J. Min. Metall. Sect. B-Metall. 59 (1) (2023) 125 - 136

Journal of Mining and Metallurgy,
Section B: Metallurgy

AB-INITIO COMBINED WITH THE CALPHAD APPROACH TO THE PHASE EQUILIBRIA IN THE TERNARY Ti-Mo-N SYSTEM

R.A. Daclan [a], M.G. Mena [a], M.R. Vasquez [a], W. Gierlotka [b,*]

[a] Department of Mining, Metallurgical, and Materials Engineering, College of Engineering, University of the Philippines-Diliman, Philippines
[b] Materials Science and Engineering Department, National Dong Hwa University, Taiwan

(Received 30 March 2021; Accepted 09 May 2023)

Abstract

The ternary Ti-Mo-N system is an important material used as a surface coating, hardener, and wear and corrosion protection layer. Knowledge of the phase equilibria, phase transformations, and phase stabilities of this alloy is important to realizeits potential applications. In this paper, formation energies of three intermetallic compounds, Mo2N-beta, Mo2N-gamma, and MoN-delta, were determined by ab-initio calculations.Then , the Calphad approach was applied to thermodynamically model the Mo-Ti, Mo-N, and Mo-Ti-N systems. The obtained Gibbs energies were used to calculate the phase diagram and thermodynamic properties of the Ti-Mo-N system. The present model is in good agreement with experimental data reported in the literature. The results of this work can be used as a basis for future investigations of the Ti-Mo-N system, as well as a basis for practical industrial applications.

Keywords: *Ab-initio; Calphad; Mo; Ti; N; Phase diagram*

1. Introduction

The titanium molybdenum nitride (TiMoN) system is highly significant in industrial applications, as it allows for the hardening, wear, and corrosion protection of metallic surfaces. To plan a technological process of surface hardening, knowledge of phase equilibria and phase stability is essential. However, determining phase equilibrium as a function of composition and temperature is almost impossible due to the experimental difficulties of high temperature and nitrogen pressure. Therefore, a reliable phase diagram of the ternary Ti-Mo-N system is yet to be established in the literature. Fortunately, computational techniques, such as ab-initio or Calphad, enable rapid materials design and development, providing a theoretical approach to phase equilibria problems. Taking into account the importance of the Ti-Mo-N system, this paper presents a phase diagram of the system, which was determined from various types of calculations.

2. Literature review.

The Mo – N binary system is composed of several phases including gas, liquid, BCC_A2, Mo2N-gamma, Mo2N-beta, and MoN-delta. The BCC_A2 phase is a solid solution of nitrogen in molybdenum, while Mo2N-gamma and Mo2N-beta are high- and low-temperature polymorphs of an intermediate phase with a homogeneity range of 0.30 – 0.35 mole fraction of nitrogen. MoN-delta is an intermediate phase with a stoichiometry of 0.5 mole fraction of nitrogen.

Experimental data on the binary Mo-N phase diagram is limited. The solubility of nitrogen in the BCC_A2 molybdenum phase was measured by Fromm and Jehn [1] at a temperature range of 1873 - 2673 K under nitrogen pressures of 0.02 to 0.53 atm. The same measurement was repeated by Jehn and Ettmayer [2] at 1573 - 2273 K under N_2 pressures of 10 to 200 atm. After reduction to 1 atm, both experimental sets agree with each other. The pressure of nitrogen in the equilibrium between the Mo2N-gamma phase and BCC_A2 phase at a temperature range of 1200 – 1800 K was also determined by Jehn and Ettmayer [2]. The heat of formation of Mo2N-beta was measured by Neumann et al. [3] and by Mah [4] using the combustion calorimetry method at 298 K. Neumann et al. [3] reported the heat of formation of Mo2N-beta as -27.3 kJ/mole per mole of atoms, whereas Mah [4] proposed -23.2 kJ/mole per mole of atoms at the same temperature. Satoh [5] quantitatively measured the heat content of the Mo2N-beta phase at three temperatures: 373 K, 599 K, and 784 K. Additionally, Ettmayer [6] studied the polymorphic transformation of Mo2N-beta to Mo2N-gamma and determined a binary Mo2N-beta

---

Corresponding author: wojtek@mail.ndhu.edu.tw

https://doi.org/10.2298/JMMB210330011D

+ Mo2N-gamma region.

The eutectic reaction Liquid = BCC_A2 + Mo_2N-gamma was described by Jehn and Ettmayer [2]. The reaction takes place at 2133 K and the following compositions: 0.0108, 0.19, 0.27 mole fraction of N were reported for BCC_A2, liquid, and Mo_2N_gamma phases, respectively.

The phase diagram of binary Mo-N proposed by Jehn and Ettmayer [2] includes the MoN_delta phase with stoichiometry 1:1. According to Shoenberg [7], the phase has an ordered hexagonal structure and can be formed in nitriding vapor-deposited molybdenum films in flowing ammonia, as reported by Troitskaya and Pinsker [8].

A revised version of the binary Mo-N phase diagram was proposed by Massalski et al. [9]. In this version, besides Mo_2N-beta, Mo_2N-gamma and MoN, two additional phases are included: Mo_3N_2 and Mo_4N_5. The stability of those two phases was marked as unknown and they were drawn by dashed lines.

Recently, the stability of different crystal structures in the Mo-N system was studied with aid of ab-initio calculations by Klimashin et al. [10]. In a case of a system involving one gaseous element, important information is the equilibrium pressure of this element with the solid phase. As pointed out by Jehn and Ettmayer [2], if a certain pressure cannot be maintained, the solid phase will absorb gaseous nitrogen or the nitrogen from the solid phase will be given off. Therefore, Jehn and Ettmayer [2] measured and calculated equilibrium nitrogen pressure for the molybdenum-rich part of a phase diagram.

Solubility of nitrogen in the liquid phase was measured by Domke and Frohberg [11] at a temperature of 2923 K and pressure of nitrogen up to 0.65 atm.

The Mo – N phase diagram calculated by Frisk [12] using the Calphad method shows some simplifications of phase equilibria for a concentration of nitrogen greater than 0.19 mole fraction. Frisk [12] proposed only one intermediate phase, called MoN, with a homogeneity range of 0.3-0.5 mole fraction of N instead of three intermediate phases: Mo_2N-beta, Mo_2N-gamma and MoN-delta phase.

The eutectic reaction Liquid = BCC_A2 + Mo2N-gamma was first described by Jehn and Ettmayer [2], who reported that the reaction takes place at 2133 K and the following compositions: 0.0108, 0.19, and 0.27 mole fraction of N for the BCC_A2, liquid, and Mo2N_gamma phases, respectively.

The binary Mo-N phase diagram proposed by Jehn and Ettmayer [2] includes the MoN_delta phase with a stoichiometry of 1:1. According to Shoenberg [7], this phase has an ordered hexagonal structure and can be formed in nitriding vapor-deposited molybdenum films in flowing ammonia, as reported by Troitskaya and Pinsker [8].

A revised version of the binary Mo-N phase diagram was proposed by Massalski et al. [9], in which two additional phases, Mo_3N_2 and Mo_4N_5, are included. The stability of these two phases is marked as unknown and they are drawn by dashed lines. However, the stability of different crystal structures in the Mo-N system was recently studied with the aid of ab-initio calculations by Klimashin et al. [10].

In a system involving one gaseous element, important information is the equilibrium pressure of this element with the solid phase. As pointed out by Jehn and Ettmayer [2], if a certain pressure cannot be maintained, the solid phase will absorb gaseous nitrogen, or the nitrogen from the solid phase will be given off. Therefore, Jehn and Ettmayer [2] measured and calculated the equilibrium nitrogen pressure for the molybdenum-rich part of the phase diagram.

The solubility of nitrogen in the liquid phase was measured by Domke and Frohberg [11] at a temperature of 2923 K and a nitrogen pressure of up to 0.65 atm.

The Mo-N phase diagram calculated by Frisk [12] using the Calphad method shows some simplifications of phase equilibria for a nitrogen concentration greater than 0.19 mole fraction. Frisk [12] proposed only one intermediate phase, called MoN, with a homogeneity range of 0.3-0.5 mole fraction of N instead of three intermediate phases: Mo2N-beta, Mo2N-gamma, and MoN-delta phase.

