

Thermodynamic analysis of the Ti-Al-N system

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Abstract: Motivated by the application of (Ti, Al)N alloy compound in the coating layer, the ternary phase diagram of Ti-Al-N was analyzed by the calculation of the phase diagram (CALPHAD) technique. The isothermal sections of the Ti-Al-N ternary system were constructed and compared with the literature experimental results. The thermodynamic parameters of the Ti-Al-N ternary system and the related Ti-N and Al-N binary systems were adopted from literatures, whereas, those of the Ti-Al binary from the literatures were adjusted according to both the ternary and the binary phase equilibria. The consistency between the calculated results and the experimental data shows that considering the ternary thermodynamic relationship, the adjustments to the thermodynamic parameters of the related binaries are necessary.

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Key words: Ti-Al-N ternary system; Ti-Al binary system; phase diagram optimization; thermodynamic analysis

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Nomenclature:

x_i —mole fraction of element i ;

y_i —site fraction of component i ;

y_i^1 and y_i^2 —site fractions of component i in the first and the second sublattices, respectively;

v_i and v_j —valencies of anion i and cation j ;

R —gas constant, 8.314 J/(mol K);

P and Q —introduced variables to maintain electroneutrality;

A , B and C —parameters to be evaluated;

GHSE_i —molar Gibbs energy of element i in its SER (stand element reference) state;

GFCC_i —molar Gibbs energy of element i in fcc state;

${}^{\circ}G_{i_m:j_n}^L$ —Gibbs energy for one mole $i_m j_n$ in liquid state;

${}^{\circ}G_i^L$ —molar Gibbs energy of the element i in the liquid state;

${}^{\circ}G_{ij}^L$ —Gibbs energy for one mole ij in liquid state;

$G_{i,j}^{\circ}$ —molar Gibbs energy of the hypothetical stoichiometric compound ij ;

$\text{HSER}(298.15\text{ K})$ —molar enthalpy at 298.15 K in the SER state;

$L_{i,j}^L$ —interaction parameter between elements i and j in liquid state;

$L_{k,i,j}$ —interaction parameter between components i and j in the second sublattice while the first one is occupied only by component k ;

$L_{i,j,k}$ —interaction parameter between components i and j in the first sublattice while the second one is occupied only by component k ;

$L_{i,j,k,l}$ —interaction parameter among components i , j , k , and l .

1. Introduction

Phase equilibria of the ternary system Ti-Al-N were investigated to better understand the behavior of technologically attractive materials such as (Ti, Al)N

coating and AlN/Ti joining. The Ti-Al-N ternary system and the related Ti-Al, Ti-N, and Al-N binary systems have been optimized by many authors [1-6]. On the basis of the literature reported thermodynamic data, the consistency between the calculated isothermal sections and the experimental data of the Ti-Al-N ternary system is reasonable at high temperature $T > 1000$ K, whereas, some differences exist at low temperature. In the present article, much attention is paid to adjust the thermodynamic parameters so that the phase equilibria of the ternary system as well as the related binary systems can be reproduced theoretically not only at high temperature but also at low temperature.

2. Optimization of the binary systems

2.1. Ti-Al system

Saunders [1] and Zhang *et al.* [2] have calculated the Ti-Al system successively, however, it is impossible to use their descriptions to fit the measured $(\delta\text{TiN}_{1-x})+\text{AlN}+(\text{TiAl}_3)$ three-phase equilibria at 600 [7] and 900°C [8] during the optimization of the Ti-Al-N ternary system (the phases with homogeneity ranges are indicated with the round brackets around the related phase names). Taking into account this problem, Saunders re-examined the system closely and concluded that a small adjustment of the stabilities of (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 could solve the problem of the $(\text{Ti}_3\text{Al})+\text{AlN}+(\delta\text{TiN}_{1-x})$ three-phase equilibrium in the Ti-Al-N system, still keeping the Ti-Al phase diagram nearly unchanged. Although the modification was addressed by Saunders *et al.*, the data were not published publicly.

