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Solid-State Phase Equilibria in the Titanium-Aluminum-Nitrogen System

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The 1273 K isothermal section of the Ti-Al-N phase diagram was studied using modern methods of physical and chemical analyses. The data obtained by various techniques are in good agreement and in harmony with the results of thermodynamic calculations. It has been reliably established that AlN can coexist with TiN_{1-x}, Ti_2AlN, and $TiAl_3$; the ternary nitride Ti_2AlN can be in equilibrium with $TiAl_3$, AlN, $TiAl_2$, TiAl, TiN_{1-x}, and Ti_3AlN; the solid solution based on α(Ti) coexists with Ti_3Al, Ti_3AlN, TiN_{1-x}, and Ti_2N. Literature data on phase equilibria in the Ti-Al-N system were analyzed, and a 1273 K isothermal section of the phase diagram has been suggested.

1. Introduction

Considerable attention has recently been given to development of advanced composite materials based on aluminum nitride (AlN) and elements of the IVB or VB groups. For example, the authors of [1995Kim], [1997Pet], and [2001Kim] proposed a series of methods of producing multilayer composites based on the Ti-Al-N system. In [1995Ino], a method of deposition of the nitride thin films on the Ti-Al alloy surface with the aim to raise their oxidation resistance was described. Development of these types of materials requires knowledge of the phase equilibria. The Ti-Al-N phase diagram is relatively complicated due to formation of ternary nitrides (Ti_3AlN, Ti_2AlN, $Ti_3Al_2N_2$). The major part of the available data on the phase equilibria in this system was obtained by Schuster et al. [1984Sch, 1985Sch], who examined the phase compositions of annealed samples prepared by pressing powders of binary constituents. Other experimental approaches used in later works [1998Che, 1999And, 2000Pro1] often led to contradictory results. Moreover, the question about whether equilibrium was established in all investigated cases remains open. The purpose of the present research is to resolve the contradictions and to construct the solid-state part of the isothermal section of the Ti-Al-N phase diagram at 1273 K in the temperature neighborhood where the composite materials are usually fabricated.

2. Materials and Experimental Procedures

Modern physical and chemical methods used in the present work allowed the attainment of the same final state of alloys from various starting points and via different paths and in this manner to obtain exhaustive proofs that equilibria were reached in the experiments. The investigations were performed by prolonged heating of alloys for attainment of equilibrium by the method of diffusion pairs and by nitriding from a gaseous phase.

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To accomplish the first approach, ternary Ti-Al-N alloys were prepared by arc melting of AlN powder (99.0%), iodide titanium (99.99%), and Al (99.999%) under a pure argon atmosphere. The synthesized samples were subjected to prolonged (~670 h) isothermal annealing in evacuated quartz tubes at 1273 K. Two types of diffusion pairs that can be schematically described as AlN/Ti and AlN/Ti/AlN were used in experiments. They were obtained by overlaying of Ti on an aluminum nitride plate in an arc furnace, or by diffusion welding of AlN and Ti plates in vacuum at 1273 K. The resultant composites were then annealed at 1273 K for 200 h. Nitriding from a gaseous phase required a more complicated procedure [2002Abr]. Initially binary Ti-Al alloys were synthesized in an electric arc furnace and homogenized in evacuated quartz tubes at 1273 K. Then samples of these alloys in the powdered form prepared by diamond filing of the arc furnace ingots or as plates were exposed to pure nitrogen atmosphere at 1273 K under a pressure 5 MPa. The duration of treatment varied from 1 to 9 h.

The alloy composition and the distribution of elements in the diffusion zones were investigated by electron probe microanalysis (EPMA), optical and scanning electron microscopy (SEM), with use of CAMEBAX-microbeam and JEOL devices. The phase composition of the samples was determined by powder x-ray diffraction analyses (XRD; DRON-4, STADI-P).

3. Binary Systems, Composition and Crystal Structure of Compounds

The binary Ti-Al phase diagram was investigated rather thoroughly [1990Mur, 1996Spe]. However, the results of these studies differ considerably. The phase diagram proposed by [1996Spe*], shown in Fig. 1, seems to be more realistic because it was confirmed by the results of later researches [1999Jun, 2000Oka]. The composition and the crystal structure of the Ti-Al phases are presented in Table 1. The compound Ti_5Al_{11} seems to exist in the range of 1258 K [1996Spe] to 1423 K [1990Mur], although the

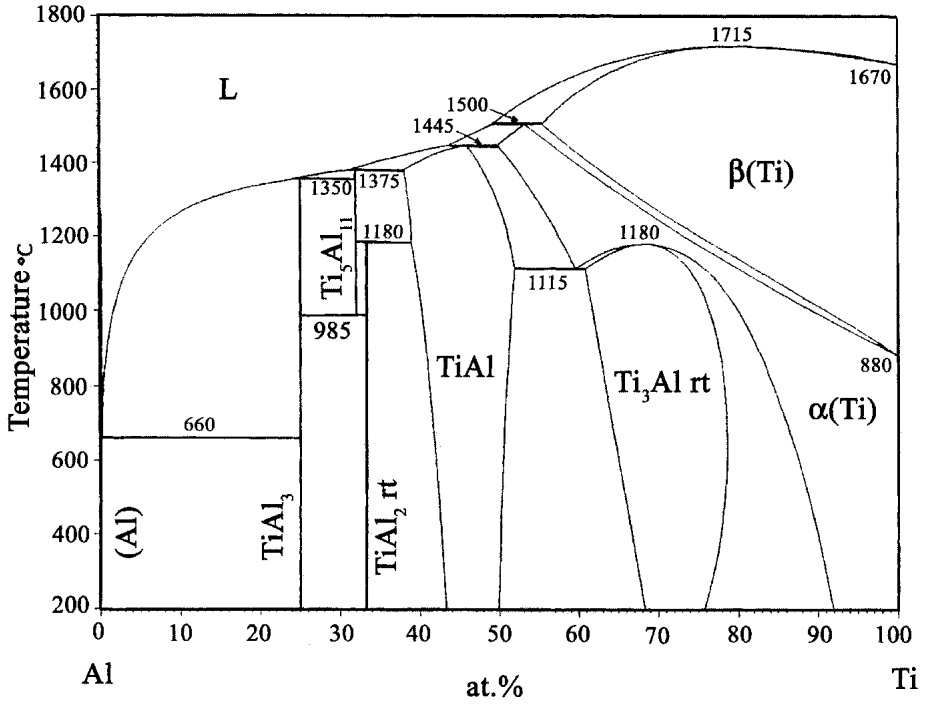

Fig. 1 Phase diagram of the Ti-Al system [1996Spe]