Mo-Ti is a simple binary system that exhibits a continuous solid solution of BCC_A2 and a limited HCP_A3 phase on the Ti side. The system was assessed by Murray [13], who collected available experimental information for his analysis. The solid phase equilibrium of the system was examined by Hansen et al. [14] and Flower et al. [15], who determined the binary HCP_A3 – BCC_A2 region. However, there is a controversy about whether a miscibility gap exists in the BCC_A2 phase. Dupouy and Averbach [16], as well as Morniroli and Gantois [17], reported short-range ordering, while Chandrasekar et al. [18] provided information on clustering in the BCC_A2 phase. According to Chandrasekar et al. [18], who found two BCC_A2 phases, the separation is an effect of a metastable miscibility gap and short-range clustering. Terauchi et al. [19] used resistivity measurement, X-ray diffraction, metallography, and transmission electron microscopy methods to determine a miscibility gap in the BCC_A2 phase.

The solidus line of the system was determined by Rudy [20] and Hansen et al. [14]. The data agree with each other, except for the Ti-rich side of the phase diagram, where the disagreement is due to the use of two different melting temperatures of pure Ti by the two investigators: 1993 K and 1943 K used by Hansen et al. [14] and Rudy [20], respectively.

The activity of Ti in the BCC_A2 phase was determined by Kuz'min and Palatnik [21], who applied the Langmuir method, as well as by Hoch and Viswanatha [22], who used the Knudsen cell technique, and by Yao et al. [23], who used pressure measurement to determine activities of both elements. The techniques used by Hoch and Viswanatha [22] and Yao et al. [23] were described in details by Hachworth et al. [24] The results from all sources do not agree with each other. Kuz'min and Palatnik's [21] data show a positive deviation from Raoult's Law, whereas Hoch and Viswanatha [22] reported a negative one. The second dataset is preferable because the Knudsen effusion method used by Hoch and Viswanatha [22] belongs to equilibrium techniques. Therefore, it can be assumed that the method gives more reliable information than the Langmuir method. The information given by Yao et al. [23] does not provide information on a reference state; hence, it is impossible to use it for the optimization procedure.

The heat of formation of the BCC_A2 phase was not determined by experiment; however, results of ab-initio calculations are available in the literature. Raabe et al. [25] calculated the heat of formation of both BCC_A2 and HCP_A3, while Marker et al. [26] calculated the heat of formation of the BCC_A2 phase only. Both datasets show a similar, exothermic characteristic of BCC_A2 formation enthalpy.

To the best knowledge of the authors, there is no experimental measurement of the thermodynamic properties of liquid Mo – Ti. The binary Mo – Ti system was thermodynamically modeled by Santhy and Hari Kumar [27], Zeng and Schmid-Fetzer [28], and Chung et al. [29]. The thermodynamic modeling of this binary system was also included in the COST 507 [30] thermodynamic database. According to the information given in the COST 507 report [30], the system was assessed by Saunders.

Since the thermodynamic descriptions of the Ti-N [31] system were obtained from the literature, a review of experimental data describing this system is not provided in this study. The ternary Mo – N – Ti system has been investigated by a limited number of researchers. Barabash and Shurin [32] investigated the isopleth Mo-TiN using optical microscopy and differential thermal analysis techniques. According to their results, the composition of the liquid in the reaction L = Mo+TiN is equal to 5-6% TiN, and the reaction occurs at 2623 K. They also presented the isothermal section of the Mo – N – Ti system at 1673 K. However, they did not report nitrogen pressure, and their data cannot be used in thermodynamic optimization. Ettmayer and Hormanseder [33] reported the isothermal section at 1373 K under nitrogen pressure of 30 and 300 bar, revealing mutual immiscibility of TiN and MoN-delta phases despite a very small lattice difference equal to ≈2%. Lengauer et al. [34] [35] [36] reported the isothermal section at 1423 K based on electron-probe microanalysis and X-ray diffraction (XRD) analysis. They reported a temperature of the reaction L = Mo+TiN equal to 2500K. Holleck [37] reported an isothermal section of this ternary system at 1273 K. However, it is apparent that Holleck's [37] isothermal section is incomplete due to the lack of experimental data that allowed for more precise drawing. The ternary Ti-Mo-N system was thermodynamically described by Chung et al. [29], who reassessed the Mo – Ti system and used binary descriptions of Mo – N and Ti – N given by Frisk [12] and Zeng and Schmid-Fetzer [28], respectively. Since that thermodynamic modeling is based on Frisk's [12] simplified description of the Mo – N system, it seems reasonable to recalculate the ternary system and compare the obtained results with available experimental information. The summary of experimental information discussed above is presented in Table 1.

3. Ab initio Calculations

The stabilities of Mo2N-beta, Mo2N-gamma, and MoN-delta were calculated using ab-initio calculations performed within the Density Functional Theory (DFT) implemented in the ABINIT [38] software. The calculations were spin-non-polarized, and the Projector Augmented Wave (PAW) [39] method, along with the Generalized Gradient Approximation (GGA) pseudopotential functional parameterized by Perdew, Burke, and Ernzerhof (PBE) [40], was used in this work, obtained from the ABINIT [38] website. As mentioned previously, three crystal structures were considered in this calculation: $I4_1/amd$, $Fm\bar{3}m$ as, and $P6_3/mmc$ for Mo_2N-beta, Mo_2N-gamma, and MoN-delta, respectively. It can also be discerned that the stoichiometry of the $Fm\bar{3}m$ crystal lattice is 1:1 instead of 2:1. The proper ratio of molybdenum to nitrogen is obtained by the vacancy occupation of nitrogen sites. On the modeling part, Special Quasirandom Structure (SQS) [41] approach was used as implemented in the Alloy Theoretical Automated Toolkit (ATAT) code [42] to obtain desired composition of the Mo_2N-gamma phase.

Before the calculation, convergence tests were conducted with respect to the k-points of the Monkhorst-Pack mesh and the cut-off energies. It was assumed that the system had converged when the energy change was smaller than 0.001 eV. Based on this assumption, the following settings were used for the calculation the k-samplings were set to: 9 9 8, 10 10 10, 13 13 6, for $I4_1/amd$, $Fm\bar{3}m$, and $P6_3/mmc$ structures, respectively, cut-off energy set to 490 eV, and double-grid cut off energy set to 871 eV. In the calculations, all the structures were relaxed and equilibrium lattice constants were obtained along with

Table 1. *Summary of experimental information on Mo – N, Mo – Ti, and Mo – N – Ti systems*

Experiment	Temperature [K]	System	Used	Ref.
Solubility of N_2 in Mo	1873 - 2673 K	Mo-N	yes	[1]
Solubility of N_2 in Mo	1573 - 2273 K	Mo-N	yes	[2]
Equilibrium BCC_A2/Mo_2N-gamma	1200-1800 K	Mo-N	yes	[2]
Heat formation of MoN-beta	298 K	Mo-N	no	[3]
Heat formation of MoN-beta	298 K	Mo-N	no	[4]
Heat formation of MoN-beta	373, 599, 784 K	Mo-N	no	[5]
Transformation Mo_2N-gamma/delta	1000-1100 K	Mo-N	yes	[6]
Eutectic Liquid=BCC_A2+Mo_2N-gamma	2133 K	Mo-N	yes	[2]
Stability of MoN-beta	300-3000 K	Mo-N	yes	[2]
Structure of MoN-beta	300-3000 K	Mo-N	yes	[7]
Stability of Mo_2N-gamma, Mo_2N-delta,MoN-delta	0K	Mo-N	no	[10]
Solubility of N_2 in liquid Mo-N	2923 K	Mo-N	yes	[11]
Equilibrium HCP_A3/BCC_A2	300-1300 K	Mo-Ti	yes	[14]
Equilibrium HCP_A3/BCC_A2	300-1300 K	Mo-Ti	yes	[15]
Clustering in BCC_A2	300-1200 K	Mo-Ti	no	[18]
Short-range ordering in BCC_A2	300-1200 K	Mo-Ti	yes	[16]
Short-range ordering in BCC_A2	300-1200 K	Mo-Ti	yes	[17]
Miscibility gap in BCC_A2	900-1200 K	Mo-Ti	no	[19]
Solidus line	1900-3000 K	Mo-Ti	yes	[20]
Solidus line	1900-3000 K	Mo-Ti	yes	[14]
Activity of Ti in BCC_A2	1800-1900 K	Mo-Ti	no	[21]
Activity of Mo and Ti in BCC_A2	1800-1900 K	Mo-Ti	yes	[22]
Activity of Mo and Ti in BCC_A2	1800-1900 K	Mo-Ti	no	[23]
Heat of formation of BCC_A2 and HCP_A3	0 K	Mo-Ti	yes	[25]
Heat of formation of BCC_A2	0 K	Mo-Ti	yes	[26]
Isopleth Mo-TiN	300-3500 K	Mo-N-Ti	yes	[32]
Isothermal section	1673 K	Mo-N-Ti	no	[32]
Isothermal section	1373 K	Mo-N-Ti	yes	[33]
Isothermal section	1423	Mo-N-Ti	yes	[36] [34] [35]
Isothermal section	1273 K	Mo-N-Ti	yes	[37]
Eutectic L=Mo+TiN	2500 K	Mo-N-Ti	yes	[35]

energies of each intermediate phase as well as pure molybdenum in body-centered cubic structure as well as gaseous nitrogen (N_2). By then, formation energy per atom of phase was calculated from the well-known equation below (Eq. 1):

$$\Delta E^0 = \left(E^0_{Mo_nN_m} - nE^0_{Mo} - mE^0_N\right) / \left(m+n\right) \tag{1}$$

