

## A THERMODYNAMIC EVALUATION OF THE Ti–N SYSTEM

C. VAHLAS

*Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, E.N.S.E.E.G., BP. 75, 38402 Saint Martin d'Hères (France)*

B. DROUIN LADOUCE

*ATOCHEM CERDATO Serquigny 27470 (France)*

P.Y. CHEVALIER

*THERMODATA THERMA, BP. 66, 38402 Saint Martin d'Hères (France)*

C. BERNARD

*Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, E.N.S.E.E.G., BP. 75, 38402 Saint Martin d'Hères (France)*

L. VANDENBULCKE

*CRCCHT, 10 Av. Recherche Scientifique, 45071 Orleans Cedex 2 (France)*

(Received 3 August 1990)

### ABSTRACT

A thermodynamic analysis of phase equilibria in the Ti–N binary system was done. The different solution phases and intermetallic compounds were analysed using thermodynamic models of the Gibbs energy. A set of self-consistent parameters has been obtained using the optimization procedure developed by Lukas et al. Good agreement is observed between the experimental information and the calculated phase diagrams and thermodynamic functions.

### INTRODUCTION

Since the mid-1980s, titanium nitride has become more and more important in high technology applications such as protective coatings against corrosion and wear or electronic components and even coatings for decorative uses. TiN layers are usually produced by chemical or physical vapour deposition (CVD or PVD). In the case of CVD, thermodynamic predictions are of interest but are based on thermodynamic data such as the Gibbs free energy of formation of non-stoichiometric phases for example. These data must be calculated in accordance with the phase diagram.

Until now, the phase diagram of the Ti–N binary system has been far less well known than the Ti–C one. The aim of the present study therefore was to optimize this phase diagram and the thermodynamic data used in calculation of multicomponent systems.

## PRESENTATION OF THE DIFFERENT PHASES

The selected phase diagram is based on the one reported in the critical review by Wriedt and Murray [1] on the crystal structure, phases boundaries and thermodynamic properties of the Ti–N binary system. The diagram was completed by using the work of Grieveson [2], Nowotny et al. [3], Ehrlich [4], Khaenko et al. [5], Lashko et al. [6] and Holmberg [7]. There are five different phases.

(1) The liquid phase L.

(2) The terminal titanium-rich solution with the hexagonal close packed (h.c.p.) structure from the pure titanium low temperature structure at  $T \leq 1155$  K with a high nitrogen solubility (Ti- $\alpha$ ).

(3) The titanium-rich solution with the body-centred cubic (b.c.c.) structure from the pure titanium high temperature structure at a higher temperature than 1155 K and with, as for Ti-h.c.p., a large composition field (Ti- $\beta$ ).

(4) The tetragonal  $\text{Ti}_2\text{N}$  solid solution with a narrow composition field centred on 33.3 at.% N. In the following, this phase is considered as an intermetallic compound containing 33.3 at.% N (Ti<sub>2</sub>N- $\epsilon$ ).

(5) The  $\text{Ti}_x\text{N}_{1-x}$  cubic face centred solid solution with a broad field of composition (Ti<sub>x</sub>N<sub>1-x</sub> -  $\delta$ ).

(6) The  $\text{Ti}_x\text{N}_{1-x}$  tetragonal centred solid solution with a narrow field of composition centred on 37.5 at.% N. As for  $\epsilon$ , this solution is considered here as an intermetallic compound containing 37.5 at.% N (Ti<sub>0.625</sub>N<sub>0.375</sub>- $\delta'$ ).

## EXPERIMENTAL INFORMATION

### *Diagram*

The first diagram elaborated from experimental data was reported by Palty et al. [8] and was subsequently used as the basis for the studies made by, for example, Hansen and Anderko [9], McClaine and Coppel [10] and Toth [11].

However, the results reported in works published after that of Palty et al. [8] often disagree on the maximum solubility of nitrogen in Ti- $\alpha$ , TiN- $\delta$  and Ti<sub>2</sub>N- $\epsilon$ . Such differences are often due to the great sensitivities of these limits to impurities. A study by Stone and Margolin [12] showed that these limits can vary drastically even with low oxygen concentrations.

### *Terminal solid solutions Ti- $\alpha$ and Ti- $\beta$*

The Ti- $\alpha$  and Ti- $\beta$  phases are stable when nitrogen activities are low. The Ti- $\alpha$  terminal phase is stable at  $T < 1155$  K and the domain of composition stretches to higher temperatures. When the nitrogen activity increases, Ti- $\alpha$  coexists with  $Ti_xN_{1-x}$ - $\delta$  at temperatures above 1323 K and with  $Ti_2N$ - $\epsilon$  at temperatures below 1323 K.

Numerous works on this part of the phase diagram have been published. Jaffee et al. [13] have determined the composition of the coexisting Ti- $\alpha$  and Ti- $\beta$  terminal solutions by a metallographical method. At 1173 K and 1273 K, the maximum solubility of nitrogen in Ti- $\beta$  increases from 0.08 at.% at 1173 K to 0.7 at.% at 1273 K, with 1.2 at.% N in Ti- $\alpha$  at 1173 K. Stone and Margolin [12] as well as Palty et al. [8] have studied this titanium rich part of the diagram up to 1673 K by metallographic analysis and their results are in good accordance with one another. According to Stone and Margolin [12], the frontier between Ti- $\beta$ /Ti- $\beta$  + Ti- $\alpha$  varies from 0.43 at.% N at 1173 K to 3.15 at.% at 1273 K and the Ti- $\alpha$ /Ti- $\alpha$  + Ti- $\beta$  limit increases from 1.18 at.% to 9.9 at.% N at 1673 K.