Following the idea proposed by Saunders as men-

tioned in Ref. [3], the re-optimization of the parameters of (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 was carried out using the Thermo-Calc package, a major computer program used to calculate the phase diagram [9]. Considering the fact that the calculated Ti-Al binary phase diagram and the Ti-Al-N ternary phase diagram were in good agreement with a large set of selected experimental data of phase equilibria, the thermodynamic data of the Ti-Al binary were modified.

The adjusted parameters of (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 in the Ti-Al system are given in Table 1. The other parameters as well as GHSE_{Al} , GHSE_{Ti} , and GFCC_{Ti} in Table 1 are still adopted from Ref. [1]. The invariant phase equilibria relating to (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 phases are given in Table 2 together with the experimental results from literatures, for comparison. The calculated phase diagram is plotted in Fig. 1, showing a better consistency with the experimental data using the present adjusted parameters than the original ones from Ref. [1].

2.2. Ti-N system

The Ti-N system has been assessed by many authors. For a consistent dataset, the data of the Ti-N system were taken from Jonsson [4] who successfully calculated the Ti-C-N and Ti-W-N systems.

2.3. Al-N system

The Al-N system has been investigated by Lukas [5] and Hillert and Jonsson [6]. The description of the AlN phase is nearly the same in both assessments. Hillert and Jonsson's parameters are accepted in this study.

Table 1. Re-optimized parameters of (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 phases in the Ti-Al system

Phases	Standard reference states	Thermodynamic parameters
		$\phi G_{\text{Al,Ti}}^{\text{TiAl}_3} = -37520.344 + 10.1 \times T + 0.75 \times \text{GHSE}_{\text{Al}} + 0.25 \times \text{GHSE}_{\text{Ti}}$
(TiAl_3)	hcp-Ti and fcc-Al	$\phi G_{\text{Ti,Ti}}^{\text{TiAl}_3} = \text{GFCC}_{\text{Ti}}$ $\phi G_{\text{Al,Ti,Ti}}^{\text{TiAl}_3} = -15000$
$\text{Ti}_5\text{Al}_{11}^*$	hcp-Ti and fcc-Al	$\phi G_{\text{Ti,Al}}^{\text{Ti}_5\text{Al}_{11}} = -38739.4 + 9.392 \times T + 0.68 \times \text{GHSE}_{\text{Al}} + 0.32 \times \text{GHSE}_{\text{Ti}}$
TiAl_2	hcp-Ti and fcc-Al	$\phi G_{\text{Ti,Al}}^{\text{TiAl}_2} = -39715.98 + 9.863 \times T + 0.667 \times \text{GHSE}_{\text{Al}} + 0.333 \times \text{GHSE}_{\text{Ti}}$

Note: *The stoichiometry of $\text{Ti}_5\text{Al}_{11}$ was chosen as $\text{Ti}_8\text{Al}_{17}$ in this calculation based on Ref. [1].

Table 2. Invariant phase equilibria relating to (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 phases in the Ti-Al system

Reaction	Calculated results		Experimental results		
	Composition of the respective phase (x_{Al})	T / K	Composition of the respective phase (x_{Al})	T / K	Ref.
$(\text{TiAl})+\text{Ti}_5\text{Al}_{11}=\text{TiAl}_2$	0.613, 0.680, 0.667	1477.0	~0.60, 0.710, 0.667	1478.0	[10]
$\text{Ti}_5\text{Al}_{11}=\text{TiAl}_2+(\text{TiAl}_3)$	0.680, 0.667, 0.743	1265.6	0.70, 0.667, 0.751	1263.2	[11]
	0.680, 0.667, 0.743	1265.6	—	1268.0	[12]

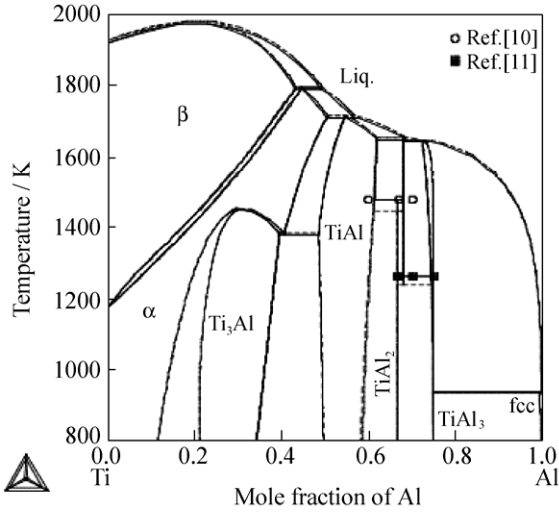


Fig. 1. Assessed Ti-Al phase diagram with adjustment (solid line) by the authors and without adjustment (dashed line) by Saunders [1].

