

# CALPHAD MODELLING OF CERAMIC SYSTEMS

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## ABSTRACT

Thermodynamic modelling based on Calphad approach is a powerful tool for understanding the behaviour and designing materials with optimized properties. This method relies on the availability of relevant Gibbs energy functions. The present work is concerned with developing the Gibbs energy functions for Si-Zr-N and Ti-Zr-N systems. The outcome of implementing such an approach is a set of internally consistent Gibbs energy functions for various phases. These functions are typically used to build Gibbs energy databases for multicomponent systems that are accessible to Gibbs energy minimization software. They can be used to compute the thermochemical and constitutional information that would help in understanding the behaviour of these materials and optimizing their compositions for different applications.

## 1 INTRODUCTION

TiN and ZrN are used as protective coatings for cutting and forming tools due to their high hardness and wear resistance. Though these coatings possess excellent mechanical properties, their oxidation resistance at elevated temperature are poor. It was reported that the oxidation resistance of these coatings can be enhanced by the incorporation of silicon [1]. The highest oxidation resistance was achieved in Si-Zr-N coatings containing about 10 mol.% Si as reported by [2]. Cemented carbide tips coated with the mixed nitride (Ti,Zr)N has shown improved cutting performance due to the alloying effect of Zr with Ti in fcc-TiN unit cell [3]. At high cutting speeds, spinodal decomposition can be expected to occur because of increase in temperature at the contact zone, leading to further increase in hardness and wear resistance [4].

The main aim of this work is to explore the phase equilibria and thermochemistry of ternary nitride coatings for tribological applications using Calphad method. It is possible to obtain the thermochemical and constitutional information with the help of Gibbs energy functions for individual phases using this method. This information will be beneficial for the selection, processing and application of these materials for various applications. In this study, internally consistent set of Gibbs energy functions for various phases are obtained using Calphad approach combined with *ab initio* calculations for Si-Zr-N and Ti-Zr-N systems. These functions are integral part of Gibbs energy databases for multicomponent systems that are accessible to Gibbs energy minimization software such as Thermo-Calc [5].

## 2 THE CALPHAD METHOD

The term Calphad is the acronym for CALculation of PHase Diagrams. This method combines the classical thermodynamic principles with mathematical formulations that

facilitates the calculation of thermochemical properties and phase equilibria of multi-component multiphase systems. The Calphad approach is based on the principle that state variables corresponding to thermodynamic equilibrium can be computed using Gibbs energy minimization. The required functions for multicomponent systems can be obtained by combining the Gibbs energy functions of the bounding binary systems. Correction terms are usually required to account for the higher order effects, usually not exceeding the ternary effects. Hence, the central theme of this approach is Gibbs energy modelling. The main task of this approach is, thus, to develop consistent set of Gibbs energy functions for relevant phases in the bounding binary and ternary systems that reproduce the experimental information satisfactorily.

## 2.1 Gibbs energy models

### 2.1.1 Elements

Elements and stoichiometric compounds have fixed composition and hence, their Gibbs energies will be dependent only on pressure and temperature. The Gibbs energy of an element in a chosen structural state can be expressed as the following.

$$G(T, p) = G^{\text{ch}} + G^{\text{ph}} + G^{\text{pr}} \quad (1)$$

where,  $G^{\text{ch}}$  is the chemical (lattice) contribution,  $G^{\text{ph}}$  is the physical contribution, typically due to magnetic ordering and  $G^{\text{pr}}$  is the pressure contribution. The functions recommended by Scientific Group Thermodata Europe (SGTE) [6] are to be used for  $G^{\text{ch}}$ , which has the following format (Meyer-Kelly polynomial).

$$G_i^{\circ}(T) = H_i^{\text{SER}} + a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 + \dots \quad (2)$$

where, a, b, c, . . . are the model parameters.  $^{\circ}$  indicates that standard pressure (1 bar) is used. SER refers to the Stable Element Reference i.e., with respect to the enthalpy at 298.15 K and 1 bar ( $H_i^{\text{SER}}$ ) and entropy at 0 K, which is zero according to third law of thermodynamics.