The composition of the border between the Ti- $\alpha$  and Ti- $\beta$  domains has been reported by Wood [14] for a maximum temperature of 1798 K by diffusion couple analysis. This author puts the Ti- $\beta$ /Ti- $\beta$  + Ti- $\alpha$  border at around 6 at.% N at 1458 K and at 7 at.% N at 1798 and 1768 K.

Only Palty et al. [8] have examined the curves of solidus of phases  $\alpha$  and  $\beta$  and peritectic  $L + \alpha + \beta$  at  $2323 \pm 25$  K. The compositions of Ti- $\alpha$  and Ti- $\beta$  reported by Wriedt and Murray [1] were deduced from extrapolations of the limits of the field Ti- $\alpha$  + Ti- $\beta$ . According to Palty et al. [8], the solidus of Ti- $\alpha$  starting from the peritectic  $L + \alpha + \beta$  at 2323 K ends up in a peritectic  $L + \alpha + \delta$  localized at 2623 K with 20.5 at.% N in the  $\alpha$  phase. Wood [14] and Toth [11] indicated 25 at.% N and 17.5 at.% N respectively in the Ti- $\alpha$  solution at this point.

The limit Ti- $\alpha$ /Ti- $\alpha$  + TiN- $\delta$  starts from the peritectic previously quoted to join the compound balance  $Ti-\alpha + Ti_xN_{1-x} = Ti_2N$ . According to most authors, this balance is by nature peritectoid. Ehrlich [4] had located the limit of nitrogen solubility in Ti- $\alpha$  at 19 at.% N. Palty et al. [8] stated that the limit moves from 20 at.% N at 2623 K to 21.2 at.% N at 1323 K. Nowotny et al. [3] found at 1673 K a composition of 24 at.% N at about this limit.

Moreover, the diagram displayed by McClaine and Coppel [10] matches the results of Palty et al. [8] regarding the peritectic at 1323 K. Wolff et al. [15], working from 1123 to 2073 K, set the limit of nitrogen solubility in Ti- $\alpha$  at about 22 at.% N to 25 at.% N between 1673 and 1573 K. The peritectoid composition should be situated between 25 and 26 at.% N.

The localization and the nature of the compound balance between Ti- $\alpha$ ,  $Ti_xN_{1-x}$ - $\delta$  and  $Ti_2N$ - $\epsilon$  varies, depending on the authors, owing to the difficulty of establishing the temperature of decomposition of the  $Ti_2N$ -

phase. McDonald and Wallwork [16] stated that  $Ti_2N-\epsilon$  is unstable at 1383 K, whereas Wolff et al. [15] placed the peritectoid at a temperature below 1473 K. However, Bars et al. [17] asserted that  $Ti_2N-\epsilon$  remains stable beyond 1773 K, and according to Wood [14] the equilibrium temperature should be 1908 K. Wriedt and Murray [1], after a critical analysis of the experimental methods used by the authors, suggested 1383 K for the temperature of the congruent decomposition of  $Ti_2N-\epsilon$  and 1323 K for the temperature of the peritectoid  $(Ti-\alpha)-(Ti_2N-\epsilon)-(Ti_xN_{1-x}-\delta)$ .

*The limit  $Ti-\alpha / Ti-\alpha + Ti_2N-\epsilon$ .* Data available at the temperatures of interest here are very scarce compared with previous fields. By and large, the solubility of nitrogen in  $Ti-\alpha$  decreases with temperature. Results reported by Palty et al. [8] and Holmberg [7] are in accordance with one another: the limit evolves from 21.2 at.% N at 1323 K to 13 at.% N at 973 K, and to 17 at.% N at 1173 K. Measurements made by Wood [14] at 1068, 1218 and 1458 K indicate compositions ranging from 16.5 at.% N to 22 at.% N with a maximum at 1458 K.

According to Wolff et al. [15], nitrogen solubility in  $Ti-\alpha$  evolves from 25.9 at.% N at 1373 K to 18.5 at.% N at 1123 K. These values are slightly higher than those recommended by Wriedt and Murray [1].

#### *Phase $Ti_2N-\epsilon$*

This phase was first mentioned by Palty et al. [8] without indicating its exact composition. Its existence was confirmed by Nowotny et al. [3], and its composition is supposed to be close to 33.3 at.% N with a narrow field of homogeneity.

Holmberg [7] established the crystalline structure of this phase and brought in evidence a narrow field of composition centred on  $Ti_2N$ . Wolff et al. [15] mentioned a field of homogeneity between 28.5 and 29.7 at.% N, from 1123 to 1373 K, while Lashko et al. [6] set the limit  $Ti_2N + Ti_xN_{1-x} / Ti_2N$  at 47.5 at.% N at 1233 K.

Wood [14] framed this field with compositions stretching from a lower limit of 24–28.5 at.% N to an upper limit of 31–35 at.% N between 1068 and 1798 K. These results contradict those reported by all the other authors.

Wriedt and Murray [1] therefore took into account the results of Holmberg [7], McClaine and Coppel [10] and Arbuzov et al. [18] to assess the diagram in this area.

#### *Phase $Ti_xN_{1-x}-\delta$*

This phase is to be found in a wide range of compositions: from 30 to about 53 at.% N from the lowest temperatures to the solidus starting from 2623 K.

The only measurements related to this solidus affect the point of congruent fusion of  $Ti_xN_{1-x}$  at about 3223 K according to Friederich and Sittig [19], Agte and Moers [20] and more recently Ettmayer et al. [21], and 3563 K

according to Eron'yan et al. [22]. Wriedt and Murray [1] stated that only the point of fusion measured by Eron'yan at 47.5 at.% N is congruent and therefore accurate.

The terminal composition of the peritectic at 2623 K as measured by Palty et al. [8] is of 27 at.% N. Other authors have suggested higher figures: 29 at.% N [10,15] 38 at.% N [11] and even 42.3 at.% N [14].