3. Study on the Ti-Al-N ternary system

3.1. Thermodynamic model descriptions

(1) Description of the ionic solution model.

Based on the assessment of Chen and Sundman [3], a thermodynamic database of the Ti-Al-N ternary system has been developed. The ionic two-sublattice model for ionic liquids [13-14] was applied by Hillert and Jonsson [6], to describe the binary liquid phase in the Al-N system and by Chen and Sundman [3], to describe the ternary liquid phase in the Ti-Al-N system, whereas, the substitutional model was used for the binary Ti-N liquid [4] and the binary Ti-Al liquid. To keep the consistency of the thermodynamic description, it is necessary to transform the substitutional model into the ionic two-sublattice model.

The ionic liquid model of the Ti-Al-N system is $(Al^{3+}, Ti^{4+})_P(N^0, N^{3-}, Va^{Q-})_Q$, where Va represents a vacancy, P and Q vary with composition to maintain electroneutrality and are given by

$$P = \sum y_i(-v_i) = 3y_{N^{3-}} + Qy_{Va^{Q-}} \quad (1)$$

$$Q = \sum y_j\nu_j = 3y_{Al^{3+}} + 4y_{Ti^{4+}} \quad (2)$$

The Gibbs energy of the liquid is given by

$$G_m^L(T) - H^{SER}(298.15 \text{ K}) = \sum_i \sum_j y_i y_j {}^\ominus G_{i-v_j; j-v_i}^L + PRT(y_{Al^{3+}} \ln y_{Al^{3+}} + y_{Ti^{4+}} \ln y_{Ti^{4+}}) + QRT(y_{N^{3-}} \ln y_{N^{3-}} + y_{N^0} \ln y_{N^0} + y_{Va^{Q-}} \ln y_{Va^{Q-}}) + {}^E G_m^L \quad (3)$$

The excess Gibbs energy of the Ti-Al-N system, ${}^E G_m^L$, described by Chen and Sundman [3] is written

as

$${}^E G_m^L = y_{Al^{3+}} y_{Ti^{4+}} y_{Va^{Q-}} L_{Al^{3+}, Ti^{4+}; Va^{Q-}}^L + y_{Ti^{4+}} y_{Va^{Q-}} y_{N^0} L_{Ti^{4+}; Va^{Q-}, N^0}^L + y_{Al^{3+}} y_{Va^{Q-}} y_{N^{3-}} L_{Al^{3+}; Va^{Q-}, N^{3-}}^L + y_{Al^{3+}} y_{Va^{Q-}} y_{N^0} L_{Al^{3+}; Va^{Q-}, N^0}^L \quad (4)$$

For the liquid phase of the Ti-Al-N system, by comparing the ionic solution model with the substitutional model, the following relations are obtained:

$${}^\ominus G_{Al^{3+}; Va^{Q-}}^L = 3{}^\ominus G_{Al}^L \quad (5)$$

$${}^\ominus G_{Ti^{4+}; Va^{Q-}}^L = 4{}^\ominus G_{Ti}^L \quad (6)$$

$${}^\ominus G_{Al^{3+}; N^{3-}}^L = 3{}^\ominus G_{AlN}^L \quad (7)$$

$${}^\ominus G_{Al^{3+}; N^0}^L = 3{}^\ominus G_N^L \quad (8)$$

$${}^\ominus G_{Ti^{4+}; N^0}^L = 4{}^\ominus G_N^L \quad (9)$$

$$L_{Al^{3+}, Ti^{4+}; Va^{Q-}}^L = Q L_{Al, Ti}^L \quad (10)$$

$$L_{Ti^{4+}; Va^{Q-}, N^0}^L = 4 L_{Ti, N}^L \quad (11)$$

where ${}^\ominus G_{Ti^{4+}; N^{3-}}^L$, $L_{Al^{3+}; Va^{Q-}, N^{3-}}^L$, and $L_{Al^{3+}; Va^{Q-}, N^0}^L$ are adopted from Ref. [3].