Where ΔE^0 is a formation energy per atom, $E^0_{Mo_nN_m}$ is energy of phase, E^0_{Mo} is energy of Mo, E^0_N is the energy of N, *m* and *n* are numbers of atoms Mo and N, respectively.

4. Thermodynamic modeling

Thermodynamic descriptions of six phases: Gas, Liquid, BCC_A2, HCP_A3, Mo_2N-beta, Mo_2N-gamma, and MoN-delta are presented in this work.

The Gibbs free energies of pure elements with respect to temperature are given as follows: ${}^0G_i(T) = G_i(T) - H_i^{SER}$ are represented by Eq. 2:

$$\begin{aligned}{}^0G_i(T) = a + bT + cTln(T) + dT^2 + \\ eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9}\end{aligned} \tag{2}$$

The ${}^0G_i(T)$ data are referred to the constant enthalpy value of the standard element reference H_i^{SER} at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [43]. The reference states are: BCC_A2 (Mo), and Gas (½N_2). The expression may be given for several temperature ranges, where the coefficients *a, b, c, d, e, f, i, j, k* have different values. The ${}^0G_i(T)$ functions are taken from SGTE Unary TDB v.5 [43]. The FCC_A1, BCC_A2, and HCP_A3 are described by a compound energy formalism (CEF) where Mo and Ti atoms occupy the first sublattice and N and vacancies the second, interstitial one. The Gibbs energy of one mole of phase is given as follows (Eq. 3):

$$\begin{gathered} {}^{m}G = y^{I}_{Mo}y^{II}_{Va}\,{}^{0}G_{Mo:Va} + y^{I}_{Mo}y^{II}_{N}\,{}^{0}G_{Mo:N} + y^{I}_{Ti}y^{II}_{Va}\,{}^{0}G_{Ti:Va} + \\ y^{I}_{Ti}y^{II}_{N}\,{}^{0}G_{Ti:N} + {}^{id,mix}G + {}^{xs}G_{Mo,Ti:N,Va} \end{gathered} \tag{3}$$

Where a is a given phase (FCC_A1, BCC_A2, or HCP_A3), I and II represent sublattices. The first four terms describe the Gibbs energy of end-members, the fifth one defines the Gibbs energy of ideal mixing, and the last one describes excess Gibbs energy.

The liquid phase was described by a substitutional solution model where the Gibbs energy of one mole of the binary phase is given as follows (Eq. 4):

$$\begin{gathered} {}^{m}G^{Liquid}_{Mo,N,Ti} = \sum_{i} x_i\,{}^{0}G^{Liquid}_{i} + RT\sum_{i}\left(x_i \ln x_i\right) + \\ \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{v}\left({}^{v}A_{i,j} + {}^{v}B_{i,j}T\right)\left(x_i - x_j\right)^{v}\right] + \\ x_{Mo}x_{N}x_{Ti}\left({}^{0}L^{Liquid}_{Mo,N,Ti}x_{Mo} + {}^{1}L^{Liquid}_{Mo,N,Ti}x_{N} + {}^{2}L^{Liquid}_{Mo,N,Ti}x_{Ti}\right) \end{gathered} \tag{4}$$

where i, j are components (Mo, N, Ti), R is the gas constant, T is absolute temperature, ${}^{v}A_{i,j}$ and ${}^{v}B_{i,j}$ are adjustable parameters, and v is integer (v = 0, 1, 2…).The ${}^{v}A_{i,j}+{}^{v}B_{i,j}\,T$ term in the Equation 4 is identified as a binary interaction parameter. The ternary interaction parameters ${}^{w}L_{Mo,N,Ti}$ are given in the last part of Equation 4 (w = 0, 1, 2). The ${}^{v}A_{i,j}$ is interpreted as excess enthalpy and ${}^{v}B_{i,j}$ as excess entropy.

The MoN-delta phase was treated as a line compound; therefore, its Gibbs energy is described by Eq. 5:

$${}^{0}G^{MoN\_delta}_{Mo:N} = a + bT + GHSERMO + GHSERNN \tag{5}$$

where a and b are adjustable parameters, T is absolute temperature, and GHSERMO and GHSERNN are Gibbs energies of Mo and N in their SER reference state, respectively.

According to Jehn and Ettmayer [2], intermediate phases Mo_2N-beta, Mo_2N-gamma exhibit some homogeneity range from an ideal stoichiometry 2:1 toward molybdenum. Therefore, it was proposed to describe them by a CEF where the first sublattice is occupied by molybdenum and the second sublattice by vacancy and nitrogen.

The Gibbs energies of both phases, Mo_2N-beta and Mo_2N-gamma, is given by Equation 6:

$$\begin{gathered} {}^{m}G^{Mo_2N-} = y^{I}_{Mo}y^{II}_{N}\,{}^{0}G^{Mo_2N-}_{Mo:N} + y^{I}_{Mo}y^{II}_{Va}\,{}^{0}G^{Mo_2N-}_{Mo:Va} + \\ {}^{id,mix}G^{Mo_2N-} + {}^{xs}G^{Mo_2N-}_{Mo:N,Va} \end{gathered} \tag{6}$$

where ${}^{id,mix}G^{Mo_2N}$ is the Gibbs free energy of ideal mixing, ${}^{xs}G^{Mo_2N}_{Mo,N:Va}$ is the excess Gibbs free energy, y^{m}_{i} is a m (m = I or II) site fraction occupied by species i (i = Mo, N, Va), ${}^{0}G^{Mo_2N}_{i,j}$ is the Gibbs energy of end-member when a sublattice I is occupied by element i and sublattice II is occupied by specie j, a indicates a polymorphic form of the Mo_2N phase (a = beta, gamma) The ideal mixing term is given by Eq. 7:

$${}^{id,mix}G^{Mo_2N-}_{m} = RT\left(y^{II}_{N} ln y^{II}_{N} + y^{II}_{Va} ln y^{II}_{Va}\right) \tag{7}$$

While the excess Gibbs energy is expressed by Eq. 8:

$${}^{xs}G^{Mo_2N-}_{m} = y^{I}_{Mo}y^{II}_{N}y^{II}_{Va}\sum_{k}{}^{k}L^{Mo_2N-}\left(y^{II}_{N} - y^{II}_{Va}\right)^{k} \tag{8}$$

Where y^{m}_{i} is a site fraction m (m = I or II) occupied by species i (i = Mo,N,Va), and ${}^{k}L^{Mo_2N}_{i,j}$ is adjustable parameter in a form ${}^{k}A + {}^{k}BT$.

Thermodynamic description of the gas phase was directly taken from SGTE substance database (SSUB3) [44]

5. Results and Discussion

The binary Mo-N system has not been thoroughly investigated thermodynamically, so ab-initio calculations were used in this study. The ground state energies of molybdenum, nitrogen, and the intermediate phases Mo2N-beta, Mo2N-gamma, and MoN-delta were calculated, and the relaxed lattice constant of Mo BCC_A2 was found to be 3.162 Å, in good agreement with a previous value of 3.178 Å reported by Wang et al. [45]. The interatomic distance in the N2 molecule was also calculated, and the result of 1.105 Å is in fair agreement with the experimental value of 1.0975 Å [46]. By using Eq. 1, formation energies per atom were calculated for Mo2N-beta, Mo2N-gamma, and MoN-delta as -0.27048 eV/atom, -0.21877 eV/atom, and -0.39129 eV/atom, respectively. The obtained formation energies were compared with literature values [10] [47] [48] [49] and are summarized in Table 2.