Localization of the  $Ti_2N + Ti_xN_{1-x}/Ti_xN_{1-x}$  limit depends on the final composition of the peritectoid at the lowest temperature. Ehrlich [4], at 1473 K, sets the lower limit of nitrogen solubility in  $Ti_xN_{1-x}$  at 29.6 at.% N. According to McClaine and Coppel [10] this point is situated at about 29 at.% N. Khaenko et al. [5] report the same point at 34.5 at.% N and 1673 K, and Toth [11] and Wood [14] gave 38 at.% N and 42 at.% N respectively. It seems that the majority of authors gave a composition of the order of 30 at.% N for this limit. Wriedt and Murray [1] chose the description made by McClaine and Coppel [10] between 2623 and 1323 K.

Localization of the peritectoid  $Ti-\alpha-Ti_2N-\epsilon-Ti_xN_{1-x}-\delta$  has already been discussed as the composition of the  $Ti_2N-\epsilon$  phase.

Starting from 1323 K, the limit  $Ti_xN_{1-x}/Ti_xN_{1-x} + Ti_2N$  follows the congruent decomposition of  $Ti_2N$  to about 1073 K. In this temperature range, Holmberg [7] indicated a composition of about 40 at.% N at 1173 K and Khaenko et al. [5] gave 38 at.% N at 1073 K. From these data and those of Arbuzov et al. [18], Wriedt and Murray [1] placed the peritectoid  $\delta'-(Ti_2N-\epsilon)-(Ti_xN_{1-x}-\delta)$  at 1073 K with a terminal composition of 39 at.% N.

#### *Phase $Ti_5N_3-\delta'$*

This phase has been obtained by Lobier and Marcon [23] at a temperature of 773 K. Other authors have been able to obtain a phase presenting certain similarities at 773 K. Nagakura and Kusunoki [24] produced a structure close to  $\delta'$  in an alloy at 38 at.% N. Arbuzov et al. [18,25] found this phase associated with  $Ti_2N-\epsilon$  in a row of compositions stretching from 34 to 37 at.% N and with  $\delta$  for a nitrogen concentration from 38 to 40.5 at.% N.

The version given by Arbuzov et al. [18] was adopted by Wriedt and Murray [1].

#### *Thermodynamic data*

Much of the thermodynamic data related to the Ti-N system deals with the  $\delta$  phase.

The nitrogen pressure above titanium nitride has been measured by many different authors: Grieveson [2], nitrogen pressure at 1273 and 1673 K for  $X_N = 0.475-0.523$ ; McClaine and Coppel [10],  $P_{N_2}$  and  $P_{Ti}$  at 1479 and 2550 K for  $X_N = 0.447-0.495$ ; Andrievskii et al. [26],  $P_{N_2}$  and  $P_{Ti}$  at 1500 and 2550 K for  $X_N = 0.242-0.480$ ; Fesenko and Bolgar [27],  $P_{N_2}$  and  $P_{Ti}$  at

2241 K and for  $X_N = 0.50$ ; Dregger [28],  $P_{N_2}$  and  $P_{Ti}$  at 1727 and 2099 K for  $X_N = 0.50$ ; and Hoch et al. [29],  $P_{N_2}$  and  $P_{Ti}$  at 1987 and 2241 K for  $X_N = 0.44$ .

The standard enthalpies of formation have been also studied by Bolgar et al. [30] for  $X_N = 0.4623$ , Gal'braikh and Ariya [31] for  $X_N = 0-0.50$ , Morozova and Kernberg [32] for  $X_N = 0.125-0.495$ , and Stearns and Kohl [33] and Humphrey [35] for  $X_N = 0.50$ . Naylor [34] measured  $H_T - H_{ST}$  for  $X_N = 0.50$  for temperatures between 360 and 1735 K.

A few works can be found related to the specific heat. McDonald et al. [36] measured  $\Delta C_p$  for stoichiometric TiN over the temperature range 1300–2000 K.

## OPTIMIZATION OF THE PHASE DIAGRAM

The optimization of the Ti–N diagram was done using the optimization procedure developed by Lukas et al. [37] and based on the following data. (1) The experimental works on phase diagram are those reported by Wriedt and Murray [1], Grieveson [2], Nowotny et al. [3], Ehrlich [4], Khaenko et al. [5], Lashko et al. [6] and Holmberg [7]. (2) Selected thermodynamic data have been measured by McClaine and Coppel [10], Grieveson [2] for nitrogen and titanium partial pressures. The heats of formation taken into account were extracted from the work of Bolgar et al. [30], Humphrey [35] and Hoch et al. [29]. (3) Calculation of the partial Gibbs free energy of titanium, from the work of McClaine and Coppel [10], was done using the partial vapour pressure of pure titanium reported by Hultgren et al. [38].

A comparison of the partial vapour pressure measurements used is presented in Fig. 1.

The results of Hoch et al. [29] corroborate well enough the work of Andrievskii et al. [26] but are related to  $P_{N_2}$  measurements lower than those reported by McClaine and Coppel [10]. The latter authors compared their results with the partial vapour pressure measurements above stoichiometric titanium nitride reported in the Janaf tables [39] and with the study of Hoch et al. [29] and showed that the results are coherent. The results of Grieveson [2] are quite different from those quoted above. According to Hultgren et al. [38], Grieveson's measurements [2] are wrong because of the experimental method used.

### *Assessment method*

Considering the few measurements available on  $Ti_2N-\epsilon$  and  $Ti_5N_3-\delta'$  solid solutions, and their narrow fields of composition, these two phases ( $\epsilon$  and  $\delta'$ ) were considered to be intermetallic compounds with the formulae  $Ti_2N$  and  $Ti_5N_3$  respectively.