### 2.1.2 Solutions

The general form of Gibbs energy of a solution is

$$G = G^{\text{ref}} + G^{\text{conf}} + G^{\text{E}} + G^{\text{ph}} + G^{\text{pr}} \quad (3)$$

where  $G^{\text{ref}}$  is the reference term and can be considered as Gibbs energy of a mechanical mixture of the constituents.  $G^{\text{conf}}$  refers to the contribution from ideal mixing of constituents and  $G^{\text{E}}$  is the excess contribution that accounts for deviation from ideal behaviour. The exact form of these terms depend on the Gibbs energy model chosen for a phase.

**Random substitutional solutions** A substitutional solution is one of the simplest mixing models, where the solute atoms substitute the solvent atoms randomly. For a multicomponent random substitutional solution at standard pressure, the  $G^{\text{ref}}$  in Equation 3 can be written as

$$G^{\text{ref}} = \sum_i x_i (G_i^{\circ} - H_i^{\text{SER}}) \quad (4)$$

where,  $x_i$  is the mole fraction of component  $i$ . The  $G^{\text{conf}}$  can be represented as

$$G^{\text{conf}} = RT \sum_i x_i \ln x_i \quad (5)$$

The composition dependence of  $G^E$  term in Equation 3 can be expressed by Redlich-Kister (R-K) polynomial [7]. Using this polynomial, the  $G^E$  for a random substitutional solution in a system A-B can be written as

$$G^E = x_A x_B \sum_{\nu=0}^n {}^{\nu}L_{A,B} (x_A - x_B)^{\nu} \quad (6)$$

where,  ${}^{\nu}L_{A,B}$  is the R-K polynomial coefficient of  $\nu^{\text{th}}$  order. The temperature dependence of these parameters can be represented as

$${}^{\nu}L_{A,B} = {}^{\nu}a + {}^{\nu}bT + {}^{\nu}cT \ln T \quad (7)$$

In the case of multicomponent solutions, the excess Gibbs energy ( $G_{\text{m-c}}^E$ ) can be written in terms of the excess Gibbs energies of the constituent binaries ( $G_{i-j}^E$ ) using geometrical extrapolation. Although there are many geometrical extrapolation schemes available, the Muggianu extrapolation [8] along with R-K polynomials is preferred due to its simplicity. Hence, for a multicomponent solution with random mixing, the excess Gibbs energy can be represented as

$$G_{\text{m-c}}^E = \sum_{i=1}^{c-1} \sum_{j=i+1}^c G_{i-j}^E(x_i, x_j) + \text{correction terms} \quad (8)$$

where,  $c$  is the number of components. The correction terms represent the contributions from the higher order systems, generally not exceeding ternary or quaternary systems.

**Sublattice formalism** A simple mixing model such as random substitutional solution is not usually adequate since many phases have more than one type of sites in which mixing takes place. This leads to a general modelling concept known as sublattice formalism. The concept of subdividing configuration space into sublattices was introduced by [9] to describe the thermodynamics of reciprocal salt systems. In this model, it was proposed that the anions and cations occupy separate sublattices and the mixing is random in each sublattice. The generalized sublattice formalism with arbitrary number of sublattices as well as constituents within each sublattice was proposed by [10]. According to this a formula unit of a phase can be represented by

$$(A, B, C \dots)_{a_1} : (A, C, E \dots)_{a_2} : \dots (B, D, E \dots)_{a_n} \quad (9)$$

where, the constituent species A, B, C... may be atoms, molecules, charged species or vacancies (Va) and  $a_s$  is the relative number of sites in sublattice  $s$ . It is also assumed that there is random mixing among the constituents in each sublattice.