(2) Descriptions of solutions and compounds.

The gas phase was treated as an ideal mixture of the species, the thermodynamic properties of which were taken from the SGTE (Scientific Group Thermodata Europe) substance database [15].

The binary compound solutions, $(TiAl_3)$, (Ti_3Al) , $(TiAl)$, are ordered phases with a general formula $(Al_{y_{Al}^1}, Ti_{y_{Ti}^1})_p (Al_{y_{Al}^2}, Ti_{y_{Ti}^2})_q$. The Gibbs energy per mole formula unit is given by

$$G_m^{(Al_{y_{Al}^1}, Ti_{y_{Ti}^1})_p (Al_{y_{Al}^2}, Ti_{y_{Ti}^2})_q} = y_{Al}^1 y_{Al}^2 G_{Al:Al}^* + y_{Al}^1 y_{Ti}^2 G_{Al:Ti}^* + y_{Ti}^1 y_{Al}^2 G_{Ti:Al}^* + y_{Ti}^1 y_{Ti}^2 G_{Ti:Ti}^* + RT[p(y_{Al}^1 \ln y_{Al}^1 + y_{Ti}^1 \ln y_{Ti}^1) + q(y_{Al}^2 \ln y_{Al}^2 + y_{Ti}^2 \ln y_{Ti}^2)] + y_{Al}^1 y_{Ti}^1 [y_{Al}^2 L_{Al, Ti: Al} + y_{Ti}^2 L_{Al, Ti: Ti}] + y_{Al}^2 y_{Ti}^2 [y_{Al}^1 L_{Al: Al, Ti} + y_{Ti}^1 L_{Ti: Al, Ti}] + y_{Al}^1 y_{Ti}^1 y_{Al}^2 y_{Ti}^2 L_{Al, Ti: Al, Ti} \quad (12)$$

The ternary solution phases include (αTi) , (βTi) , and (δTi) , the solutions of Al and N in hcp-Ti, bcc-Ti, and fcc-Ti, respectively. These phases are described as $(Ti, Al)_1(N, Va)_a$ with $a=1, 3$ and 0.5 for fcc, bcc, and hcp phases correspondingly. The Gibbs energy per mole formula unit is given by

$$G_m^{(Ti, Al)_1(N, Va)_a} = y_{Al} y_N G_{Al: N}^* + y_{Al} y_{Va} G_{Al: Va}^* +$$

$$\begin{aligned}
 & y_{Ti}y_N G_{Ti:N}^* + y_{Ti}y_{Va} G_{Ti:Va} + \\
 & RT[(y_{Al} \ln y_{Al} + y_{Ti} \ln y_{Ti}) + \\
 & a(y_N \ln y_N + y_{Va} \ln y_{Va})] + \\
 & y_{Al}y_{Ti}(y_N L_{Al,Ti:N} + y_{Va} L_{Al,Ti:Va}) + \\
 & y_N y_{Va}(y_{Ti} L_{Ti:N, Va} + y_{Al} L_{Al:N, Va}) + \\
 & y_{Al}y_{Ti}y_N y_{Va} L_{Al,Ti:N, Va}
 \end{aligned} \tag{13}$$

The stoichiometric compounds, AlN, Ti₂N, Ti₅Al₁₁, TiAl₂, Ti₂AlN, Ti₃AlN, and Ti₃Al₂N₂, are of the general formula Ti_aAl_bN_c and the Gibbs energy per mole formula unit is treated as

$$G_m^{Ti_aAl_bN_c} = aG_{Ti}^* + bG_{Al}^* + cG_N^* + A + BT + CT \ln T \tag{14}$$

3.2. Calculation of isothermal sections

So far, little information about the Ti-Al-N isothermal sections at temperatures below 1173 K has been reported. In 1984, Beyers *et al.* [7] proposed a Ti-Al-N ternary isothermal section at 873 K (Fig. 2) and emphasized that the Ti-Al-N ternary isothermal section was imperfect and a deeper research on it was needed. In 1990, Bhansali *et al.* [16] proposed an improved Ti-Al-N ternary phase diagram (Fig. 3).