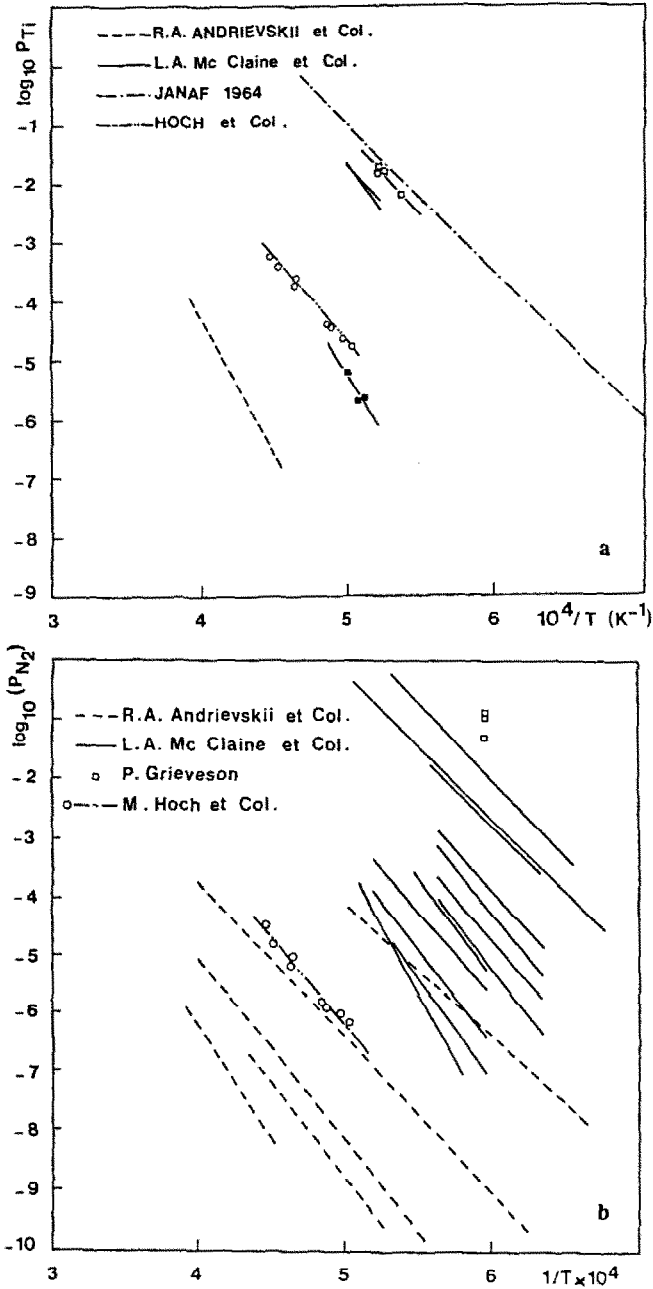


Fig. 1. Plots of  $\log_{10}(P_{Ti})$  (a) and  $\log_{10}(P_{N_2})$  (b) vs.  $1/T$ . Comparison between the measures of Hoch et al. [29], McClaine et al. [10], Andrievskii et al. [26] and Janaf [39].

The Gibbs free energy of the different solid solutions considered here have been described using an interstitial sublattice model [40] for Ti- $\alpha$ , Ti- $\beta$  and  $Ti_xN_{1-x}$ - $\delta$ , and with a simple substitution model for the liquid phase.

The interstitial sublattice model was first described by Hillert and Staffanson [40] and corresponds to a structure made of two sublattices: the first is full, filled with titanium atoms, and the second is composed of nitrogen atoms and vacancies. The solid-solution composition varies according to the substitution at the nitrogen vacancies within the second sublattice.

In the following,  $a$  and  $c$  denote the number of sites of each sublattice. The solid phase can then be described as  $(\text{Ti})_a(\text{Va},\text{N})_c$  where Va is the vacancy. With the site fraction  $Y_{\text{Ti}}$  for titanium,  $Y_{\text{Va}}$  for vacancies and  $Y_{\text{N}}$  for nitrogen atoms, the Gibbs free energy can be written as

$$G = Y_{\text{Ti}}Y_{\text{Va}}G_{\text{Ti}_a\text{Va}_c} + Y_{\text{Ti}}Y_{\text{N}}G_{\text{Ti}_a\text{N}_c} + cRT[Y_{\text{Va}} \ln Y_{\text{Va}} + Y_{\text{N}} \ln Y_{\text{N}}] \\ + Y_{\text{Va}}Y_{\text{N}}[L_{\text{VaN}}^0 + L_{\text{VaN}}^1(Y_{\text{Va}} - Y_{\text{N}})]$$

This last term represents the excess free energy resulting from interactions between the vacancies and the nitrogen atoms where  $L_{\text{Va,N}}^i$  is a function of temperature:

$$L_{\text{Va,N}}^i = A_{\text{Va,N}}^i - B_{\text{Va,N}}^i \cdot T$$

The site fractions are defined as

$$Y_{\text{Ti}} = 1 \quad Y_{\text{Va}} = \frac{n_{\text{Va}}}{n_{\text{Va}} + n_{\text{N}}} \quad Y_{\text{N}} = 1 - Y_{\text{Va}}$$

According to the study done by Frisk [41] on the systems Cr–N, Fe–N, Mo–N and Cr–Mo–N the following values were found:  $a = 1$ ,  $c = 0.5$  for Ti- $\alpha$ ;  $a = 1$ ,  $c = 3$  for Ti- $\beta$ ; and  $a = 1$ ,  $c = 1$  for Ti $_x$ N $_{1-x-\delta}$ .