A composition variable called site fraction ( $y_{i\#s}$ ) is introduced in order to formulate the Gibbs energy using the sublattice formalism. It is defined as the mole fraction of a constituent species  $i$  in sublattice  $s$ , i.e.,

$$y_{i\#s} = \frac{N_{i\#s}}{N_s} \quad (10)$$

where,  $N_{i\#s}$  is the number of constituent species  $i$  and  $N_s$  is the total number of sites in sublattice  $s$ , including vacant sites. Using the sublattice formalism, the Gibbs energy per mole of formula unit (mfu) of a phase is given as

$$G_{\text{mfu}} = \sum_{I(0)} \left( \prod_{I(0)} y_{i\#s} \right) G_{I(0)}^\circ + RT \sum_s a_s \sum_i y_{i\#s} \ln y_{i\#s} + \sum_{I(z)} \left( \prod_{I(z)} y_{i\#s} \right) L_{I(z)} \quad (11)$$

where,  $I(z)$  is the constituent array of  $z^{\text{th}}$  order. A  $0^{\text{th}}$  order constituent array ( $I(0)$ ) has only one species occupying each sublattice. It is commonly referred to as an end-member since it resembles a stoichiometric compound. The first term in Equation 11 represents the reference term that is formed by the weighted sum of the Gibbs energies of all the end-members  $I(0)$ . Second term is the contribution of configurational entropy to Gibbs energy due to random mixing of constituents within each sublattice. The excess contribution to Gibbs energy is given by the third term. It consists of several interaction energy terms  $L_{I(z)}$  which arise due to the interaction of constituents within a sublattice. The interaction terms beyond the second order constituent array are not considered since their contribution to Gibbs energy is negligible.

### 3 AB INITIO CALCULATIONS

With the advancements in high performance computing, it is now possible to carry out intensive low length scale calculations for systems with large number of atoms and molecules. Amongst these calculations, total energy calculations based on density functional theory (DFT) has gained much use in the context of Calphad. Results from these calculations often serve as input in the thermodynamic modelling, greatly improving the quality of the Gibbs energy functions. The predictive capability of DFT can be utilized to obtain the structural, electronic and thermodynamic properties of materials.

Thermochemical properties such as enthalpy of formation, enthalpy of mixing, *etc.* serve as important input quantities in the optimization of Gibbs energy functions. When the experimental values are unavailable, calculated values of these properties can be used in the optimization. Besides, the enthalpy of formation of hypothetical end-members of the sublattice formulation (Equation 11) may be required. These quantities can also be obtained using *ab initio* calculations based on DFT. In the past, empirical methods such as Miedema model [11] was used for estimating the enthalpy of formation. At present, methods based on DFT are being used for generating thermochemical information such as, enthalpy of formation and enthalpy of mixing of a solid solution at absolute zero of temperature with good accuracy.

In the present work DFT calculations are performed using Vienna Ab initio Simulation Package (VASP) [12]. General settings used for the calculations are listed in Table 1. The enthalpy of formation ( $\Delta_f H_{298}^\circ$ ) is estimated by calculating the difference between the total energies of compound and pure elements in the chosen structural state

$$\Delta_f H_{298}^\circ \approx E_0(\text{A}_y\text{B}_z) - yE_0(\text{A}) - zE_0(\text{B}) \quad (12)$$

where,  $E_0(\text{A}_y\text{B}_z)$ ,  $E_0(\text{A})$  and  $E_0(\text{B})$  are the total energies of compound  $\text{A}_y\text{B}_z$  and elements, A and B, respectively.

The *mcsqs* [15] code of Alloy Theoretic Automated Toolkit (ATAT) [16] is used for generating the SQS supercells at different compositions. This code generates SQS

Table 1: Typical settings used for VASP calculations.

Pseudopotential	PAW
Exchange-correlation functional	GGA-PBE
Energy cut-off	600 eV
$k$ -point spacing	$\leq 0.02 \text{ \AA}^{-1}$
$k$ -point sampling scheme	Monkhorst-Pack [13]
Force convergence	$2 \times 10^{-3} \text{ eV \AA}^{-1}$
Energy convergence	$10^{-7} \text{ eV}$
Integration scheme	Tetrahedron method with Blöchl corrections [14]

structures using stochastic techniques such as Monte Carlo method which are more efficient in finding the optimum supercell. The enthalpy of mixing,  $\Delta_{\text{mix}}H$  obtained from these calculations are useful input for thermodynamic assessments. In the present work, SQS has been used to generate random mixing of the substitutional atoms in the nitrides of Ti-Zr-N and Al-B-N systems.