The motivation for performing ab-initio calculations was to address the significant discrepancies in the available information on the formation energies of intermediate phases in the molybdenum-nitrogen system. For instance, Klimashin et al. [10] reported a formation energy of -25953 J/mol atom for Mo2N-beta, while The Open Quantum Materials Database [49] reported a value of -35989 J/mol atom for the same compound. Therefore, our own ab-initio calculations were performed, and the results were used during the optimization procedure. GGA functionals were used in this work as they are known to produce more reliable results for calculating formation energies compared to LDA functionals [50].

The results obtained in this study are in good agreement with the data reported by Klimashin et al. [10]. However, the formation energies of MoN-delta

Table 2. *Formation energies of intermediate phases in the Mo – N system*

Phase	Crystal structure	Formation energy		Reference
		[eV/atom]	[J/mol atom]	
Mo2N-beta	$I4_1 / amd$	-0.27048	-26097	This work
		-0.26898	-25953	[10]
		-0.373	-35989	[47]
Mo2N-gamma	$Fm\bar{3}m$	-0.21877	-21108	This work
		-0.22884	-22079	[10]
MoN-delta	$P6_3 / mmc$	-0.39129	-37753	This work
		-0.40681	-39251	[10]
		-0.537	-51812	[48]
		-0.459	-44286	[49]
		-0.557	-53742	[47]

Table 3. *Interaction parameters of phases in the Mo-Ti-N system*

Phase	Parameter	Ref.
Liquid (Mo,N,Ti)	${}^{0}L^{Liquid}_{Mo,N} = -126812.93 + 31.7978*T$	This work
	${}^{1}L^{Liquid}_{Mo,N} = -63380.43 + 2.5311*T$	This work
	${}^{0}L^{Liquid}_{Mo,Ti} = 50546.77 - 56.8279*T$	This work
	${}^{0}L^{Liquid}_{N,Ti} = -376736$	[31]
	${}^{1}L^{Liquid}_{N,Ti} = -102480$	[31]
	${}^{0}L^{Liquid}_{Mo,N,Ti} = -250000$	This work
	${}^{1}L^{Liquid}_{Mo,N,Ti} = -10000$	This work
	${}^{2}L^{Liquid}_{Mo,N,Ti} = -10000$	This work
FCC_A1 (Ti):(N,Va)	${}^{0}L^{FCC\_A1}_{Ti:N,VA} = -47739$	[31]
	${}^{1}L^{FCC\_A1}_{Ti:N,VA} = -9877$	[31]
BCC_A2 (Mo,Ti):(N, Va)$_3$	${}^{0}G^{BCC_{A2}}_{Mo:N} = 299700 - 25.4821*T + GHSERMO + 3*GHSERNN$	This work
	${}^{0}L^{BCC\_A2}_{Mo:N,VA} = -48841.69$	This work
	${}^{0}L^{BCC\_A2}_{Ti:N,VA} = -984397$	[31]
	${}^{0}L^{BCC\_A2}_{Mo,Ti:VA} = -38129.29 - 18.0564*T$	This work
	${}^{1}L^{BCC\_A2}_{Mo,Ti:VA} = -30201.38 + 4.1680*T$	This work
HCP_A3 (Mo,Ti):(N, Va)$_{0.5}$	${}^{0}G^{HCP\_A3}_{Mo:N} = 0$	This work
	${}^{0}L^{HCP\_A3}_{Ti:N,VA} = -4743$	[27]
	${}^{0}L^{HCP\_A3}_{Mo,Ti:VA} = 68953.76 + 23.8599*T$	This work
	${}^{1}L^{HCP\_A3}_{Mo,Ti:VA} = 33727.54 + 79.0211*T$	This work
MoN_delta (Mo):(N)	${}^{0}G^{MoN_{delta}}_{Mo:N} = -75509.38 + 90.2104*T + GHSERMO + GHSERNN$	This work
Ti2N (Ti)$_2$:(N)	${}^{0}G^{Ti2N}_{Ti:N} = -63220.14 + 22.4200*T + 2*GHSERTI + GHSERNN$	[31]
Mo2N_beta (Mo)$_2$:(N,Va)	${}^{0}G^{Mo2N_{beta}}_{Mo:N} = -78292.41 + 85.9746*T + 2*GHSERMO + GHSERNN$	This work
	${}^{0}G^{Mo2N_{beta}}_{Mo:VA} = 211092.42 - 21.3920*T + 2*GHSERMO$	This work
	${}^{0}L^{Mo2N\_beta}_{Mo:N,VA} = -341168.64 + 33.7743*T$	This work
	${}^{1}L^{Mo2N\_beta}_{Mo:N,VA} = 136817.5$	This work
Mo2N_gamma (Mo)$_2$:(N,Va)	${}^{0}G^{Mo2N_{gamma}}_{Mo:N} = -63327.06 + 70.5488*T + 2*GHSERMO + GHSERNN$	This work
	${}^{0}G^{Mo2N_{gamma}}_{Mo:VA} = 54580.40 + 0.5512*T + 2*GHSERMO$	This work
	${}^{0}L^{Mo2N\_gamma}_{Mo:N,VA} = -82973.78 + 9.9716*T$	This work
	${}^{1}L^{Mo2N\_gamma}_{Mo:N,VA} = 44489.38$	This work

reported in open databases [48] [49] [47] show more negative values, which could be attributed to the use of different pseudopotentials. These ab-initio calculated formation energies of intermediate phases were then used in the thermodynamic optimization process. The optimization was carried out in a step-by-step manner. Firstly, the thermodynamic parameters of the liquid and BCC_A2 phases were optimized based on the solubility of nitrogen in both phases and the equilibrium pressure of nitrogen. Secondly, the thermodynamic parameters of intermediate phases were calculated. Finally, all the obtained parameters were assessed together to obtain a consistent thermodynamic model of the binary Mo-N system. During the optimization process, equal weight was given to the experimental information used, as there was no information available regarding the experimental errors.

To optimize the ternary Mo-Ti-N system, the data provided by Ettmayer and Hormanseder [33] and Langauer et al. [36] were utilized. The optimized parameters of the Liquid, BCC_+A2, and HCP_A3 phases allowed for a satisfactory reproduction of the experimental data. Barabash and Shurin's [32] data was excluded from the study due to significant discrepancies with Ettmayer and Hormanseder's [33] findings, whose data for the isothermal section was also employed. Chung et al.'s [29] data was also excluded due to its computational origin.

The thermodynamic parameters obtained in this work are tabulated in Table 3.

Based on the parameters presented in Table 2, the phase diagram for the binary Mo-N system was computed, as shown in Figure 1, with the gas phase being suspended. During this optimization, experimental data such as the solubility of nitrogen in molybdenum, equilibrium pressure of nitrogen, the Mo2N-beta to Mo2N-gamma transformation, and the L = Mo + Mo2N-gamma eutectic reaction were used from Jehn and Ettmayer [2]. Additionally, the melting temperature of MoN-delta was obtained from the Springer Handbook of Materials Data [51], while the information on the Mo2N-beta to Mo2N-gamma transformation was taken from Oyama [52].