The Gibbs free energies of formation of the stoichiometric compounds were calculated using Lukas' optimization in accordance with equation

$$\Delta G(T) = A - BT + CT(1 - \ln T) - DT^2/2 - ET^{-1}/2 - FT^3/6$$

where the last four terms are linked to the specific heat as follows:

$$\Delta C_p(T) = C + DT + ET^{-2} + FT^2$$

The thermodynamic functions and the terms  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ ,  $F$  optimized by Lukas have been calculated with respect to Ti-h.c.p. and  $1/2 N_{2g}$ .

The values used for the lattice stabilities of the pure components come from the SGTE assessment [42] except for liquid nitrogen, the value for which was extracted from the work of Frisk [41].

The following values were used:

$$G_{\text{Ti,h.c.p.}}^{\circ} - G_{\text{Ti,h.c.p.}}^{\circ} = 0$$

For  $298.15 < T < 900.00$

$$G_{\text{Ti,h.c.c.}}^{\circ} - G_{\text{Ti,h.c.p.}}^{\circ} = 6787.882 + 1.098987T - 1.5835T \ln(T) + 4.11413E - 3T^2 \\ - 0.385519E - 6T^3 - 65428T^{-1}$$



TABLE 1

Data for the  $\alpha$ ,  $\beta$ ,  $\delta$  and  $\epsilon$  forms of TiN: all data in J (g atom)<sup>-1</sup>*Liquid phase (L)*Formula: (Ti, N)<sub>1</sub>

$$\Delta G^E(L) = x_{Ti}x_N(-166556.8 - 59.72463T)$$

*b.c.c. solid solution (Ti- $\beta$ )*Formula: (Ti)<sub>0.25</sub>(Va,N)<sub>0.75</sub>

$$\Delta G^E(Ti-\beta) = Y_{Va}Y_N(-1785086.5)(0.25)$$

$$G_{Ti_{0.25}N_{0.75}-\beta} - 0.25G_{Ti_{b.c.c.}}^{\circ} - 0.75G_{\frac{1}{2}N_2(g)}^{\circ} = 229649.6 + 44.82970T$$

*h.c.p. solid solution (Ti- $\alpha$ )*Formula: (Ti)<sub>0.667</sub>(Va,N)<sub>0.333</sub>

$$\Delta G^E(Ti-\alpha) = Y_{Va}Y_N(16332.2 - 15.26016T)(2/3)$$

$$G_{Ti_{0.667}N_{0.333}-\alpha} - (2/3)G_{Ti_{h.c.p.}}^{\circ} - (1/3)G_{\frac{1}{2}N_2(g)}^{\circ} = -120698.6 + 31.11770T$$

*Ti<sub>x</sub>N<sub>1-x</sub>- $\delta$  solid solution*Formula: (Ti)<sub>0.5</sub>(Va,N)<sub>0.5</sub>

$$\Delta G^E(Ti_xN_{1-x}-\delta) = Y_{Va}Y_N[-40381.7 - 2.41202T + 5199.3(Y_{Va} - Y_N)](0.5)$$

$$G_{Ti_{0.5}N_{0.5}-\delta} - 0.5G_{Ti_{h.c.p.}}^{\circ} - 0.5G_{\frac{1}{2}N_2(g)}^{\circ} = -175519.5 + 119.33832T + 12.061226T(1 - \ln T)$$

$$+ 0.01205317T^2/2 + 1100959T^{-1}/2 - 2.9956 \cdot 10^{-6}T^3/6$$

*Ti<sub>2</sub>N- $\epsilon$* 

$$G_{Ti_{0.667}N_{0.333}-\epsilon} - (2/3)G_{Ti_{h.c.p.}}^{\circ} - (1/3)G_{\frac{1}{2}N_2(g)}^{\circ} = -125000 + 32.4157T$$

*Ti<sub>0.625</sub>N<sub>0.375</sub>- $\delta'$* 

$$G_{Ti_{0.625}N_{0.375}-\delta'} - (0.625)G_{Ti_{h.c.p.}}^{\circ} - (0.375)G_{\frac{1}{2}N_2(g)}^{\circ} = -148000 + 49.37758T$$

TABLE 2

Three-phase equilibria and congruent transformations in the Ti-N system

Equilibrium	Calculated			Wriedt and Murray [1]				
	T (K)	at.% N		T (K)	at.% N			
L + Ti- $\alpha$ = Ti- $\beta$	2318	4.51	14.45	9.71	2293 ± 25	4.0	12.5	6.2
L + TiN- $\delta$ = Ti- $\alpha$	2621	11.65	30.25	20.51	2623 ± 25	15.2	28	20.5
TiN- $\delta$ = Ti- $\alpha$ + Ti <sub>2</sub> N	1393	29.69	23.08	33.33	1323 ± 60	30	23	33.3
Ti <sub>2</sub> N- $\epsilon$ + TiN- $\delta$ = Ti <sub>5</sub> N <sub>3</sub> - $\delta$	874	33.33	43.80	37.50	1073 ± 100	34	39	37.5
<i>Congruent transformations</i>								
Ti- $\alpha$ = Ti- $\beta$	1155	0	1156 ± 3	0				
Ti- $\beta$ = L	1941	0	1943 ± 6	0				
Ti <sub>2</sub> N- $\epsilon$ = T : N- $\delta$	1435	33.33	1373	33.33				
TiN- $\delta$ = L	3625	48.41	3563	47.4				

For  $900.00 < T < 1155.00$

$$G_{\text{Ti}_{\text{b.c.c.}}}^{\circ} - G_{\text{Ti}_{\text{h.c.p.}}}^{\circ} = 6539.775 + 1.726127T - 1.5881T \ln(T) \\ + 3.539455E - 3T^2 - 0.187926E - 6T^3 - 35472T^{-1}$$

For  $1155.00 < T < 1941.00$

$$G_{\text{Ti}_{\text{b.c.c.}}}^{\circ} - G_{\text{Ti}_{\text{h.c.p.}}}^{\circ} = 5758.572 + 38.389865T - 7.4305T \ln(T) \\ + 9.363565E - 3T^2 - 1.048054E - 6T^3 - 525093T^{-1}$$