DFT calculations are capable of predicting the total energy ( $E_0$ ) of a structure at 0 K. In order to obtain accurate Gibbs energy parameters, thermodynamic properties at finite temperature (above 0 K) is crucial. In this work, both harmonic and quasiharmonic approximations are used for calculating the finite temperature thermodynamic properties. Harmonic approximation is implemented using PHONON code [17]. Phonopy [18] was used for estimating the thermodynamic properties using quasiharmonic approximation (QHA).

## 4 THERMODYNAMIC OPTIMIZATION

Thermodynamic optimization was performed using PARROT [19] module of ThermoCalc. Details about the optimization of Si-N, Zr-N, Ti-Zr-N and Si-Zr-N are given below.

### 4.1 Si-N system

Thermodynamic functions for this system is available from the work of [20]. However, it was not possible to reproduce the phase relations in Si-Zr-N system using that description. Hence, the Si-N system has been re-optimized in this work. The enthalpy of formation ( $\Delta_f H_{298}^\circ$ ) as well as heat capacities ( $C_p$ ) of  $\alpha$  and  $\beta\text{Si}_3\text{N}_4$  are calculated using the *ab initio* calculations mentioned above. The computed values of  $\Delta_f H_{298}^\circ$  for  $\alpha$  and  $\beta\text{Si}_3\text{N}_4$  are  $-790012$  and  $-788858$  J/mol, respectively. The  $C_p$  as a function of temperature, obtained using QHA for  $\alpha$  and  $\beta\text{Si}_3\text{N}_4$  is shown in Figure 1. The  $C_p^\circ(T)$  values are fitted to appropriate expressions down to 0 K and integrated to obtain the Gibbs energy functions (Equation 13).

$${}^\circ G^{\text{Si}_3\text{N}_4} - 3H_{\text{Si}}^{\text{SER}} - 4H_{\text{N}}^{\text{SER}} = \begin{cases} a + bT + \gamma T^4 \\ a + bT + cT \ln T + dT^{-1} + eT^{-2} + fT^3 \end{cases} \quad (13)$$

The model parameters for this system are optimized using thermochemical (experimental and *ab initio*) and constitutional data as input. The calculated phase diagram is shown in Figure 2a. There is good agreement between the experimental data and the

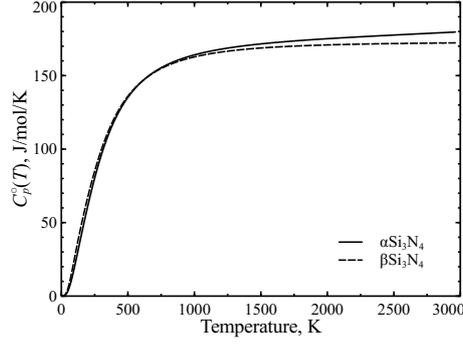


Figure 1: Calculated  $C_p^o$  for  $\alpha$  and  $\beta$ Si<sub>3</sub>N<sub>4</sub> using QHA.