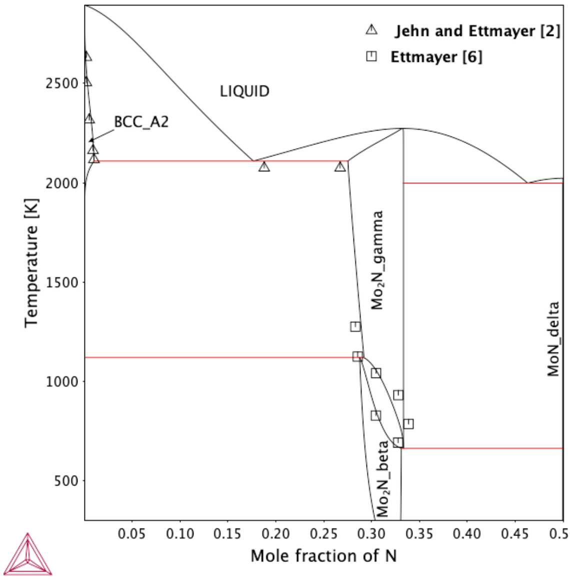

Figure 1. *Calculated phase diagram of Mo-N system superimposed with experimental data given by Jehn and Ettmayer [2] and Ettmayer [6]. The gas phase was suspended in this calculation*

The solubility of nitrogen in molybdenum is shown to be reproduced quite accurately in this work. The three-phase equilibrium calculated by Jehn and Ettmayer [2] at 2073 K is reproduced at 2074 K, and the composition of the liquid phase calculated in this work is in good agreement with the value proposed by Jehn and Ettmayer [2] at 0.2 mole fraction of nitrogen. Additionally, the calculated melting temperature of Mo2N-gamma is 2273 K, which agrees well with the prediction given by Jehn and Ettmayer [2]. It can be concluded that the modeled temperature of the Mo2N-beta to Mo2N-gamma phase transformation is dependent on the concentration of nitrogen. According to Jehn and Ettmayer [2], the transformation occurs at 1123 K for low nitrogen concentration, whereas Oyama [52] reported a temperature of 973 K for high nitrogen concentration in the Mo2N-beta phase. In this work, the transformation temperature was modeled at 1124 K for low nitrogen concentration, and while it was not possible to reproduce 973 K for a low concentration of nitrogen in the intermediate phase, the calculated transformation temperature was found to be 1051 K. The discrepancy between the calculation and experiment can be explained by the difficulty of maintaining samples in equilibrium during the experimental procedure, which can introduce uncertainties in the results.

Figure 2a shows the calculated activity of nitrogen in liquid phase at 2923 K superimposed with data given by Domke and Frohberg [11]. In this calculation, the following reference states were used: liquid state and gaseous state for molybdenum and nitrogen, respectively.

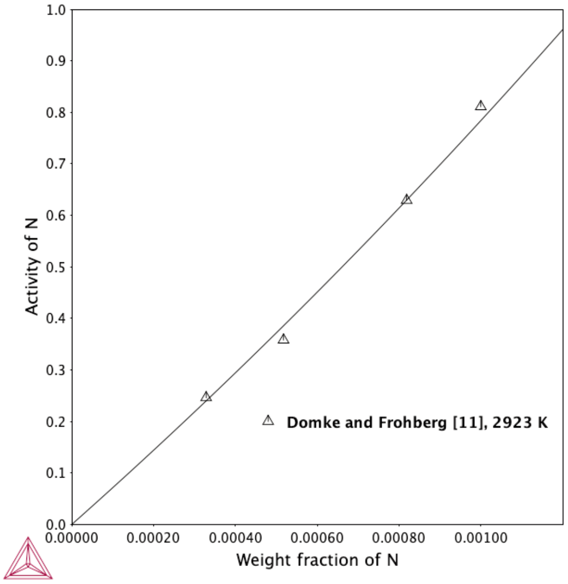

Figure 2a. *Calculated activity of nitrogen in liquid phase at 2923 K superimposed with data given by Domke and Frohberg [11]*

The calculated activity agrees with experimental data fair and follows the trend given by experiment. It can be noticed that the activity obeys Henry's Law for a dilute solution.

Figure 2b shows calculated pressure of N_2 over liquidus line.

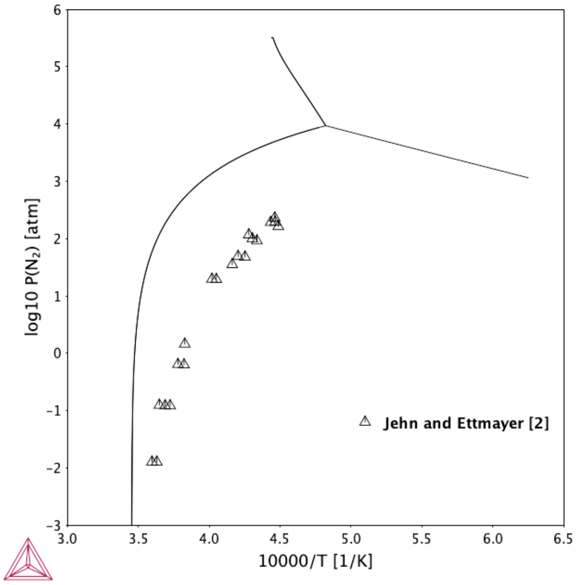

Figure 2b. *Calculated pressure of N_2 over liquidus line together with data given by Jehn and Ettmayer [2]*

As depicted in Figure 2b, discrepancies can be observed between the calculated and experimental data. There are two possible reasons for this issue:

a) Thermodynamic model has to describe a whole system, not only a single phase, therefore, thermodynamic parameters are adjusted to all available data. In many cases there is a lack of information on experimental error thus setting reasonable weight of data is difficult.

b) Experimental data at high temperature are affected by quite a big error due to a strong influence of temperature on pressure.

Initially, the ternary Mo-Ti-N system was computed using the literature description of the Mo-Ti system [27]. However, the calculated isothermal section at 1423 K did not match well with the experimentally determined tie-lines reported by Langauer et al. [36]. Therefore, it was decided to re-optimize the binary Mo-Ti system using available experimental data on the solidus line [14] [20], BCC_A2-HCP_A3 phase equilibria [14] [15], formation enthalpy of BCC_A2 [25] [26], formation enthalpy of HCP_A3 [25], and activity of Ti in BCC_A2 phase [22]. The optimization process was performed step by step, starting with the BCC_A2 phase and then simultaneously assessing the liquid and HCP_A3 phases. Finally, all phases were optimized together to obtain the best set of interaction parameters.

The calculated binary phase diagram of the Mo-Ti system is presented in Figure 3a, which also displays the experimental data obtained by Hansen et al. [14], Flower et al. [15], and Rudy [20], as well as calculations made using thermodynamic parameters provided by Santhy and Hari Kumar [27] and Chung et al. [29].

It can be seen that the phase boundary BCC_A2-HCP_A3 agrees well with the experimental data given by Hansen et al. [14]. The models proposed by Santhy and Hari Kumar [27] and Chung et al. [29] show almost identical phase equilibria in this area. The difference between the models can be observed in the area not covered by the experimental data. The calculation made with the Santhy and Hari Kumar [27] parameters shows a much bigger binary HCP_A3+BCC_A2 region in comparison to the present work. Chung et al. [29] followed the information given by Terauchi et al. [19], who suggested a miscibility gap in the BCC_A2 phase. However, as discussed by Murray [13], there is some controversy about whether the miscibility gap exists. In this work, it was decided to omit the separation in BCC_A2 as it was also omitted by Santhy and Hari Kumar [27] and in the COST 507 database [30]. The liquidus and solidus lines calculated from all three databases look very similar and agree well with the experimental data provided by Rudy [20].

Figure 3b displays calculated formation enthalpy of BCC_A2 phase superimposed with DFT calculations given by Raabe et al. [25], and Marker et al. [26]as well as with Calphad-type calculation given by Santhy and Hari Kumar [27], and Chung et al. [29]. It can be seen that parameters proposed in this work agree well with DFT calculation and lay between both calculated datasets [25] [26]. The formation enthalpy proposed by Santhi and Hari Kumar [27] shows endothermic characteristic for whole concentration range and doesn't agree with DFT prediction. Chung et al. [29] proposed exothermic enthalpy of formation; however, the values are less negative than it appears from ab-initio modeling.

Figure 4 shows calculated binary Ti-N phase diagram. The calculation was done using thermodynamic model given by Sridar et al. [31].

The calculated isothermal section of the ternary Ti-Mo-N system at 1051 K is presented in Figure 5a.