For  $1941.00 < T < 3000.00$

$$G_{\text{Ti}_{\text{b.c.c.}}}^{\circ} - G_{\text{Ti}_{\text{h.c.p.}}}^{\circ} = -1376.09 - 0.158585T + 4.17375E31T^{-9}$$

For  $298.15 < T < 1941.00$

$$G_{\text{Ti}_{\text{liq}}}^{\circ} - G_{\text{Ti}_{\text{h.c.p.}}}^{\circ} = 12862.13 - 7.355375T - 1.565748E - 21T^7$$

For  $1941.00 < T < 3000.00$

$$G_{\text{Ti}_{\text{liq}}}^{\circ} - G_{\text{Ti}_{\text{h.c.p.}}}^{\circ} = 14595.653 - 8.293138T - 2.96577E31T^{-9}$$

For  $298.15 < T < 6000.00$

$$G_{\text{N}_{\text{liq}}}^{\circ} - G_{\frac{1}{2}\text{N}_2(\text{g})}^{\circ} = 29950 + 59.02T$$

The Gibbs free energy of formation of  $\text{Ti}_{0.5}\text{N}_{0.5}$  f.c.c. with respect to Ti h.c.p. and  $\frac{1}{2}\text{N}_2(\text{g})$  was calculated from the results reported in the 1985 Janaf tables [39].

The different terms of the Gibbs free energy of each solid solution were calculated using the program developed by Lukas et al. [37], taking into account all the thermodynamic data quoted above.

TABLE 3

Comparison between the values reported by McClaine et al. [10] at 1900 K and the results obtained with the Lukas procedure

$X_{\text{Ti}}$	$G_{\text{int}}^{1900}$	$G_{\text{int}}^{1900}$
	McClaine et al. [10]	Present work
0.71	-59008	-58101
0.68	-64187	-63164
0.65	-69023	-67792
0.60	-76404	-74313
0.55	-80747	-78799
0.53	-80642	-79764
0.52	-80927	-79986
0.51	-80751	-79960
0.5	-79923	-79406

### Results and discussion

The excess Gibbs free energy  $\Delta G^E$ , coefficients for the liquid phase (L), the b.c.c. (Ti- $\beta$ ), h.c.p. (Ti- $\alpha$ ) and  $Ti_xN_{1-x}$ - $\delta$  solid solutions in the temperature range 298.15–4000 K and the Gibbs energy of formation of the stable stoichiometric compounds (Ti<sub>2</sub>N- $\epsilon$ , Ti<sub>0.625</sub>N<sub>0.375</sub>- $\delta$  and TiN- $\delta$ ) and of the metastable ones (TiN<sub>3</sub>- $\beta$ , Ti<sub>2</sub>N- $\alpha$ ) are presented in Table 1.

In doing the optimization by the procedure developed by Lukas et al. [37], the enthalpies of formation of the intermetallic compounds were estimated in order to keep the temperature of the three phases in equilibrium (Ti<sub>2</sub>N-