Table 1 Crystalline structure and lattice parameters of the phases in the Ti-Al-N system

Phase	Structure type	Space group	Lattice parameters, Å			Reference
			a	*b*	*c*	
α(Ti)	Mg	$P6_3/mmc$	2.950(1)	…	4.681(2)	[1985Mro]
β(Ti)	W	$Im\bar{3}m$	3.28	…	…	[1963Jam]
	Ti	$P6/mmm$	4.625	…	2.813	[1983Sri1]
Ti_3Al	Mg_3Cd	$P6_3/mmc$	5.793	…	4.623	[1983Sri2]
TiAl	CuAu	$P4/mmm$	4.001	…	4.071	[1983Sri2]
$TiAl_2$	$ZrGa_2$	$Cmmm$	12.0944	3.9591	4.0315	[1990Sch]
	$HfGa_2$	$I4_1/amd$	3.971(1)	…	24.313(1)	[2000Bra]
Ti_5Al_{11}	$Ti(Ti_{0.5}Al_{0.5})Al_2$	$Pmmm$	4.0262	3.9617	4.0262	[1990Sch]
	$CuTi_3$	$P4/mmm$	4.030(1)	…	3.955(1)	[1994Bra]
	$Ti(Ti_{0.25}Al_{0.75})Al_2$	$I4/mmm$	3.9230	…	16.5349	[1990Sch]
	$Ti(Ti_{0.14}Al_{0.86})Al_2$	$P4/mmm$	3.9053	…	29.1963	[1990Sch]
$TiAl_3$	$TiAl_3$	$I4/mmm$	3.8537	…	8.5839	[1990Kum]
AlN	…	$P6_3mc$	3.1114	…	4.9792	[1986Wri]
$TiN_{0.43}$	TiS	$R\bar{3}mh$	2.9809(4)	…	21.6642(85)	[1996Len]
$TiN_{0.58}$	$Sc_{0.67}Te$	$R\bar{3}mh$	2.9795	…	28.9649	[1986Len]
δ′	$TiN_{0.5}$	$I4_1/amd$	4.1493(2)	…	8.7858(5)	[1985Chr]
Ti_2N	TiO_2	$P4_2/mnm$	4.9452	…	3.0342	[1986Len]
TiN_{1-x}	NaCl	$Fm\bar{3}m$	4.240	…	…	[1993Jia]
TI_3AlN	Re_3B	$Pm\bar{3}m$	4.112	…	…	[1985Sch]
Ti_2AlN	Cr_2AlC	$P6_3/mmc$	2.9912	…	13.621	[1984Sch]
$Ti_3Al_2N_2$	$Ti_3Al_2N_2$	$P31c$	2.990	…	23.3854	[2000Pro1]
	$Ti_3Al_2N_2$	$P6_3mc$	2.9875	…	23.350	[1985Sch]
	Ti_4AlN_3	$P6_3/mmc$	2.9880	…	23.372(2)	[1984Sch]
	Ti_3AlN_2	$P6_3/mmc$	2.660	…	23.3854	[1997Lee]

exact temperature interval of its appearance is not finally established.

The constitution of the Al-N diagram in the nitrogen concentration range of 0-50 at.% was proposed by [1986Wri] and is shown in Fig. 2. Thermodynamic calculations of the phase equilibria in the intervals of temperature

23-3273 K and nitrogen concentrations 0-100 at.% were carried out by [1984Jon] and [1992Hil]. There is only one stoichiometric compound AlN in this system. Crystallographic data for this phase are included in Table 1.

The Ti-N phase diagram was investigated in detail [1987Etc], [1990Wri], [1991Vah], [1991Etc], and [1993Gus] with results shown in Fig. 3. Three intermediate phases: TiN_{1-x}, Ti_2N, and δ′-phase were found in the system (Table 1). The δ′-compound decomposes at 1073 K to TiN_{1-x} and Ti_2N via a peritectoid reaction.

There are three ternary nitrides Ti_3AlN, Ti_2AlN, and $Ti_3Al_2N_2$ in the Ti-Al-N system in addition to binary compounds [1984Sch] with some third-component solubility. Crystallographic data are included in Table 1. The Ti_3AlN