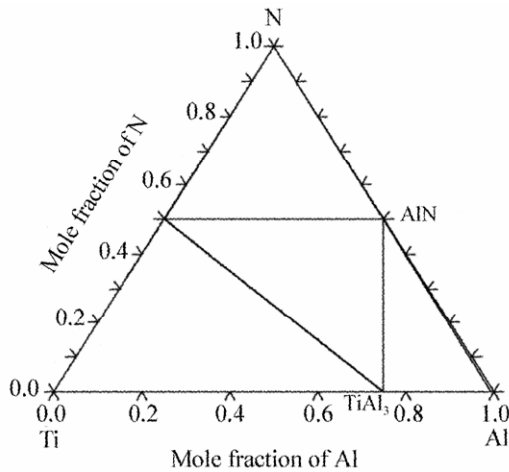


Fig. 2. Calculated isothermal section of the Ti-Al-N system at 873 K by Beyers *et al.* [7].

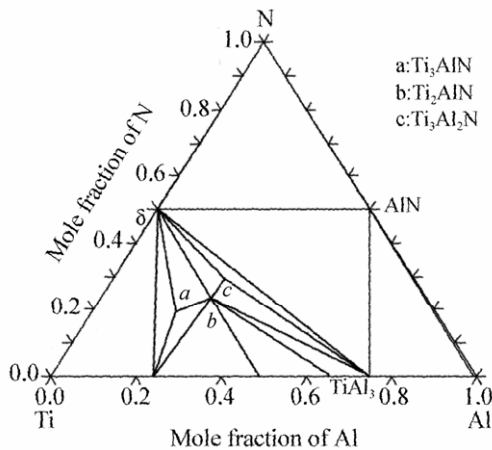


Fig. 3. Calculated isothermal section of the Ti-Al-N system at 873 K by Bhansali *et al.* [16].

As for the isothermal section given by Bhansali *et al.* [16], there are several aspects that are not consistent with the latest experimental results. First, (Ti₃Al) and (TiAl) were treated as stoichiometric compounds, whereas, actually both of them are compound solutions with small homogeneity ranges [1]. Second, Ti₂N [4] was reported by many researchers, but it was not mentioned by Bhansali *et al.* [16]. Third, Ti₃Al₂N₂ was not stable at 1473 K or below [17], but it was mentioned by Bhansali *et al.* [16].

The isothermal sections at different temperatures were constructed using the thermodynamic parameters of the assessed Ti-Al-N ternary and the related three binaries, Ti-Al, Ti-N, and Al-N, as shown in Figs. 4-7. The present calculations are not only consistent with high temperature experimental results [8, 17], such as 1273 and 1573 K, but also consistent with low temperature results [8], such as 1173 K. Additionally, the isothermal section of the Ti-Al-N at 873 K is predicted, which is an improvement over the isothermal section given by Beyers *et al.* [7] and Bhansali *et al.* [16].

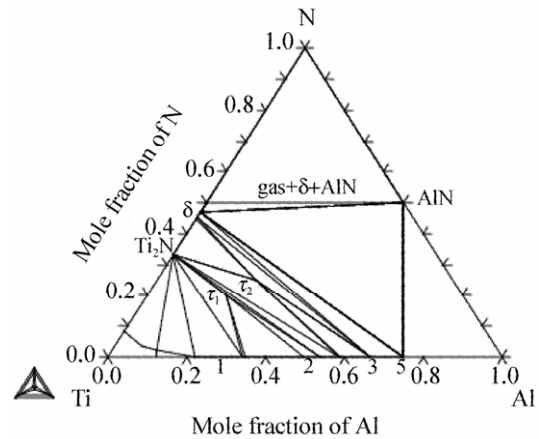


Fig. 4. Calculated isothermal section of the Ti-Al-N system at 873 K: τ_1 —Ti₃AlN; τ_2 —Ti₂AlN; 1—(Ti₃Al); 2—(TiAl); 3—TiAl₂; 5—(TiAl₃).