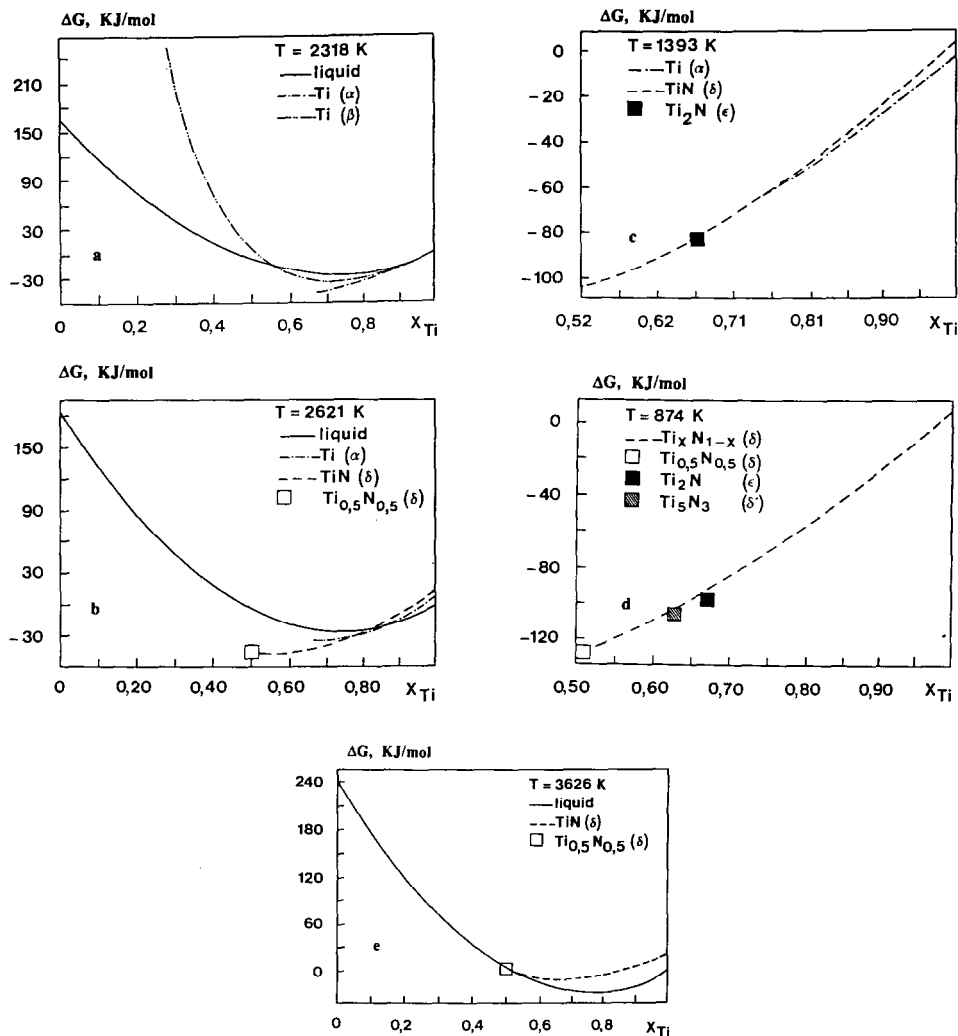


Fig. 2. Gibbs free energies of formation of the various compounds and solutions in equilibrium at the three-phase equilibria and the congruent transformations: (a)  $T = 2318$  K; (b)  $T = 2621$  K; (c)  $T = 1393$  K; (d)  $T = 874$  K; (e)  $T = 3626$  K.

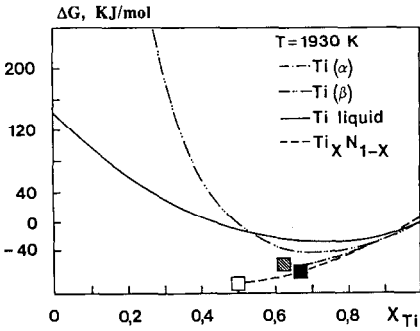


Fig. 3. Gibbs free energies of formation of the various compounds and solutions at  $T = 1930$  K.

$Ti_5N_3 - Ti_xN_{1-x}$ ) high enough to be in accordance with the diagram reported by Wriedt and Murray [1]. The temperatures and compositions of the three-phase equilibria and congruent transformations calculated with the optimized Gibbs free energies of formation are compared with the selected values of Wriedt and Murray [1] in Table 2. The data given in Table 2 show that all the equilibria of the three phases are in agreement with the results

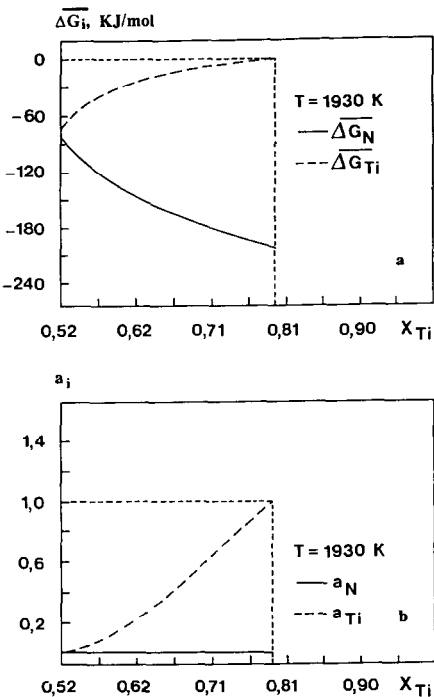


Fig. 4. Partial Gibbs free energies (a) and activities (b) of nitrogen and titanium in the  $Ti_x N_{1-x}$ - $\delta$  phase.

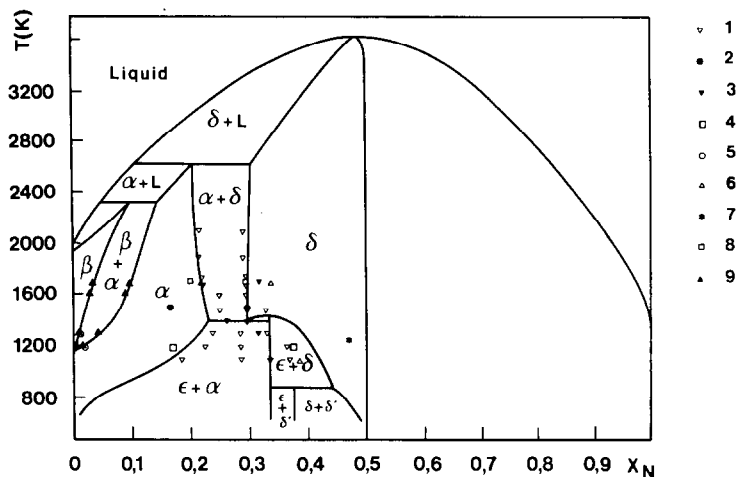


Fig. 5. Phase diagram of the Ti-N system, without the gaseous phase, calculated with the Lukas optimization procedure and comparison with the experimental results linked to the limit between the various fields according the following authors: (1) Andrievskii et al. [26]; (2) Ehrlich [4]; (3) Grieveson [2]; (4) Holmberg [7]; (5) Jaffee et al. [13]; (6) Khaenko et al. [5]; (7) Lashko et al. [6]; (8) Stone and Margolin [12].

selected by Wriedt and Murray [1], except for  $Ti_2N-\epsilon + Ti_xN_{1-x}-\delta = Ti_5N_3-\delta'$  for the reasons quoted above. Moreover, there is a lack of data in this domain.

Variations in the Gibbs free energies of formation of the phases are reported as functions of the composition at the temperatures of the various three-phase equilibria in Fig. 2. In addition, the Gibbs free energy of formation of the various species at 1930 K is given in Fig. 3. The activity and the partial Gibbs free energies of the titanium and the nitrogen at this temperature are shown in Fig. 4.

In Table 3, the integral Gibbs free energies of formation of titanium nitride referred to the stable state at 1900 K are compared with the values deduced from the work of McClaine and Coppel [10] by Teyssandier et al. [43] as a function of  $X_{Ti}$ . The results obtained are in accordance with the values reported by McClaine and Coppel [10]. In spite of a slight difference between the selected values of the thermodynamic functions and the available results, this optimization led to a good computational model of the experimental results taken into account in the Lukas procedure.