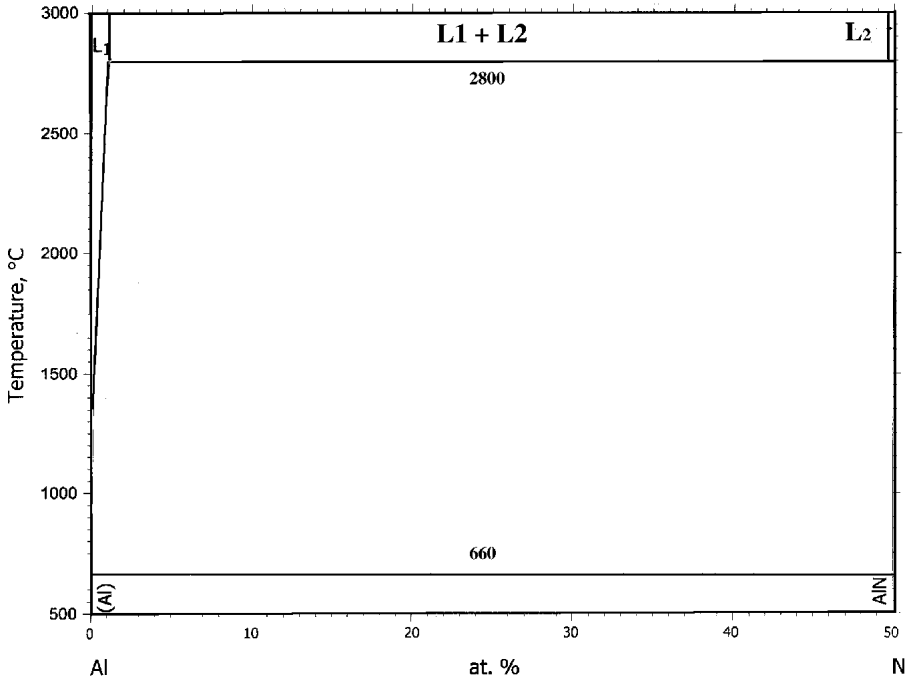

Fig. 2 Phase diagram of the Al-N system [1986Wri]

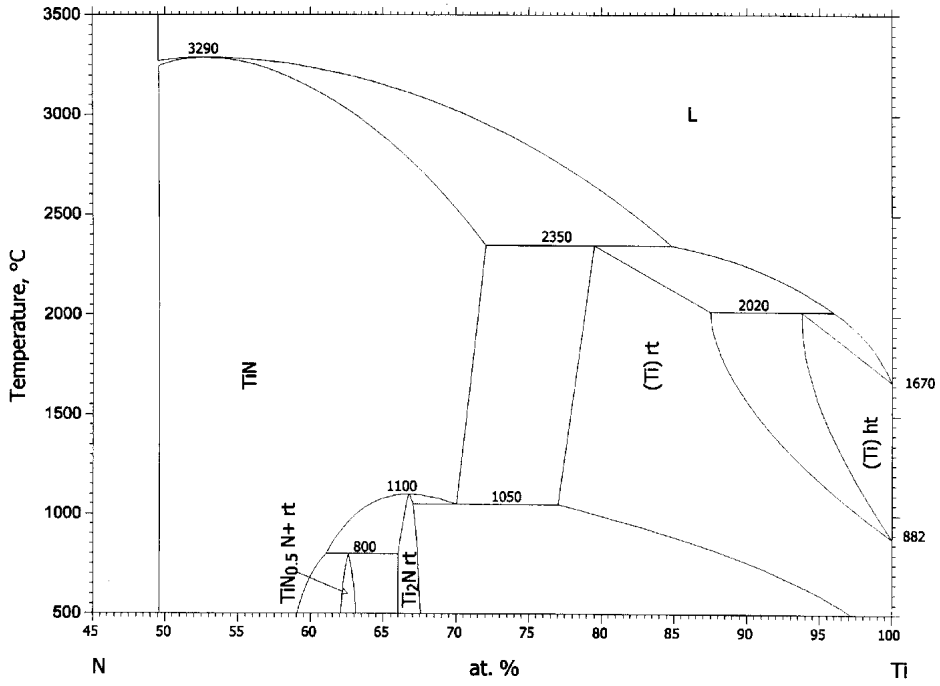

Fig. 3 Phase diagram of the Ti-N system [1990Wri]

phase has an insignificant field of homogeneity. The hexagonal H-phase, Ti_2AlN is isostructural with the similar phase, Ti_2AlC, (structure type Cr_2AlC) and possesses some area of homogeneity, with a deficit of nitrogen [1984Sch, 1985Sch, 1997Dur]. The $Ti_3Al_2N_2$ compound exists in the temperature interval 1473-1673 K [1984Sch, 1998Che]. Its composition is not established exactly. According to [1997Lee] and [1999Iva] this phase is isostructural with the Ti_3AlC_2 compound and its composition can be characterized by the formula $Ti_3Al_{1-x}N_2$. [1998Bar] confirmed the conclusions of [1984Sch] and supported the $Ti_3Al_2N_2$ formula for the compound composition. However, in later works [2000Pro1] they changed their point of view and decided that the most Al-rich ternary nitride had the composition Ti_4AlN_{3-x}. Some physical properties of this compound were investigated [2000Pro2, 2000Bar].

4. Experimental Results

The results of preliminary experiments have revealed that the most effective and informative method of determining phase equilibria in the Ti-Al-N system consists of nitriding powdered samples. The chemical and phase compositions of the Ti-Al alloys used in these types of experiments are given in Table 2. The XRD analysis of the binary samples quenched after prolonged heating at 1273 K allowed specifying the Ti-Al phase diagram. It was established that Ti_5Al_{11} phase is not stable at 1273 K so that the lowest temperature of its existence is higher than suggested in [1996Spe]. According to the XRD results, 1 h isothermal annealing at 1273 K in nitrogen atmosphere under pressure of 5 MPa results in formation of the ternary compound Ti_2AlN in the first five alloys of Table 2. The lattice parameters of the Ti_2AlN phase showed no significant dependence on the composition of the initial samples and amounted to $a = 2.986(9)$ Å and $c = 13.622(5)$ Å, which counts in favor of the narrowness of its homogeneity range. The relative quantities of the coexisting phases in the samples subjected to nitriding were evaluated from the XRD patterns, and the results are presented in Fig. 4. They confirm the existence in the Ti-Al-N system of following three-phase regions: $TiAl_3$-Ti_2AlN-AlN, Ti_2AlN-AlN-TiN_{1-x}, $TiAl_3$-$TiAl_2$-Ti_2AlN, and Ti_2N-TiN_{1-x}-α(Ti).

