Calphad 62 (2018) 148–153

Contents lists available at ScienceDirect

Calphad

journal homepage: www.elsevier.com/locate/calphad

Thermodynamic optimization of Si-Zr-N system using Calphad approach coupled with *ab initio* methods

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ARTICLE INFO

Keywords:
ab initio
Si-N
Si-Zr-N
Zr_5Si_3N
Si_3N_4

ABSTRACT

Gibbs energy model parameters for Si-Zr-N system were obtained using Calphad approach coupled with *ab initio* calculations. The enthalpies of formation of α and βSi_3N_4 in Si-N system and Zr_5Si_3N end-member in Si-Zr-N system were calculated using density functional theory (DFT). The finite temperature thermodynamic properties were calculated using quasiharmonic approximation (QHA). The computed heat capacities were fitted to appropriate expressions valid down to 0 K. The *ab initio* thermochemical data obtained in the present work and the experimental thermochemical and constitutional data from literature were used for the thermodynamic optimization of Si-N and Si-Zr-N systems. The calculated phase equilibria and thermodynamic properties are in good agreement with the input data.

1. Introduction

The development of super hard materials are of high technical importance. Most of the cutting tools and other components, subjected to friction and wear are coated with these materials. Though, the durability of these coatings depends on the mechanical properties such as hardness and wear resistance, their oxidation resistance at high temperature is also important. The excessive oxidation of these coatings leads to loss of adherence and reduction in wear resistance. ZrN films are known to exhibit high hardness [1] and corrosion resistance [2] but its oxidation resistance at elevated temperature is rather poor. It was reported that the oxidation resistance of these coatings can be enhanced by the incorporation of silicon [3]. The highest oxidation resistance was achieved in Si-Zr-N films containing about 10 at.% Si and the hardness of these films were found to increase with increase in Si content as reported by [4]. Si-Zr-N films containing high Si content ($\geq$ 25 at.%), exhibited high oxidation resistance in flowing air (> 1300 °C) [3]. In order to achieve the desired attributes in these coatings, understanding the phase equilibria as a function of temperature and composition is essential.

In the present work, we report the thermodynamic optimization of Si-N and Si-Zr-N systems. The Gibbs energy functions for Zr-N system is from our previous work [5]. The Gibbs energy functions for Si-Zr system are essentially from [6]. The Zr_5Si_3 phase in this system is stoichiometric and hence a two-sublattice formulation, given by $(Si)_3(Zr)_5$, was used to model its Gibbs energy by [6]. This phase has same crystal structure as Ti_5Si_3, which is non-stoichiometric. In order to account for its non-stoichiometry [7] has used a three-sublattice formulation for Ti_5Si_3. Since the final goal of this work is to model the Si-Ti-Zr-N system, it was necessary to remodel Zr_5Si_3 phase using a similar model, in order to make the present description compatible with that of [7]. Figs. 1 and 2 depict the calculated phase diagrams for Zr-N and Si-Zr using these descriptions. A brief review of the relevant literature concerning other systems is given below.

2. Literature review

2.1. Si-N system

The experimental constitutional and thermochemical data concerning Si-N system was reviewed by [8]. Partial phase diagram of the system from 0 to 0.015 at.%N was reported by [9]. Further, the thermodynamic description of the system for the full composition range was provided by [10]. However, the constitutional data in Si-Zr-N system could not be reproduced satisfactorily when the Gibbs energy parameters from [10] were used for the modelling of the ternary. Moreover, the polymorphism of silicon nitride (Si_3N_4) was not considered in that work. In order to address these issues we have re-optimized the Si-N system in the present work.

The crystallographic information for the equilibrium solid phases present in Si-N system are listed in Table 1. According to [11], αSi_3N_4 forms preferentially at low temperatures and its formation is preferred

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https://doi.org/10.1016/j.calphad.2018.06.004
Received 1 May 2018; Received in revised form 12 June 2018; Accepted 16 June 2018

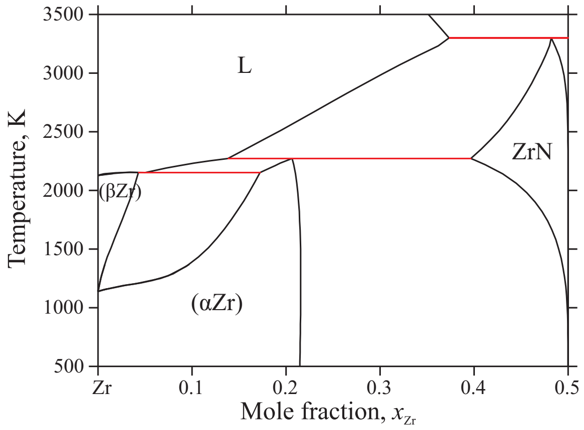

Fig. 1. The calculated Zr-N phase diagram [5].

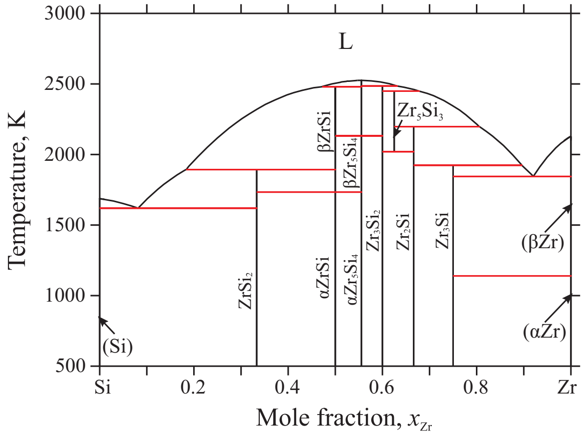

Fig. 2. The calculated Si-Zr phase diagram [6].