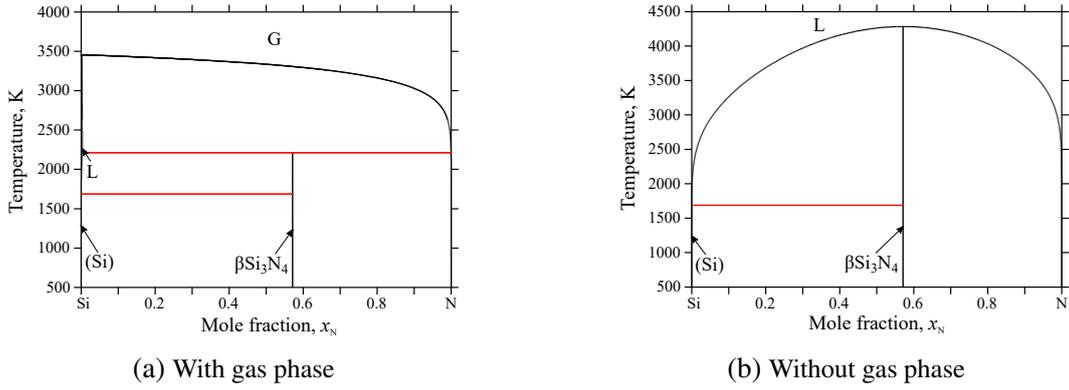


Figure 2: Calculated Si-N phase diagrams.

calculated phase boundaries. The phase diagram calculated without considering the gas phase is shown in Figure 2b.

## 4.2 Zr-N system

The Zr-N system was initially modelled by [21]. Since some of the critical experimental data available in the literature was not used in that work, a re-optimization of the system is done here. The computed  $\Delta_f H_{298}^o$  values with respect to Zr(hcp) and N<sub>2</sub>(g) using DFT are listed in Table 2. It is to be noted that ZrN<sub>3</sub> and ZrN<sub>0.5</sub> are the end-members of the sublattice formulations of bcc and hcp solid solutions. The Helmholtz energy estimated using harmonic approximation is converted to Gibbs energy with respect to SER using the following equation [22].

$$\begin{aligned}
 G_T(\text{phase}) &= \sum_{i=\text{elements}} \nu_i H_{298}^o(i) = E_0(\text{phase}) + \text{ZPE}(\text{phase}) + A_T^o(\text{phase}) \\
 &= \sum_{i=\text{elements}} \nu_i [E_0(i) + \text{ZPE}(i) + (H_{298}^o - H_0^o)(i) + (pV(i))] \quad (14)
 \end{aligned}$$

where, ZPE is the zero point energy which was obtained from these calculations. The Gibbs energy calculated using harmonic approximation for stoichiometric ZrN is shown in Figure 4.

This system was optimized with experimental thermochemical and constitutional data as well as the *ab initio* thermochemical data as input. The calculated Zr-N phase diagram and its comparison with experimental data shows that they are in good agree-

Table 2: Enthalpy of formation of end-members in Zr-N system using DFT

End-member	$\Delta_f H_{298}^\circ$ (J/mol)
ZrN (fcc)	-341593
ZrN <sub>0.75</sub> (hcn)	-148695
	80996

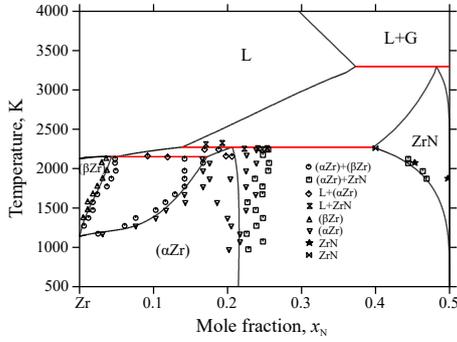


Figure 3: Comparison of calculated Zr-N phase diagram with experimental data [23].

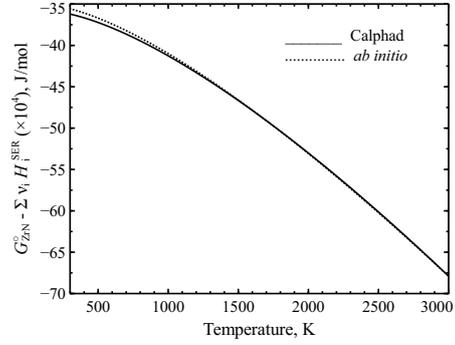


Figure 4: Comparison of calculated and *ab initio* Gibbs energy of ZrN.

ment (Figure 3). The calculated Gibbs energy of ZrN matches well with the values estimated from *ab initio* calculations, as shown in Figure 4.