Table 2 Chemical and phase compositions of the powdered Ti-Al alloys before and after annealing in nitrogen atmosphere at $T = 1273$ K, $p(N_2) = 5$ MPa

	Initial composition, at.%		Phase composition	
No.	Ti	Al	Before nitriding	After nitriding
1	25.6	74.4	$TiAl_3$, $TiAl_2$	Ti_2AlN, $TiAl_3$ AlN
2	38.3	61.7	$TiAl_2$, TiAl	Ti_2AlN, $TiAl_3$, $TiAl_2$
3	54.9	45.1	TiAl, Ti_3Al	Ti_2AlN, TiN_{1-x}, AlN
4	69.9	30.1	Ti_3Al	Ti_2AlN, TiN_{1-x}
5	77.1	22.9	Ti_3Al	Ti_2AlN, TiN_{1-x}
6	89.1	10.9	α(Ti)	TiN_{1-x}, Ti_2N, α(Ti)

The nitriding of compact samples (in the form of plates) of the Ti-Al binary alloys for time intervals varying from 1 to 9 h has shown that this approach to investigation of phase equilibria in the system under study is not effective. The analysis of the structure of the formed diffusion zones, carried out in transverse sections of the samples by means of the SEM and XRD techniques, has revealed only aluminum and titanium nitride particles with the size of 2-10 μm that were formed on the sample surfaces. No ternary nitrides were found. Thus, the interaction of the compact alloys with nitrogen resulted in rapid formation of a TiN_{1-x} + AlN surface layer that was in equilibrium with the gas atmosphere and hampered penetration of nitrogen into the metal volume.

Proofs of reliability of the data established by nitriding of powdered alloys have been obtained in the diffusion pairs experiments. The EPMA, SEM, and XRD studies of the diffusion zones have revealed that two intermediate layers appeared at the AlN/Ti boundary after 200 h annealing of the samples synthesized by overlaying of Ti on aluminum nitride plates: a layer of titanium nitride TiN_{1-x} with inclusions of the ternary nitride Ti_3AlN and a layer of the α(Ti)-based phase containing up to 19 at.% aluminum. Figure 5(a) shows the structure of the diffusion zone in the AlN/ titanium layer 150 μm thick/AlN sample formed after annealing for 200 h. The layer nearest the aluminum nitride layer was about 30 μm thick and composed of titanium nitride TiN_{1-x}. The next layer was based on the Ti_3AlN compound with inclusions of TiN_{1-x}. The numbers in this figure indicate the points where the chemical composition was determined by the EPMA technique. The results are given in Table 3. As the method did not allow measurement of nitrogen content, only the ratios of Ti concentration to Al concentration are shown in this table. The diffusion pairs experiments as a whole indicate clearly that there are the AlN-TiN_{1-x}, TiN_{1-x}-Ti_3AlN, and Ti_3AlN-α(Ti) conodes at the 1273 K isothermal section of the Ti-Al-N diagram, which is in perfect accordance with the data of Table 2.

Establishment of the equilibrium line positions in Ti-rich alloys was complicated because the ternary nitride Ti_3AlN was formed very slowly. To solve this problem, traditional experiments of prolonged heating were carried out. Two types of specimens were prepared for this purpose by melting of Ti with AlN, with a mole ratio of Ti to AlN of 3/1 in one type and 2/1 in the other. The constant phase composition TiN_{1-x} + Ti_3AlN + α(Ti) in specimens of the first type was attained after only 200 h of isothermal heating at 1273 K and remained unchanged on further annealing up to 670 h. The ratio Ti/Al in α(Ti) was about 81/19. According to the results of SEM and XRD studies, four phases, TiN_{1-x}, Ti_3AlN, α(Ti), and Ti_3Al, existed in samples of the second type after 200 h annealing (Fig. 5b), the Ti_3AlN phase was formed around titanium nitride particles (Fig. 5b). Evidently equilibrium was not reached in this latter case. Longer heating changed the phase composition to TiN_{1-x} + Ti_3AlN + α(Ti), which remained constant on further processing up to 670 h. Figure 6 shows an x-ray diffraction pattern obtained from the second type specimen after 670 h of annealing. The lattice parameter a of the Ti_3AlN phase was equal to 4.1127(17) Å.The results of the chemical analysis carried