Table 1
Crystallographic data for solid phases in Si-N system.

Phase	Pearson symbol	Space group
αSi_3N_4	hP28	$P31c$
βSi_3N_4	hP14	$P6_3$
Si	cF8	$Fd\bar{3}m$

during condensation from gaseous phase due to kinetic reasons. It was concluded by [12] that αSi_3N_4 is a metastable phase. Later, it was also established by [13] that the transformation from α to β is reconstructive at ≈ 2123 K and not reversible. Hence, [8] assumed αSi_3N_4 as metastable and considered βSi_3N_4 as a thermodynamically stable phase in his review.

The co-ordinates of the invariant equilibria are summarized in Table 2. The decomposition temperature of Si_3N_4 was measured by [14] while conducting sintering studies. It was also estimated by [15] from vapour pressure data. These are in reasonable agreement with each other. However, in both the works there is no explicit mention of the type of polymorph that was investigated and its purity. Since αSi_3N_4 can be formed easily in comparison with βSi_3N_4, we assume that the starting material is αSi_3N_4 unless it is mentioned explicitly. However, αSi_3N_4 transforms to βSi_3N_4 before decomposition. Hence, we believe that the decomposition temperatures measured by [14,15] are related to βSi_3N_4. The decomposition temperature was also calculated by [16–18], which are lesser than the experimental value and thus it is not included in the optimization.

Table 2
Co-ordinates of invariant equilibria in Si-N system.

Equilibrium	Composition (at% N)	Temperature (K)
$L + (Si) \rightleftharpoons \beta Si_3N_4$	0.02 [23], 0, 57.1	1687
	0.012 [9], 0, 57.1	1687
$L + G \rightleftharpoons \beta Si_3N_4$	0, 1, 57.1	2173 [14]
		2250 [15]

There are few thermochemical measurements reported in literature for Si_3N_4 [18–22]. The thermodynamic quantities tabulated by [18,19] did not have any reference to the polymorph for which the values are reported. Hence, it was assumed that these data are pertaining to αSi_3N_4 since it can form easily in comparison with βSi_3N_4 [11]. On the other hand, there are only limited thermochemical data available for βSi_3N_4. The Gibbs energy of formation for βSi_3N_4 was reported by [20,21]. We expect that the sample might be contaminated with carbon, since silicon nitride and graphite powders were mixed and heated in a graphite crucible. Due to the uncertainties, thermochemical data from these works were not included for the optimization. The enthalpy of formation of α and βSi_3N_4 at 298 K was measured by [22] using calorimetry which are used in the present work.

2.2. Si-Zr-N system

There is no evidence of any ternary equilibrium phase in this system. It is clear from Fig. 2 that Zr_5Si_3 phase is stable only in the temperature range 2020–2450 K in the binary. However, dissolution of nitrogen makes this phase stable at lower temperature in the ternary. According to [24], the solubility of nitrogen in Zr_5Si_3 at 1873 K is upto 5 at.%. Other than this phase, there is no significant solubility of the third element in any of the other binary phases as established from the reaction chemistry studies between Si_3N_4 and Zr by [25], Zr_5Si_3 and ZrN by [24], Si and ZrN by [26] and Si_3N_4 and ZrN by [27].

The phase equilibria at 1273 and 1573 K was determined using X-ray diffraction by [28], which were presented in the form of isothermal sections in the review by [29]. Zr_5Si_3N was found to be stable in both the sections and a change in phase relation was also observed. At 1273 K, an equilibrium was found to exist between Si_3N_4, ZrN and ZrSi, which transformed to Si_3N_4, ZrN and $ZrSi_2$ at 1573 K. Hence, a U-type solid state invariant reaction

$$Si_3N_4 + ZrSi \rightleftharpoons ZrSi_2 + ZrN$$

is expected to occur between 1273 and 1573 K.

3. Thermodynamic models

The sublattice formulations used for describing the Gibbs energies of the equilibrium phases in Si-N and Si-Zr-N systems are listed in Table 3. The Gibbs energy expressions for the elements are from the

Table 3
Sublattice formulations used in this work.

Phase	Sublattice formulation
Si-N	
Liquid	$(N, Si)_1$
(αSi_3N_4)	$(Si)_3\ (N)_4$
(βSi_3N_4)	$(Si)_3\ (N)_4$
(Si)	$(Si)_1(Va)_1$
Si-Zr-N	
Liquid	$(N, Si, Zr)_1$
(α Zr)	$(Si, \underline{Zr})_1\ (N, \underline{Va})_{0.5}$
(β Zr)	$(Si, \underline{Zr})_1\ (N, \underline{Va})_3$
(Si)	$(\underline{Si}, Zr)_1\ (N, \underline{Va})_1$
Zr_5Si_3N	$(Si, \underline{Zr})_2\ (\underline{Si}, Zr)_3\ (Zr)_3\ (N, \underline{Va})_1$

Underline denotes major constituent of the sublattice with mixed occupancy.