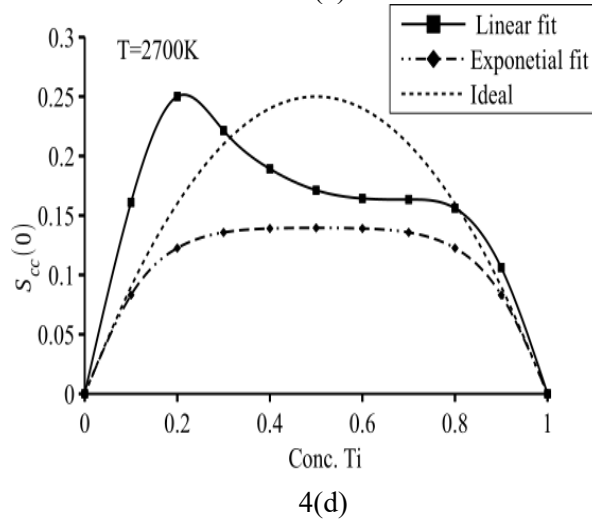
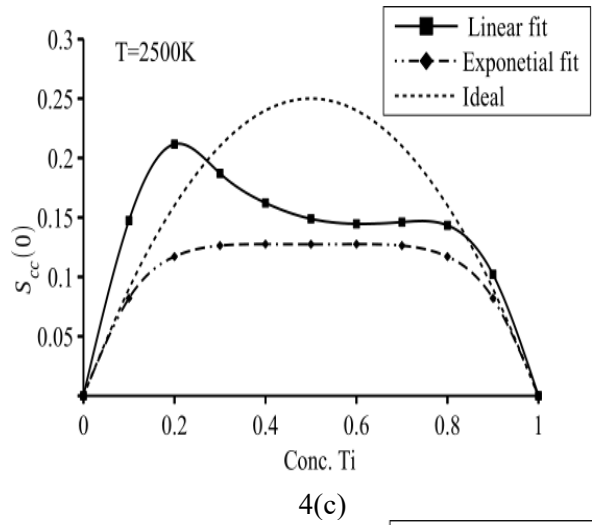
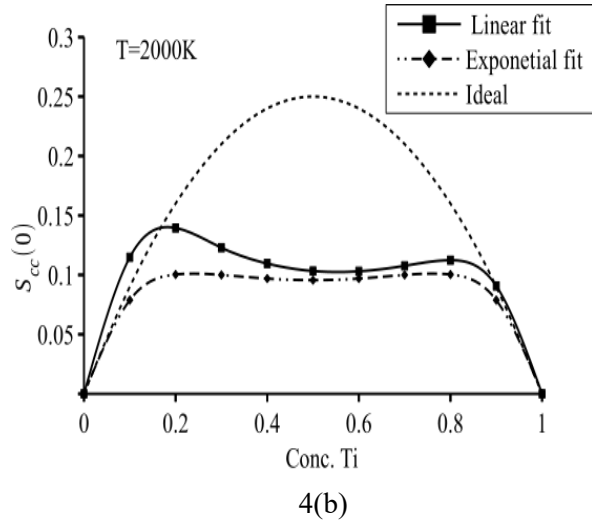
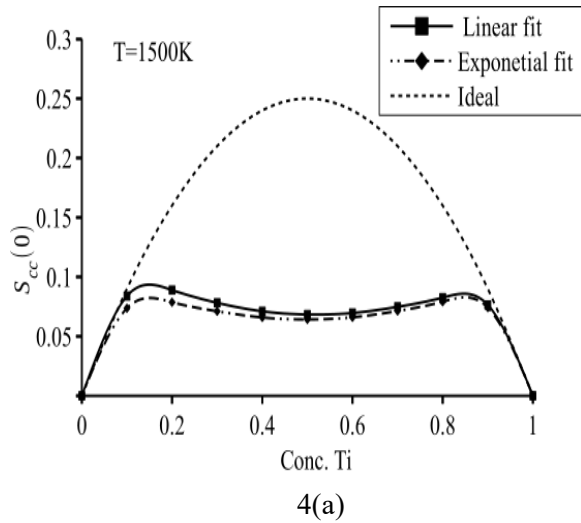
Fig. 2: Enthalpy of mixing of the liquid Al-Ti alloy versus concentration of Ti at 2000 K.



Figs. 3(a-d): Activity of the components of the liquid Al-Ti alloy versus concentration of Ti at different temperatures.

The compositional dependence of the computed values of the activities of components Al and Ti are plotted in Figs. 3(a-d). They found to be in well agreement at temperature 1500K (Fig. 3(a)). With the increase in temperature of the system, it is observed that the activity of Al computed using linear parameters shows negative deviation from Raoult's law at lower concentrations of Ti. Generally, the activity shifts towards ideal values with an increase in temperatures. In this work, this general trend is observed when exponential parameters are used.

The study of structural properties like concentration fluctuation in long-wavelength limit ($S_{cc}(0)$) gives information about the arrangement of the atoms in the initial melt. Moreover, the positive or negative deviations of $S_{cc}(0)$ with respect to its ideal value ($S_{cc}^{id}(0)$) gives information about the nature of local arrangements of atoms, such as for $S_{cc}(0) > S_{cc}^{id}(0)$ segregating or homo-coordination behaviour is expected and for $S_{cc}(0) < S_{cc}^{id}(0)$ compound forming or hetero-coordination tendency is expected.



Figs. 4(a-d): The compositional dependence of the concentration fluctuations in long-wavelength limit

($S_{cc}(0)$) of liquid Al-Ti alloy at different temperatures.

The values of $S_{cc}(0)$ have been computed using Equation (11) with the aid of the linear parameter and exponential parameters from Table 1 and are plotted in Figs. 4(a-d). It is observed that the computed values of $S_{cc}(0)$ at temperature 1500 K are in good agreement. Generally, it is observed that the computed value of $S_{cc}(0)$ gradually shifts toward the ideal value with the increase in the temperature of the liquid alloys [22]. But in the present work, it is observed that the computed values of $S_{cc}(0)$ using the linear parameters shifts beyond respective ideal values at the low concentrations of Ti (Figs. 1(b-d)) with the increase in the temperature of the system. The variation of $S_{cc}(0)$ beyond the ideal value can be termed as the appearance of the artificial miscibility gap. However, the presence of such trend has been removed by using the exponential temperature-dependence parameters at high temperatures. Therefore, it can be concluded that the exponential temperature-dependent parameters of the interaction energy parameters well explain the thermodynamic and structural properties of the liquid Al-Ti system at preferred higher temperatures.

4. Conclusion

The linear as well as exponential temperature-dependent interaction parameters were used in the frame work of R-K polynomial to compute the thermodynamic and structural properties of liquid Al-Ti alloy at constrained higher temperature range, 1500-2700 K. The artificial inverted miscibility gaps (artifacts) appeared in the computed thermodynamic properties (G_M^{xs}) and activity and structural property ($S_{cc}(0)$) at higher temperatures, such as 2000 K, 2500 K, and 2700 K when the interaction parameters were assumed to be linear temperature-dependent. But these gaps were found to be removed when the interaction parameters were assumed to be exponential temperature-dependent. The present study predicts that the thermo-structural properties of the system are well explained by the exponential parameters at considered higher temperature range.

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