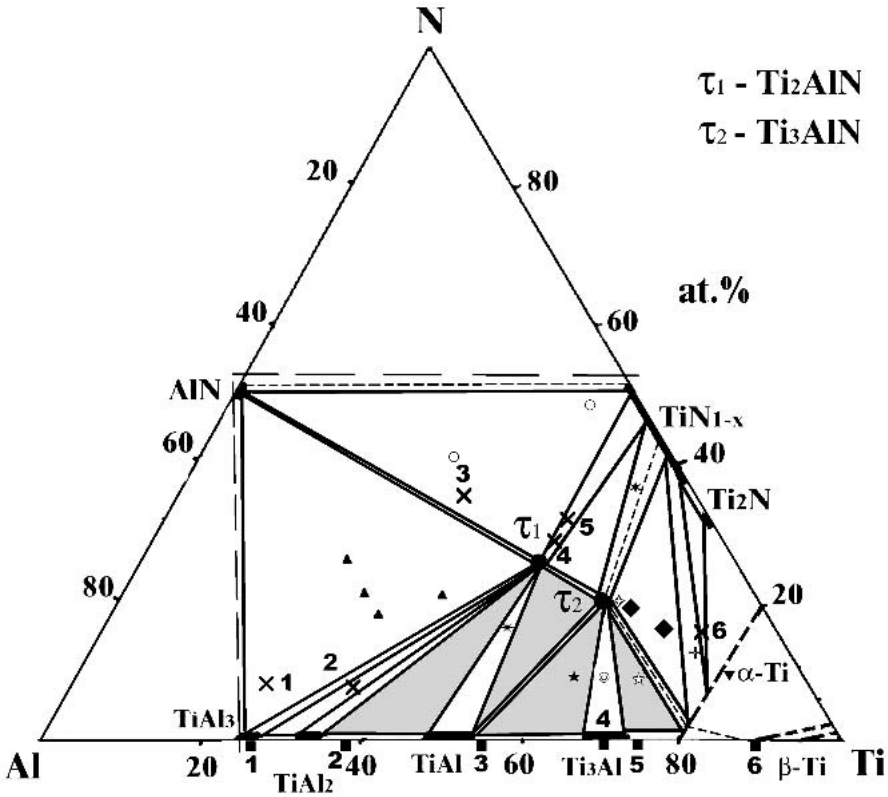

Fig. 4 Isothermal section of the Ti-Al-N phase diagram at 1273 K. Present work: ■, initial composition of titanium-aluminum alloy; ×, composition of nitrided alloy; ♦, composition of equilibria alloy; — — —, diffusion paths. Shaded triangles, results of thermodynamic calculations. Experiment points and phase areas of [1984Sch]: ▲, AlN-Ti_2AlN-TiAl; ▼, TiN_{1-x}-Ti; ○, TiN_{1-x}-AlN-Ti_2AlN; ◎, Ti_3AlN-Ti_3Al; +, TiN_{1-x}-Ti_2AlN-Ti_3AlN; ✳, Ti_2AlN-TiAl; ∗, TiN_{1-x}-Ti_2AlN-Ti_3AlN; ★, Ti_2AlN-Ti_3Al; ☆, TiN_{1-x}-Ti_3Al; ✧, TiN_{1-x}-Ti_3Al-Ti_3AlN

out by the EPMA technique at points 3-6 of Fig. 5(b) are presented in Table 3.

Thermodynamic calculations of phase equilibria at 1273 K have been carried out to ascertain the structure of the section of the Ti-Al-N phase diagram adjacent to the binary Ti-Al side in the concentration range from $TiAl_2$ to α(Ti). The data on the formation Gibbs energy $\Delta_f G$ were taken from [1978Kau] for $TiAl_3$, TiAl, and Ti_3Al, from [1992Hil] for AlN and from [1996Jon] for TiN_{1-x} and Ti_2N. All phases were supposed to be stoichiometric. The equilibria involving α- and β-solid solutions based on Ti were not analyzed as they had been investigated experimentally in detail. The equilibria with participation of Al-rich liquid phase were not considered because they were outside the area of compositions under study. At present, there are no experimental data on $\Delta_f G$ of Ti_3AlN, Ti_2AlN, or $TiAl_2$ though these functions were assessed in [1998Che]. Therefore, at the first stage of the present calculations these unknown Gibbs energies were found by using an optimizing procedure. In essence, this consisted in variation of the $\Delta_f G$ (Ti_3AlN), $\Delta_f G$ (Ti_2AlN), and $\Delta_f G$ ($TiAl_2$) with the aim of searching for the value, which describes the experimentally established regions of their appearance in the phase diagram (Fig. 4). As a consequence, the following values of the Gibbs energies of formation (in kJ/mol) of Ti_3AlN, Ti_2AlN, and $TiAl_2$ from the components stable at 1273 K have been found at −360.0, −323.3, and −80.8, respectively. These values were then used for calculation of the unexplored fields of the three-phase equilibrium. The calculated results are shown in Fig. 4 as shaded triangles and are in complete agreement with the conclusions of [1998Che] about the form of the Ti-Al-N phase diagram at 1273 K. The [1998Che] diagram was made by optimizing available data on the thermodynamic properties and phase equilibria with due regard for homogeneity ranges of the intermetallics. The $\Delta_f G$ (Ti_3AlN) and $\Delta_f G$ (Ti_2AlN) assessed in [1998Che] amount to −320.2 and −288.8 kJ/mol at 1273 K, which is rather close to the values found here.

The present experimental studies and calculations allowed construction of the solid-state part of the 1273 K isothermal section of the ternary Ti-Al-N phase diagram (Fig. 4). It includes the following crystalline phases: $TiAl_3$, $TiAl_2$, TiAl, $TiAl_3$, AlN, TiN_{1-x}, Ti_2N, Ti_3AlN, Ti_2AlN, and α- and β-Ti-based solid solutions. It is seen that aluminum nitride can be in equilibrium with TiN_{1-x}, Ti_2AlN, and $TiAl_3$, ternary nitride Ti_2AlN coexists with $TiAl_3$, $TiAl_2$, TiAl, TiN_{1-x}, and Ti_3AlN, while the α-solid solution coexists with Ti_3Al, Ti_3AlN, TiN_{1-x}, and Ti_2N.

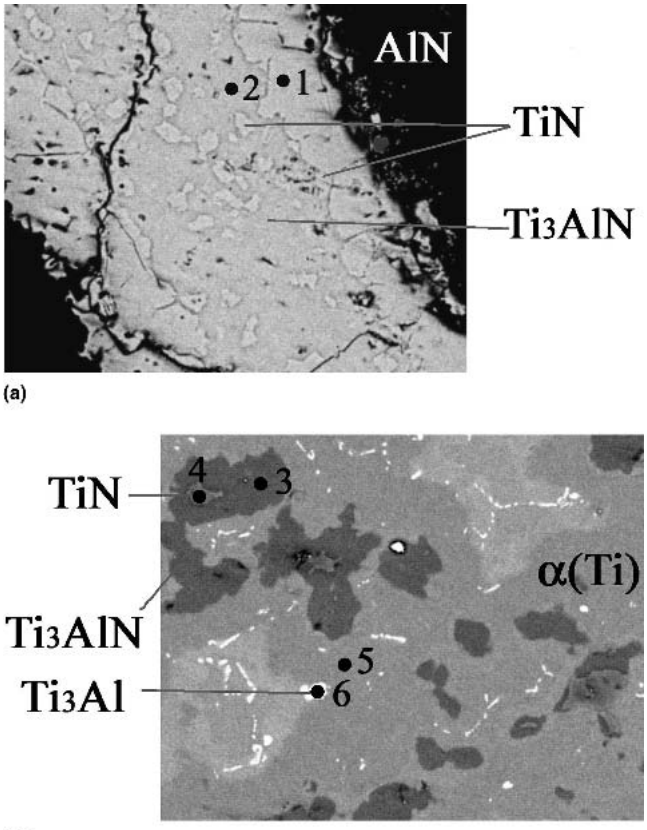

Fig. 5 **(a)** Microstructure of the diffusion zone, formed in the sample AlN/Ti/AlN after 200 h annealing at 1273 K, secondary $\bar{e}$, ×1000. **(b)** Microstructure of the AlN + 2Ti sample after 200 h annealing at 1273 K, secondary $\bar{e}$, ×1000. Numbers mark the points where chemical composition was determined using the EPMA technique.