### 4.3 Ti-Zr-N system

Experimental information indicates that TiN and ZrN are immiscible with each other below 2000 K [24]. However, there is no experimental data regarding the critical point of the miscibility gap. The enthalpy of mixing of TiN and ZrN, computed using SQS, indicate that demixing is favoured (Figure 5). The Gibbs energy of formation of one of the compositions of the mixed nitride ( $\delta$ -phase) corresponding to the formula  $Zr_{0.25}Ti_{0.75}N$  was calculated using harmonic approximation is shown in Figure 6. The calculations for other SQS structures failed due to negative phonon frequencies. In order to model the Gibbs energy functions of the Ti-Zr-N system, the thermodynamic descriptions for Zr-N from present work as well as Ti-N and Ti-Zr from [25] and [26], respectively, were combined. The model parameters for the  $\delta$  phase were optimized with the *ab*

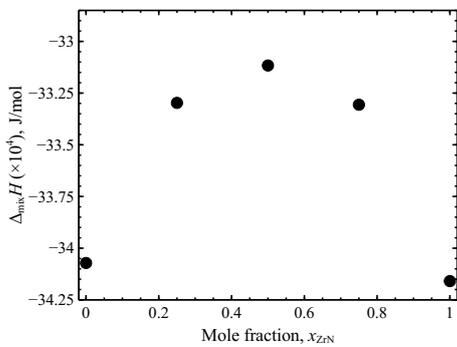


Figure 5: Enthalpy of mixing of TiN and ZrN computed using SQS.

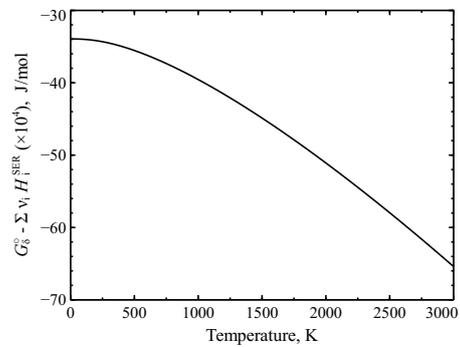


Figure 6: Gibbs energy of  $\delta$ -phase of composition corresponding to  $Zr_{0.25}Ti_{0.75}N$  calculated using PHONON.

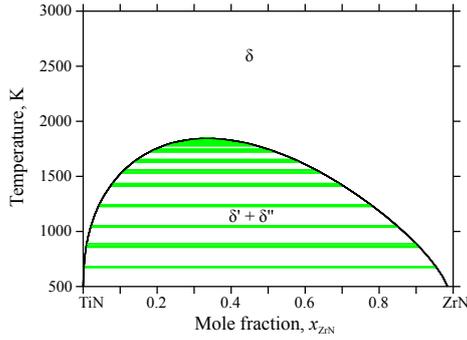


Figure 7: Calculated TiN-ZrN section.

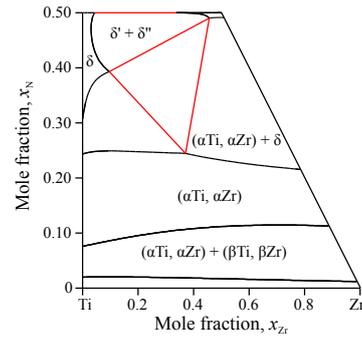


Figure 8: Calculated partial isothermal section at 1473 K.

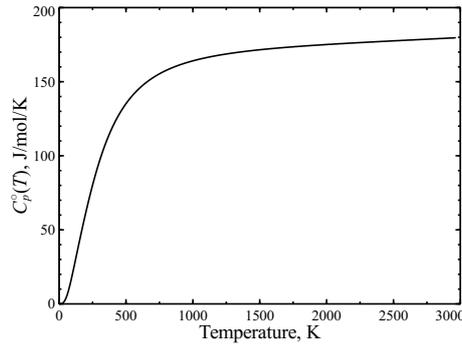


Figure 9: Calculated  $C_p^\circ$  for  $Zr_5Si_3N$  using QHA.

*initio* thermochemical data as input. Figure 7 shows the calculated TiN-ZrN section. The predicted critical temperature and composition of the miscibility gap are 1844 K and 0.34 ( $x_{ZrN}$ ), respectively. The partial isothermal section at 1473 K indicates the presence of  $\delta$ -phase miscibility gap, as shown in Figure 8.