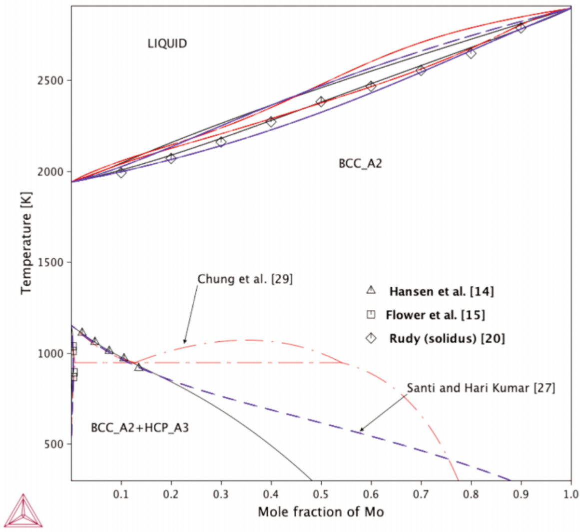

Figure 3a. *Calculated phase diagram of Mo – Ti system superimposed with previous assessments [29] [27] and experimental data [14] [15] [20]*

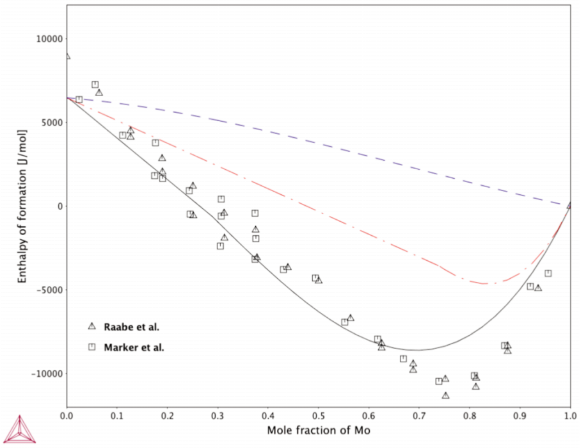

Figure 3b. *Calculated enthalpy of formation of BCC_A2 phase superimposed with previous models [27] [29] and ab-initio calculations [25] [26]*

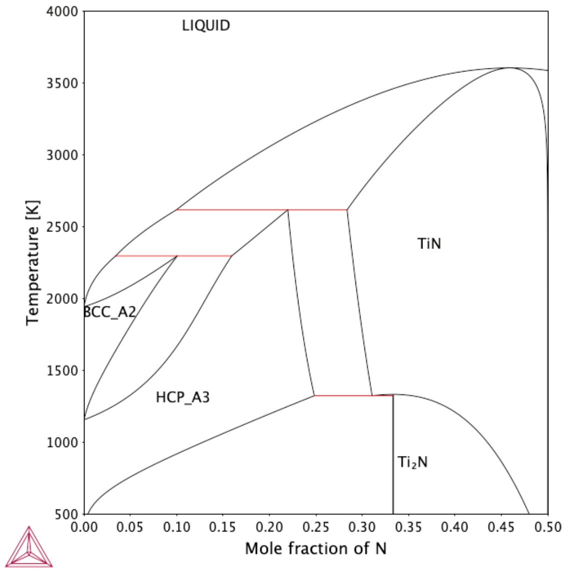

Figure 4. *Calculated phase diagram of Ti – N system based on Sridar et al. [31] model*

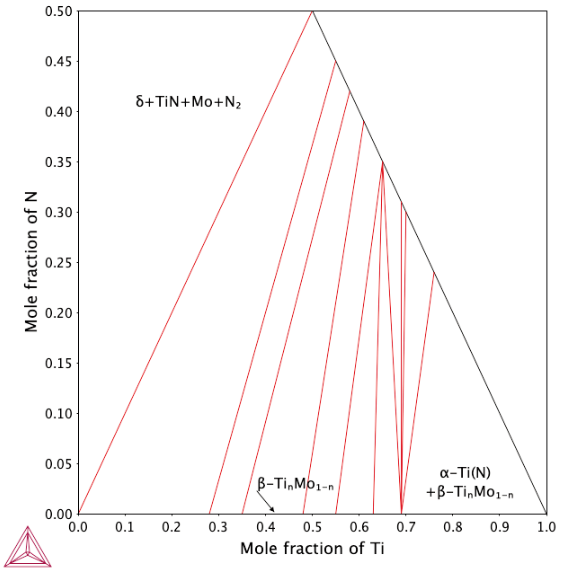

Figure 5b. *Holleck's isothermal section of Mo-Ti-N system at 1273 K, redrawn from: Transition Metalls Binäre und ternäre Carbid- und Nitridsysteme der Übergangsmetalle, StuttgarBerlin: Bebrüder Borntraeger, 1984 [37] [53]. (Obtained via license CC BY 4.0)*

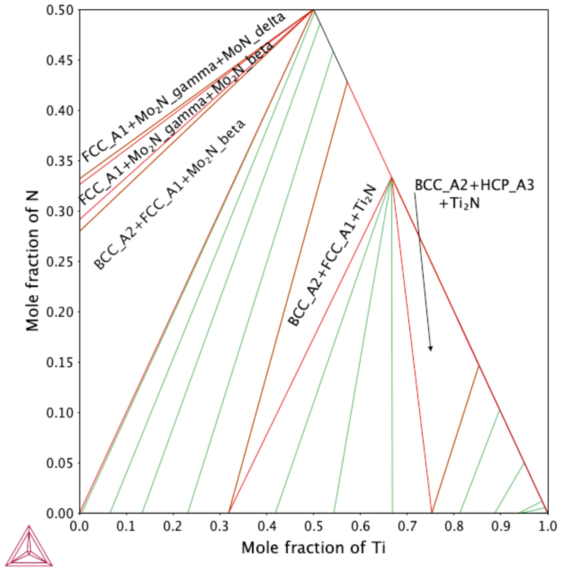

Figure 5a. *Calculated isothermal section at 1051 K of a ternary Ti-Mo-N system from this study*

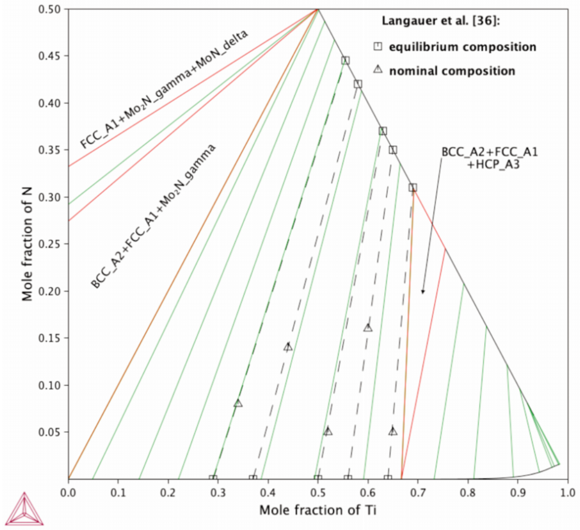

Figure 5c. *Calculated isothermal section at 1423 K of a ternary Ti-Mo-N system superimposed with data given by Langauer et al. [36]*

It can be observed that the constituent binary system created five tie-triangles. By comparing this result to the isothermal section proposed by Holleck [37], depicted in Figure 5b, it can be found that equilibria between phases existing in the binary Mo-N phase and Ti-N phase that were not listed in [37]. The proposed phase equilibria are believed to be more accurate than those reported by Holleck [37] due to the calculation of all tie-triangles that exist at 1051 K.

Figure 5c shows the calculated isothermal section of the Mo-Ti-N system at 1423 K, along with the experimental data given by Langauer et al. [36]. It can be seen that the binary region BCC_A2-FCC_A1 determined by Langauer et al. [36] is well reproduced by the calculation, and experimentally determined tie-lines are parallel to calculated ones.

Figure 5d displays the calculated isothermal section of the Mo-Ti-N system at 1373 K under 30 bar superimposed with data given by Ettmayer and Hormanseder [33] under pressure 30 bar and 300 bar. Ettmayer and Hormanseder [33] determined a binary region based on metallographic analysis and XRD experiments; therefore, information on equilibrium compositions is not available. It can be seen that the proposed model reproduces the binary region fairly well, with some discrepancies between calculation and Ettmayer and Hormansder [33] data. The calculation under 300 bar almost does not change phase equilibria; therefore, an additional calculation at 300 bar was not included in Figure 5d for the sake of clarity.