Table 3 Results of electron probe microanalysis of the diffusion zone in the samples shown in Fig. 5

Sample	Point in the diffusion zone (Fig. 5)	at.%Ti/at.%Al ratio
AlN/Ti/AlN	1	99.2/0.8
	2	73.1/26.9
2Ti + AlN	3	74.2/25.8
	4	98.8/1.2
	5	80.6/19.4
	6	75.7/24.3

5. Discussion

The isothermal sections at 1273 K of the Ti-Al-N phase diagram according to different authors [1984Sch, 1998Che] are presented in Fig. 7(a) and (b). Two types of disagreement in the data can be seen. Firstly, the authors [1984Sch] suggested that aluminum nitride could be in equilibrium with TiAl, Ti_2AlN, and TiN_{1-x} (Fig. 7a) and on this basis proposed existence of the AlN-$TiAl_3$ and AlN-$TiAl_2$ tie lines. The thermodynamic calculations [1998Che] resulted in the conclusion that AlN could coexist only with $TiAl_3$, Ti_2AlN, and TiN_{1-x} (Fg. 7b). These results have matched well with the results of this work (Fig. 4).

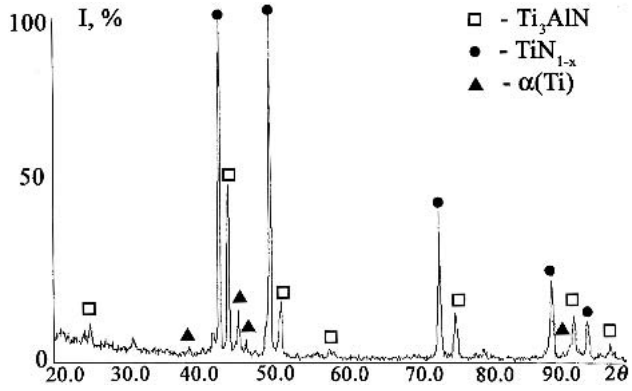

Fig. 6 Diffractogram of the AlN + 2Ti sample after 670 h annealing at 1273 K

Secondly, according to [1984Sch] the complex nitride Ti_2AlN is in equilibrium with Ti_3Al and Ti_3AlN (Fig. 7a), while Ti_3AlN forms a three-phase field with TiN_{1-x} and Ti_3Al (Fig. 7a). In addition, the TiN_{1-x}-Ti_3Al-α(Ti) and TiN_{1-x}-Ti_2N–α(Ti) heterogeneous regions were also found. However, in the later and more extensive investigation [1998Che] it was demonstrated that the character of the phase equilibria at the 1273 K isothermal sections of the Ti-Al-N phase diagram is quite different. Ternary nitrides Ti_2AlN and Ti_3AlN form the three-phase equilibrium triangle with the phase based on TiAl. There are also the following three-phase regions: $TiAl_3$-Ti_5Al_{11}-Ti_2AlN, Ti_5Al_{11}-$TiAl_2$-Ti_2AlN, $TiAl_2$-TiAl-Ti_2AlN, TiAl-Ti_3Al-Ti_3AlN, and Ti_3Al-α(Ti)-Ti_3AlN.

This scheme of phase equilibria remains practically unchanged at 1173 K. The 1173 K isothermal sections of the Ti-Al-N phase diagram according to different authors [1997Zen, 1997Dur, 1998Che, 1999And] are presented in Fig. 8(a-d). Comparing Fig. 8(b)-(d), one can see that calculations carried out in three different works [1997Zen, 1998Che, 1999And] have led to similar structure of the regions with participation of the ternary nitrides at the two isothermal sections. A minor distinction consists only in appearance at 1273 K of the Ti_5Al_{11} intermetallic compound, which is in equilibrium with the Ti-Al binary phases and Ti_2AlN (Fg. 7b). The three-phase equilibrium Ti_2AlN-Ti_3AlN-Ti_3Al at 1173 K found in experiments [1997Dur] matches the results [1984Sch] for 1273 K, but contradicts the present data and the results of works [1997Zen, 1998Che, 1999And].

In the present work, the existence of the three-phase equilibria $TiAl_3$-AlN-Ti_2AlN and $TiAl_3$-$TiAl_2$-Ti_2AlN has been experimentally established. The phase equilibria among the compounds $TiAl_2$, TiAl, Ti_3Al, α(Ti), Ti_2AlN, and Ti_3AlN were calculated (Fig. 4). The results of calculations are in agreement with the results of [1998Che] (Fig. 7b), except for participation of Ti_5Al_{11} phase. In the present work, this compound was not found in experiments with either the binary Ti-Al or ternary Ti-Al-N alloys.