#### 4.4 Si-Zr-N system

Experimental data indicate that the dissolution of nitrogen makes  $Zr_5Si_3$  phase stable down to room temperature in Si-Zr-N system. The phase equilibria at 1273 and 1573 K were presented in the form of isothermal sections in the review by [27]. *Ab initio* calculations were performed for  $Zr_5Si_3N$  end-member since there are no experimental thermochemical data available for this system. The calculations predict its  $\Delta_f H_{298}^\circ$  to be  $-968142$  J/mol. The  $C_p^\circ$  as a function of temperature, obtained using QHA is shown in Figure 9. The  $C_p^\circ(T)$  values were fitted to relevant expressions and the Gibbs energy functions similar to Equation 13 were obtained by integration. A preliminary version of the Gibbs energy description for the ternary system is obtained by combining Gibbs energy functions of Si-N and Zr-N from present work and the modified thermodynamic description of Si-Zr system from [28]. The Gibbs energy parameters for  $Zr_5Si_3N$  were optimized with the *ab initio* thermochemical data and the experimental constitutional data. The calculated isothermal sections at 1273 and 1573 K using the parameters obtained in this work and its comparison with experimental data from [27] are shown in Figures 10a and 10b, respectively. The change in disposition of the tie-triangles between  $\beta Si_3N_4$ , ZrN, ZrSi and ZrSi<sub>2</sub> at 1273 K and 1573 K indicates the presence of a U-type invariant reaction between these temperatures. The calculated U-type invariant reaction

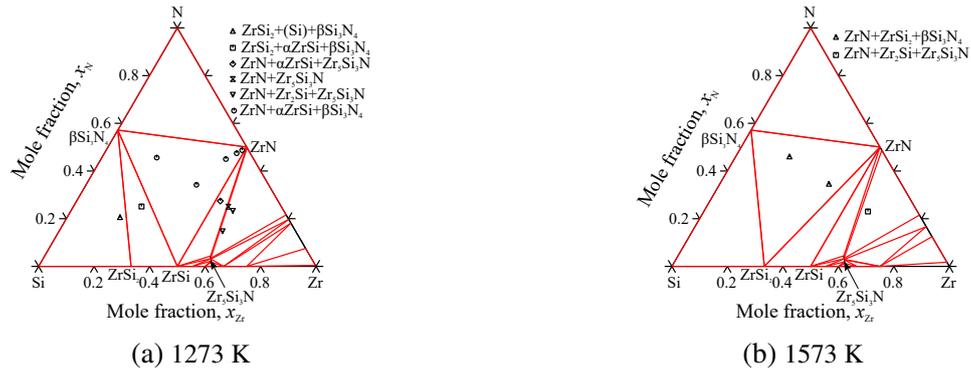


Figure 10: Comparison of calculated isothermal sections at 1273 K and 1573 K with experimental data from [27].

( $\text{Si}_3\text{N}_4 + \text{ZrSi} \rightleftharpoons \text{ZrSi}_2 + \text{ZrN}$ ) temperature is 1382 K. It is worth mentioning that when the Gibbs energy descriptions for Si-N system from [20] was used, this reaction occurred at  $<500$  K, which is inconsistent with the experimental data.

## 5 CONCLUSIONS

The present work was aimed at obtaining the thermodynamic descriptions for Si-Zr-N and Ti-Zr-N systems using Calphad method. *Ab initio* calculations were used extensively to improve the quality of the Gibbs energy functions. Some of the key findings from this work are:  $\beta\text{Si}_3\text{N}_4$  is thermodynamically more stable than  $\alpha\text{Si}_3\text{N}_4$ ; the critical point of miscibility gap in  $\delta$ -phase was estimated to be 1844 K and 0.35  $x_{\text{ZrN}}$  in Ti-Zr-N system; U-type invariant reaction temperature is calculated to be 1382 K in Si-Zr-N system.

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