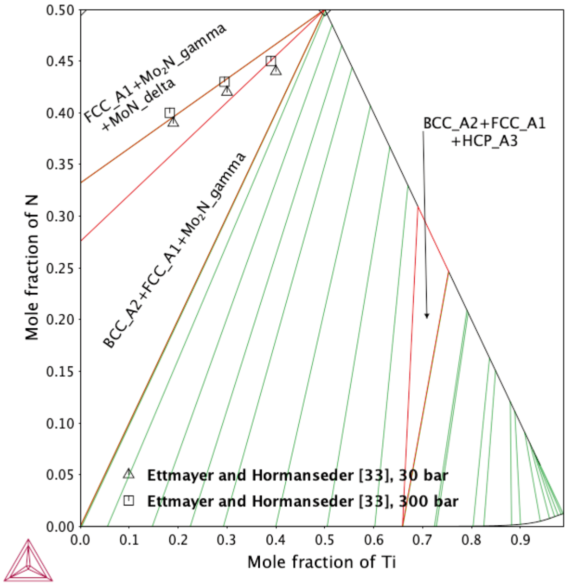

Figure 5d. *Calculated isothermal section at 1373 K under pressure of 30 bar of a ternary Ti-Mo-N system superimposed with data given by Ettmayer and Hormansder [33]*

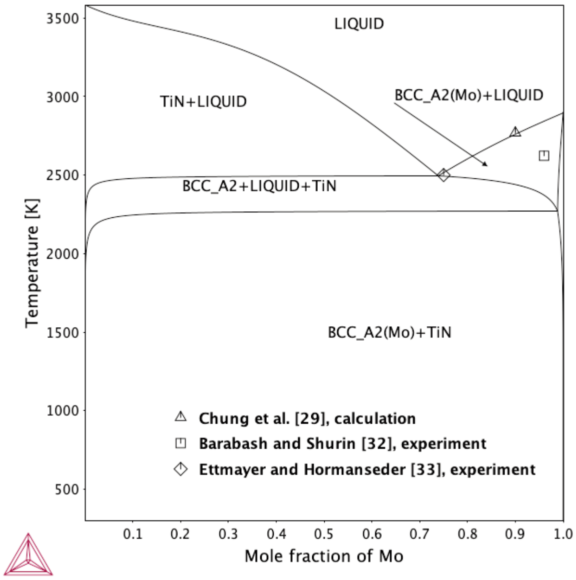

Figure 5e. *Calculated isopleth TiN – Mo together with results given by Chung et al. [29], Barabash and Shurin [32], and Ettmayer and Hormanseder [33]*

In Figure 5e, an isoplethal Mo-TiN calculation is presented, along with eutectic points reported by Barabash and Shurin [32], Ettmayer and Hormanseder [33], and Chung et al. [29]. It can be observed that there are significant differences in both temperature and composition among the reported data. In the current study, the calculation agrees with the temperature reported by Ettmayer and Hormanseder [33], although the calculated composition slightly deviates from the experimental determination. A similar situation is observed in the thermodynamic calculation presented by Chung et al. [29], who claim agreement with the results reported by Barabash and Shurin [32].

6. Summary and Conclusions

In the present study new thermodynamic models for the binary Mo-N, Mo-Ti, and ternary Mo-N-Ti systems are proposed. These models were developed using available thermodynamic and structural data, as well as ab-initio calculations. The results indicate good agreement between the calculated values and the available experimental information. By combining the new models for Mo-N and Mo-Ti with the literature model for Ti-N, isothermal sections at 1000 K, 1373 K, and 1423 K were calculated and compared with the predictions of Holleck [37], Barabash and Shurin [32], Ettmayer and Hormanseder [33], and Langauer et al. [36]. The study concludes that the new thermodynamic model for Mo-N is more accurate than the previous model proposed by Frisk [12], due to the application of ab-initio calculations and the inclusion of all experimentally determined intermediate phases, instead of the single solution phase proposed by Frisk [12]. Additionally, the new thermodynamic model of the Mo-Ti system agrees well with experimental and theoretical data and provides a good reproduction of the ternary Mo-Ti-N system.

Acknowledgment

The work was supported by Ministry of Science and Technology (Taiwan) under grants 109-2221-E-259 -005 and 111-2221-E-259 -009. The authors also acknowledge the support of the Department of Science and Technology (DOST) Philippine Council for Industry, Energy and Emerging Technology Research and Development (PCIEERD) GIA Project 2: Development of Radio Frequency (RF) Plasma System for Ti-Al-N Thin Film Synthesis. One of the authors (W.G.) is thankful to the University of the Philippines for the support during his visit to the Department of Mining, Metallurgical, and Materials Engineering, College of Engineering, UP Diliman as well as to the Office of the International Affairs of the National Dong Hwa University for the support.

References

[1] E. Fromm, H. Jehn, Gleichgewichte und Entgasungskinetik in den Systemen Mo-N, W-N und Re-N (Ger.), High Temperature-High Pressures, 3 (5) (1971) 553-564.

[2] H. Jehn, P. Ettmayer, The molybdenum-nitrogen phase diagram, Journal of Less-Common Metalls, 58 (1978) 85-98. DOI: 10.1016/0022-5088(78)90073-5.

[3] B. Neumann, C. Kroger, H. Kunz, Die bildungswärmen der nitride, V. Die verbrennungswärmen iniger metalle und metallnitride (in Ger.), Zeitschrift fur Anorganische und Allgemeine Chemie, (218) (1934) 379-401.

[4] A.D. Mah, Rep. Invest. No. 5529, U. S. Bur. Mines, (1969).

[5] S. Satoh, Scientific papers of the Institute of Physical and Chemical Research, 34 (1938) 1001.

[6] P. Ettmayer, The system Mo - N, Monatshefte fur Chemie, 101 (1970) 127-140 . DOI:10.1007/BF00907533.

[7] N. Schonberg, Contributions to the knowledge of the molybdenum-nitrogen and tungsten-nitrogen systems, Acta Chemica Scandinavica, (8) (1954) 204-207. DOI:10.3891/acta.chem.scand.08-0204.

[8] N.V. Troitskaya, Z.G. Pinsker, The hexagonal nitrides of molybdenum, Kristallografiya, 6 (1961) 43-48.

[9] T.B. Massalski, P.R. Subramanian, H. Okamoto, L. Kacprzak, Binary alloy phase diagrams, in Binary Alloy Phase Diagrams, Metal Park, Ohio, 1990, ASM International.

[10] F.F. Klimashin, N. Kotuna, H. Euchner, D. Holec, P.H. Mayrhofer, The impact of nitrogen content and vacancies on structure and mechanical properties of Mo-N thin films, Journal of Applied Physics, 120 (2016) 185301. DOI: 10.1063/1.4966664.

[11] H. Domke, M.G. Frohberg, Determination of the solubility of nitrogen in liquid molybdenum, Zeitschrift fur Metallkunde, 65 (9) (1974) 615-617.

[12] K. Frisk, A thermodynamic evaluation of the Ce-N, Fe-N, Mo-N and Cr-Mo-N systems, Calphad, 15 (1) (1991) 79-106. DOI: 10.1016/0364-5916(91)90028-I.

[13] J.L. Murray, The Mo-Ti (molybdenum-titanium) system, Bulletin of Alloy Phase Diagrams, 2 (1981) 185-192. DOI: 10.1007/BF02881476.

[14] M. Hansen, E.L. Kamen, H.D. Kessler, Systems titanium-molybdenum and titanium-columbium, Transactions AIME, 191 (1951) 881-888.

[15] H.M. Flower, S.D. Henry, D.R.F. West, The alpha-beta transformation in dilute Ti-Mo alloys, Journal of Materials Science, 9 (1974) 57-60. DOI: 10.1007/BF00554755.

[16] J.M. Dupouy, B.L. Averbach, Atomic arrangements in titanium-molybdenum solid solution, Acta Metallurgica, 9 (1961) 755-763. DOI: 10.1016/0001-6160(61)90106-7.

[17] J.P. Morniroli, M. Gantois, Formation conditions for the omega phase of titanim-niobium and titanium-molybdenum alloys, Les Memories Scicientifiques de la Revue de Metalurgie, 11 (1973) 831-842.

[18] V. Chandrasekar, R. Taggart, D.H. Polonis, Phase separation process in beta phase of Ti-Mo binary system, Metallography, 5 (1972) 393-398. DOI: 10.1016/0026-0800(72)90027-4.

[19] S. Terauchi, H. Matsumoto, T. Sugimoto, K. Kamei, Investigation of the titanium-molybdenum binary phase diagram, Journal of Japanese Institute of Metals and Materials, 41 (1977) 632-637. DOI: 10.2320/jinstmet1952.41.6_632.

[20] E. Rudy, Compilation of phase diagram data, Techical Rept. AFML-TR-62-2 Part V, Wright Paterson Air Force Base, (1969).

[21] A.A. Kuz'min , L.S. Palatnik, Vapour pressure of titanium over Ti-Mo alloys, Physics of Metals and Matallography, 14 (1962) 142-144.