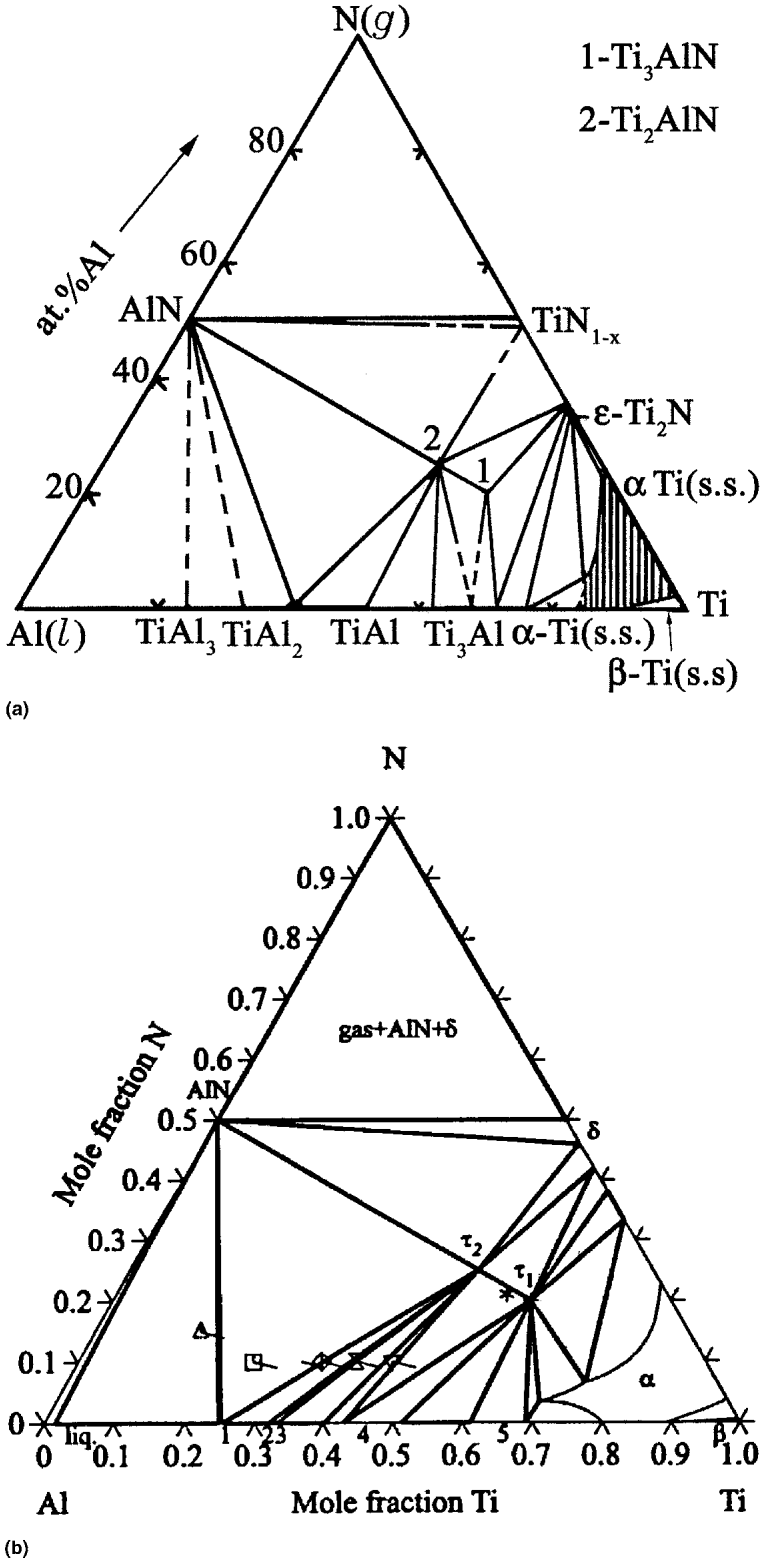

Fig. 7 The 1273 K isothermal section of the Ti-Al-N phase diagram **(a)** after [1984Sch]; **(b)** after [1998Che]: 1, $TiAl_3$; 2, Ti_5Al_{11}; 3, $TiAl_2$; 4, TiAl; 5, Ti_3Al; τ_1, Ti_3AlN; τ_2, Ti_2AlN

The thermodynamic analysis of the phase equilibria in the Ti-Al-N system at 1273 K carried out in the present work has allowed the authors to reveal why the data [1984Sch, 1997Dur] disagree both with the conclusions of [1997Zen], [1998Che], [1999And] and the present results. The calculations showed that formation of the three-phase