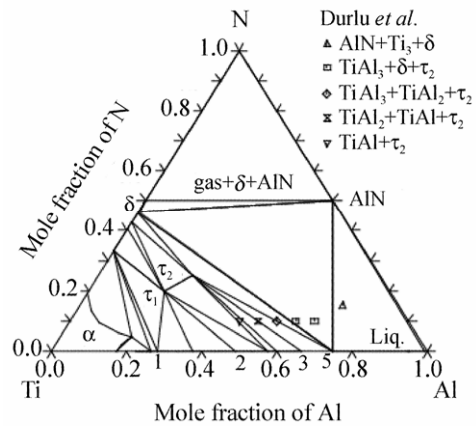


Fig. 5. Calculated isothermal section of the Ti-Al-N system at 1173 K compared with the experiments from Durlu *et al.* [8]: τ_1 —Ti₃AlN; τ_2 —Ti₂AlN; 1—(Ti₃Al); 2—(TiAl); 3—TiAl₂; 5—(TiAl₃).

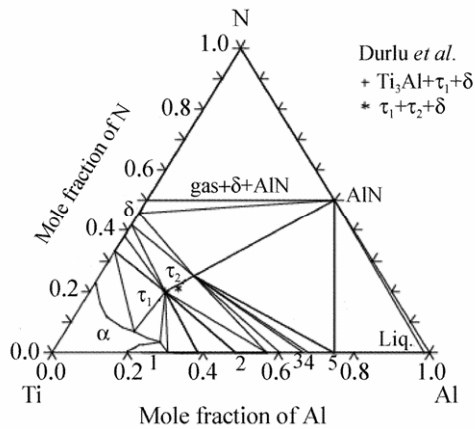


Fig. 6. Calculated isothermal section of the Ti-Al-N system at 1273 K compared with the experiments from Durlu *et al.* [8]: τ_1 — Ti_3AlN ; τ_2 — Ti_2AlN ; 1— (Ti_3Al) ; 2— (TiAl) ; 3— TiAl_2 ; 4— $\text{Ti}_5\text{Al}_{11}$; 5— (TiAl_3) .

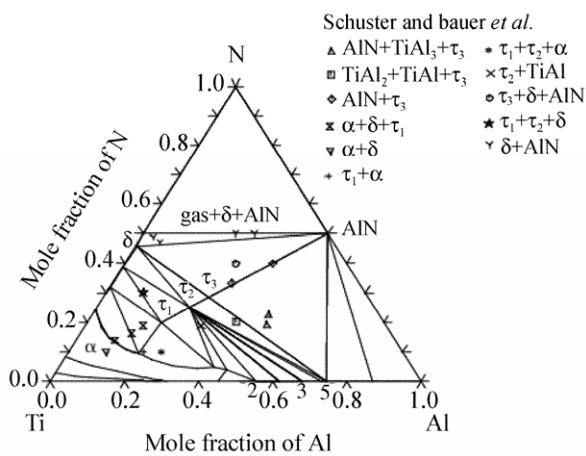


Fig. 7. Calculated isothermal section of the Ti-Al-N system at 1573 K compared with the experiments from Schuster and Bauer [17]: τ_1 — Ti_3AlN ; τ_2 — Ti_2AlN ; τ_3 — $\text{Ti}_3\text{Al}_2\text{N}_2$; 2— (TiAl) ; 3— TiAl_2 ; 5— (TiAl_3) .

4. Conclusions

In this article, the isothermal sections of the Ti-Al-N system below 1173 K are constructed by adjusting the thermodynamic parameters of the related Ti-Al binary. The reassessment of the thermodynamic parameters of (TiAl_3) , $\text{Ti}_5\text{Al}_{11}$, and TiAl_2 phases assured the consistency between the calculated phase diagrams and the experimental equilibrium data for the Ti-Al-N ternary isothermal sections not only at high temperature, but also at low temperature.

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