[22] M. Hoch, R. Viswanathan, Thermodynamics of titanium alloys III: the Ti-Mo system., Metallurgical Transactions, 2 (1971) 2765-2767. DOI: 10.1007/BF02813250.

[23] K. Yao, X. Min, S. Shi, Y. Tan, Volatilization behavior of β-Type Ti-Mo alloy manufactured by Electron beam melting, Metals, 8 (2018) 206-220. DOI: 10.3390/met8040206.

[24] J.V. Hachworth, M. Hoch, H.L. Gegel, Thermodynamics of titanium alloys: I. Development of a triple Knudsen cell and its use to study the activity of copper in the Ti− Cu system, Metallurgical Transactions, 2 (1971) 1799-1806. DOI: 10.1007/BF02913408.

[25] D. Raabe, B. Sander, M. Friak, D. Ma, J. Neugebauer, Theory-guided bottom-up design of b-titanium alloys as biomaterials based on first principles calculations: Theory and experiments, ActaMaterialia, 55 (2007) 4475-4487, DOI: j.actamat.2007.04.024.

[26] C. Marker, S.-L. Shang, J.-C. Zhao, Z.-K. Liu, Thermodynamic description of the Ti-Mo-Nb-Ta-Zr system and its implications for phase stability of Ti bio-implant materials, Calphad, 61 (2018) 72-84. DOI: 10.1016/j.calphad.2018.02.004

[27] K. Santhy, K.C. Hari Kumar, Thermodynamic assessment of Mo-Ni-Ti ternary system by coupling first-principle calculations with CALPHAD approach, Intermetallics, 18 (2010) 1713-1721. DOI: /j.intermet.2010.05.008

[28] K. Zeng, R. Schmid-Fetzer, Critical assessment and thermodynamic modeling of the Ti-N system, Zeitschrift fur Metallkunde, 87 (1996) 540-554,

[29] H.-J. Chung, J.-H. Shim, D.N. Lee, Thermodynamic evaluation and calculation of phase equilibria of the Ti-Mo-C-N quaternary system., Journal of Alloys and Compounds, 282 (1999) 142-148. DOI: 10.1016/S0925-8388(98)00711-7

[30] I. Ansara, A.T. Dinsdale, M.H. Rand, COST 507: Thermodynamic database for light metal alloys, European Communities, Brussels and Luxembourg, 1998.

[31] S. Sridar, R. Kumar, K.C. Hari Kumar, Thermodynamic modeling of Ti-Zr-N system, Calphad, 56 (2017) 102-107. DOI: 10.1016/j.calphad.2016.12.003

[32] O.M. Barabash, A.K. Shurin, Fazovyeravnovesiya v splavakh Mo-Ti-N i Mo-Hf-N, Izv AN SSSR Metally, 4 (1978) 243-246.

[33] P. Ettmayer, W. Hormanseder, Phase equilibria between high melting nitrides and refractory binder metals, High Temperatures-High Pressures, 18 (1986) 161-172.

[34] W. Langauer, P. Ettmayer, An investigation of the Ti-Mo-N System at low nitrogen activities, Zeitschrift fur

Metallkunde, 80 (1989) 726-730.

[35] W. Langauer, P. Ettmayer, Investigation of phase equilibria in the Ti-N and Ti-Mo-N systems, Materials Science and Engineering A, A105/106 (1988) 257-263. DOI: 10.1016/0025-5416(88)90504-6

[36] W. Langauer, H.J. Ullrich, P. Ettmayer, Investigations in the ternary system Ti-Mo-N by means of EPMA and XRD, Mikrochimica Acta, 1 (1987) 211-218.

[37] H. Holleck, TBinäre und ternäre carbid- und nitridsysteme der ubergangsmetalle, Stuttgard-Berlin, Germany: BebrüderBorntraeger, 1984.

[38] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty, D. C. Allan, First-principles computation of material properties: The ABINIT software project, Computational Materials Science, 25 (2002) 478-492. DOI: 10.1016/S0927-0256(02)00325-7

[39] G. Kresse, D. Joubert, From ultrasoftpseudopotentials to the projector augmented-wave method, Physical Review B, 59 (1999) 1758. DOI: 10.1103/PhysRevB.59.1758

[40] J. P. Padrew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Physical Review Letters, 77 (1996) 3865. DOI: doi.org/10.1103/PhysRevLett.77.3865

[41] A. Zunger, S.-H. Wei, L. G. Ferreira, J. E. Bernard, Special quasirandom structures, Physical Review Letters, 65 (1990) 353. DOI: 10.1103/PhysRevLett.65.353

[42] A. van de Walle, Multicomponent multisublattice alloys, nonconfigurational entropy and other additions to the Alloy Theoretic Automated Toolkit, Calphad, 33 (2009) 266-278. DOI: 10.1016/j.calphad.2008.12.005

[43] Scientific Group Thermodata Europe, Unary Database v. 5.0, France, 2015.

[44] Scientific Group Thermodata Europe, SGTE Substance Database 3.2, 2004.

[45] Y. Wang, S. Curtarolo, C. Jiang, R. Arroyave, T. Wang, G. Ceder, L.-Q. Chen, Z.-K. Liu, Ab initio lattice stability in comparison with CALPHAD lattice stability, Calphad, 28 (2004) 79-90. DOI: j.calphad.2004.05.002

[46] M. D. Fryzuk, S. A. Johnson, The continuing story of dinitrogen activation, Coordination Chemistry Review, 200-202 (2000) 379-409. DOI: 10.1016/S0010-8545(00)00264-2

[47] JARVIS National Institute of Standards and Technology, National Institute of Standards and Technology, [Online]. Available: https://www.ctcms.nist.gov/~knc6/JVASP.html. [Accessed 27 05 2020].

[48] Materials Project, [Online]. Available: https://materialsproject.org. [Accessed 19 11 2019].

[49] The Open Quantum Materials Database, [Online]. Available: http://www.oqmd.org. [Accessed 19 11 2019].

[50] D. Rappoport, N. R. M. Crawford, Approximate density functionals: which should I choose?, Encyclopedia of Inorganic Chemistry, 2008 John Willey & Sons.

[51] H. Warlimont, W. Martienssen, Springer handbook of materials data, Berlin Heidelberg 2005. Springer.

[52] S.T. Oyama, The chemistry of transition metal carbides and nitrides, Glasgow, 2012, Blackie Academic & Professional.

[53] S.B. Kislitsin, A.I. Potekaev, V.V. Uglov, A.A. Klopotov, V.D. Klopotov, Y.F. Ivanov, A.T. Parpiev, Steel surface TiCrN, TiMoN coatings structural phase state change features after low-energy alpha particles irradiation, IOP Conference Series: Materials Science and Engineering, 289 (2018) 012010. DOI: 10.1088/1757-899X/289/1/012010

AB-INITIO U KOMBINACIJI SA CALPHAD PRISTUPOM FAZNOJ RAVNOTEŽI U TERNARNOM Ti-Mo-N SISTEMU

R.A. Daclan [a], M.G. Mena [a], M.R. Vasquez [a], W. Gierlotka [b,*]

[a] Odsek za rudarskom metalurško i inženjerstvo materijala, Fakultet za inženjerstvo, Univerzitet na Filipinima -Diliman, Filipini

[b] Odsek za nauku o materijalima i inženjerstvo, Nacionalni Dong Hua univerzitet, Tajvan

Apstrakt

Trojni sistem Ti-Mo-N je važan materijal koji se koristi kao površinski premaz, učvršćivač i sloj za zaštitu od habanja i korozije. Poznavanje faznih ravnoteža, faznih transformacija i fazne stabilnosti ove legure je važno za realizaciju njenih potencijalnih primena. U ovom radu su ab-initio proračunima određene energije formiranja tri intermetalna jedinjenja, Mo2N-beta, Mo2N-gama i MoN-delta. Zatim je primenjen Calphad pristup za termodinamičko modeliranje Mo-Ti, Mo-N i Mo-Ti-N sistema. Dobijene Gibsove energije su korišćene za izračunavanje faznog dijagrama i termodinamičkih svojstava Ti-Mo-N sistema. Sadašnji model je u saglasnosti sa eksperimentalnim podacima iz literature. Rezultati ovog rada mogu se koristiti kao osnova za buduća proučavanja Ti-Mo-N sistema i kao osnova za praktičnu industrijsku primenu.

Ključne reči: *Ab-initio; Calphad; Mo; Ti; N; Fazni dijagram*