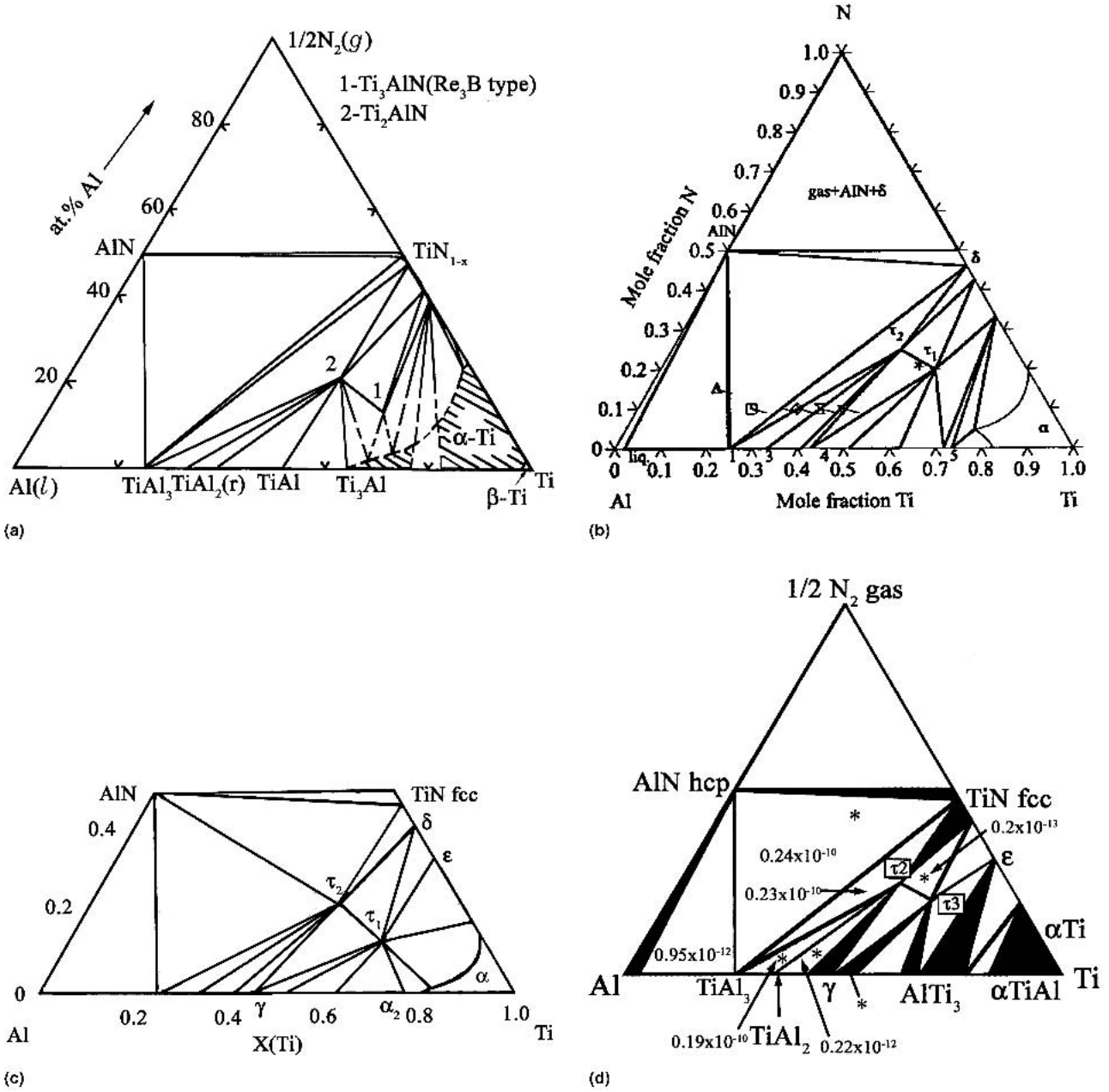

Fig. 8 1173 K isothermal section of the Ti-Al-N phase diagram: **(a)** after [1997Dur]; **(b)** after [1998Che]: 1, $TiAl_3$; 3, $TiAl_2$; 4, TiAl; 5, Ti_3Al; τ_1, Ti_3AlN; τ_2, Ti_2AlN; **(c)** after [1997Zen]: τ_1, Ti_3AlN; τ_2, Ti_2AlN; **(d)** after [1999And]: τ_2, Ti_2AlN; τ_3, Ti_3AlN

Ti-Al-N alloys from initial binary constituents is accompanied by changes in the Gibbs energy, which are quite small in the absolute value and, in most cases, do not exceed several hundred J/mole. This fact suggests that very long intervals of time were required for achievement of equilibrium in experiments [1984Sch], where the ternary alloys were prepared by sintering the mixtures of powdered binary compositions. On the contrary, the interaction of the powdered Ti-Al binary alloys with nitrogen is accompanied by significant (hundreds of kJ/mol) gains in the Gibbs energy, which provided a means for quick achievement of the state corresponding to the minimum of this function.

The most contradictory are the data on the phase equilibria in the Ti-rich part of the system. This part is described in three different ways:

1) Experimentally [1984Sch, 1997Dur], it was established that at both temperatures 1173 and 1273 K the Ti_2N compound does not extend into the ternary system and is surrounded by only binary phases, namely, by the solid solution of nitrogen in α(Ti) and by the TiN_{1-x} nitride. This is consistent with the present work. Ti_3AlN, Ti_3Al, TiN_{1-x}, and the α(Ti) solid solution form the three-phase regions Ti_3AlN-Ti_3Al-TiN_{1-x} and TiN_{1-x}-Ti_3Al-α(Ti)

[1984Sch, 1997Dur] (Fig. 7a, 8a). The thermodynamic calculation [1998Che] confirmed this scheme of phase equilibria (Fig. 8b) at 1173 K, but at 1273 K led to different results (Fig. 7b). However, the conditions under which the ternary nitride Ti_3AlN forms were not well established [1998Che] and in their calculation these authors did not take into account the lowest titanium nitride Ti_2N, though on the calculated phase diagram at 1273 K the Ti_3AlN-TiN_{1-x}-Ti_2N and Ti_3AlN-Ti_2N-α(Ti) equilibrium fields were shown, but the compound itself was not marked [Fig. 7b (Fig. 5 in [1998Che])].

2) Zeng and Schmit-Fetzer [1997Zen] found that Ti_2N could be in equilibrium with TiN_{1-x}, α(Ti), and Ti_3AlN and that there is the three-phase Ti_3Al-α(Ti)-Ti_3AlN field (Fig. 8c).
3) The thermodynamic calculation [1999And] indicated that Ti_2N could coexist with Ti_3Al and, therefore, the three-phase fields Ti_2N-Ti_3Al-Ti_3AlN and Ti_2N-Ti_3Al-α(Ti) should be present in the diagram (Fig. 8d).

Thus, despite the fact that the thermodynamic calculations [1996Car, 1998Che, 1999And] of the phase equilibria in the Ti-Al-N system at 1173 K were based on the results of the same experimental investigation [1997Dur], they did lead to ambiguous results.

6. Conclusions

A blend of modern physical and chemical techniques in combination with thermodynamic calculations was used in the present work to study solid state phase equilibria in the Ti-Al-N system at 1273 K. The experimental approach allowed the attainment of the same final state of alloys from various starting points and via different ways and in this manner it was possible to obtain exhaustive proofs that equilibrium was reached. The data found by various techniques were well coordinated among themselves and in agreement with the outcome of the thermodynamic analysis. The obtained results and literature data were used for construction of the 1273 K isothermal section of the Ti-Al-N phase diagram that can be recommended for prediction of phase equilibria in composite materials that are developing on the basis of this system.

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