The phase diagram (Fig. 5) shows good agreement between experimental measurements and the calculated diagram. While the values reported by Wolff et al. [15] were not taken into account here, they are in accordance with our results.

A more theoretical and accurate work would require more experimental knowledge of the limits between the different fields in the nitrogen-rich

domain at moderate and low temperatures. However, measurements made at high temperature are not yet available in sufficient number.

## REFERENCES

- 1 H.A. Wriedt and J.L. Murray, *Bull. Alloy Phase Diagr.*, 8 (1987) 378.
- 2 P. Grieveson, *Proc. Br. Ceram. Soc.*, 8 (1967) 137.
- 3 H. Nowotny, F. Benesovsky, C. Brukl and O. Schob, *Monatsh. Chem.*, 92 (1961) 403.
- 4 P. Ehrlich, *Z. Anorg. Chem.*, 259 (1949) 1.
- 5 V.V. Khaenko, E.T. Kachkovskaya and A. Frenkel, *Poroshk. Metall.*, 11 (1972) 34.
- 6 N.F. Lashko, A.I. Glazova and E.I. Gus'kova, *Izv. Akad. Nauk SSSR. Metal.*, 2 (1968) 224.
- 7 B. Holmberg, *Acta Chem. Scand.*, 16 (1962) 1255.
- 8 A.E. Palty, H. Margolin and J.P. Nielsen, *Trans. Am. Soc. Mater.*, 46 (1954) 312.
- 9 M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
- 10 L.A. McClaine and C.P. Coppel, *Technical Report AFML, -TR-65299, Part II*, Arthur D. Little, Cambridge, MA, 1966.
- 11 L.E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971.
- 12 L. Stone and H. Margolin, *Trans. AIME*, 197 (1953) 1498.
- 13 R.I. Jaffee, H.R. Odgen and D.J. Maykuth, *Trans. AIME*, 188 (1950) 1261.
- 14 F.W. Wood, Ph.D. Thesis, Oregon State University, 1974.
- 15 L. Wolff, G. Bastin and H. Heijligers, *Solid State Ion.*, 16 (1985) 105.
- 16 N.R. McDonald and G.R. Wallwork, *Oxid. Met.*, 2 (1970) 263.
- 17 J.P. Bars, E. Etchessahar, J. Debuigne and A. Lerous, *C. R. Acad. Sci., Ser. C*, 278 (1974) 581.
- 18 M.P. Arbutov, S.Ya. Golub and B.V. Khaenko, *Izv. Akad. Nauk SSSR, Neorg. Mat.*, 13 (1977) 1779.
- 19 E. Friederich and L. Sittig, *Z. Anorg. Chem.*, 143 (1925) 293.
- 20 C. Agte and K. Moers, *Z. Anorg. Chem.*, 198 (1931) 233.
- 21 P. Etmayer, R. Kieffer and F. Hattinger, *Metallica*, 28 (1974) 1151.
- 22 M.A. Eron'yan, R.G. Avarbeac and T.N. Danisina, *High Temp.*, 14 (1976) 359.
- 23 G. Lobier and J.P. Marcon, *C. R. Acad. Sci., Ser. C*, 268 (1969) 1132.
- 24 S. Nagakura and T. Kusunoki, *J. Appl. Crystallogr.*, 10 (1977) 52.
- 25 M.P. Arbutov, S.Ya. Golub and B.V. Khaenko, *Phys. Met. Metallogr. (USSR)*, 44 (1977) 194.
- 26 R.A. Andrievskii, Yu.F. Khromov, D.E. Svistunov and R.S. Yurkova, *Russ. J. Phys. Chem.*, 57 (1983) 996.
- 27 V.V. Fesenko and A.S. Bolgar, *Poroshk. Metall.*, 1 (1963) 17.
- 28 L.H. Dregger, Ph.D. Thesis, University of Wisconsin, *Diss. Abstr.*, 22 (1962) 3423.
- 29 M. Hoch, D.P. Dingley and H.L. Johnston, *J. Am. Ceram. Soc.*, 77 (1955) 304.
- 30 A.S. Bolgar, E.A. Ryklis and V.V. Fesenko, *Heat Trans., Sov. Res.*, 5 (1973) 71.
- 31 E.I. Gal'braikh and S.M. Ariya, *Russ. J. Phys. Chem.*, 44 (1970) 1578.
- 32 M.P. Morozova and M.M. Kernberg, *Russ. J. Phys. Chem.*, 40 (1966) 604.
- 33 C.A. Stearns and F.J. Kohl, *High Temp. Sci.*, 2 (1970) 146.
- 34 B.F. Naylor, *J. Am. Ceram. Soc.*, 68 (1946) 370.
- 35 G.L. Humphrey, *J. Am. Ceram. Soc.*, 73 (1951) 2261.
- 36 R.A. McDonald, F.L. Oetting and H. Prophet, *Report N64-18824*, The Dow Chemical Co., Midland, MI, 1963.
- 37 H.L. Lukas, E.-Th. Henig and B. Zimmermann, *Calphad*, 1 (1977) 225.

- 38 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of the Thermodynamic Properties of Binary Alloys, American Society of Materials, Ohio, 1973.
- 39 Janaf Thermochemical Tables, 3rd edn., American Chemical Society, The American Institute of Physics, National Bureau of Standards, Washington, DC, 1985.
- 40 M. Hillert and L.I. Staffanson, Acta Chem. Scand., 24 (1970) 3618.
- 41 K. Frisk, TRITA-MAC-0393, April 1989, Division of Physics and Metallurgy, Royal Institute of Technology, Stockholm, Sweden.
- 42 SGTE (Scientific Group Thermodata Europ), Data base, 1987.
- 43 F. Teyssandier, M. Ducarroir and C. Bernard, Calphad, 8 (1984) 233.