The N-Ti-V System (Nitrogen-Titanium-Vanadium)

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Introduction

Only a few studies of the phase constitution in the N-Ti-V system are available. [66Str] and [72Kie] reported the mutual solubility of TiN and VN and the lattice parameters of these compounds. For the purpose of strengthening vanadium alloys, [71Shu] and [74Bar] studied the solubility of group IV A metal nitrides in V and the phase relationships near the V corner. In these studies, electrolytic vanadium was first melted under a mixture of argon and high purity N. The alloys were prepared under argon by arc melting the nitrified vanadium alloys and iodide titanium. The phase constitution was studied by metallography, x-ray diffractometry, differential thermal analysis (DTA), and hardness testing in the temperature range 1200 to 1800 °C.

Binary Systems

The binary Ti-V phase diagram (Fig. 1) is from [87Mur]. At high temperatures, the (βTi) and (V) phases form a continuous series of bcc solid solution. Below 850 °C, a miscibility gap is present in the β phase giving rise to a monotectoid reaction, (βTi, V) ↔ (αTi) + (V). In previous assessments [Hansen, Elliott, Shunk, 81Mur], no miscibility gap with its associated monotectic reaction was shown, but [87Mur] used data of [80Nak] to construct the diagram of Fig. 1. A recent study [89Wei] showed that the reported miscibility gap in the (βTi, V) phase was possibly due to oxygen impurity and that neither a miscibility gap nor a stable monotectoid was likely to occur in the pure binary Ti-V system, which is consistent with the former assessments. Thus the presence or absence of the miscibility gap is still inconclusive.

The N-Ti phase diagram (Fig. 2), from [87Wri], is characterized for up to 50 at.% N. Two terminal solid solutions, (αTi) and (βTi), and three titanium nitrides, Ti_2N, δ′, and TiN (also designated as δTiN_{1-x}), are the solid phases reported for this system. The δ′ phase is also called $Ti_2N(\alpha)$. The solubility of N in (αTi) and the homogeneity range of TiN are quite large. More than half of the phase boundaries are not well established.

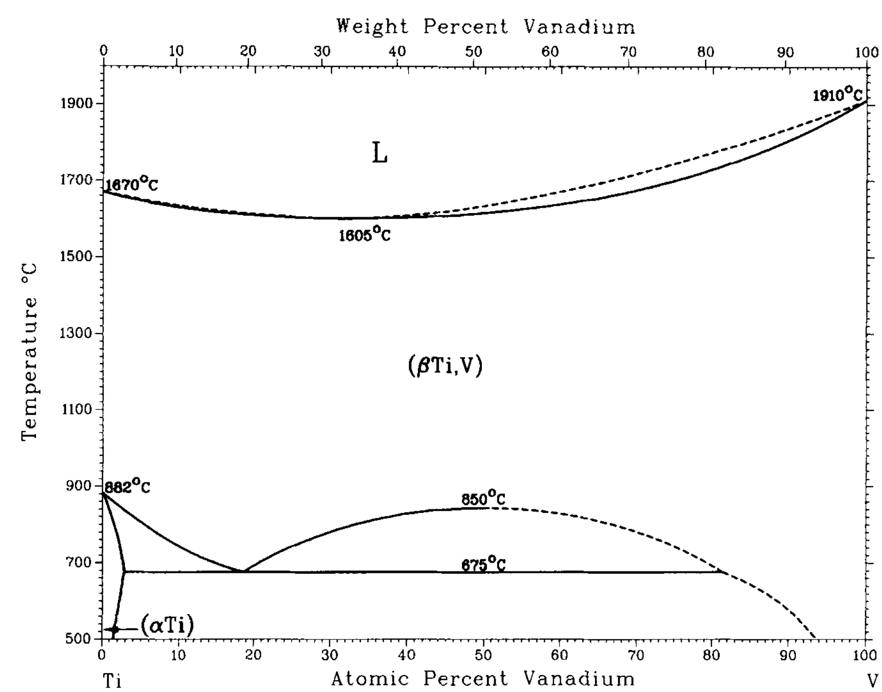

Fig. 1 Ti-V binary phase diagram. From [87Mur].

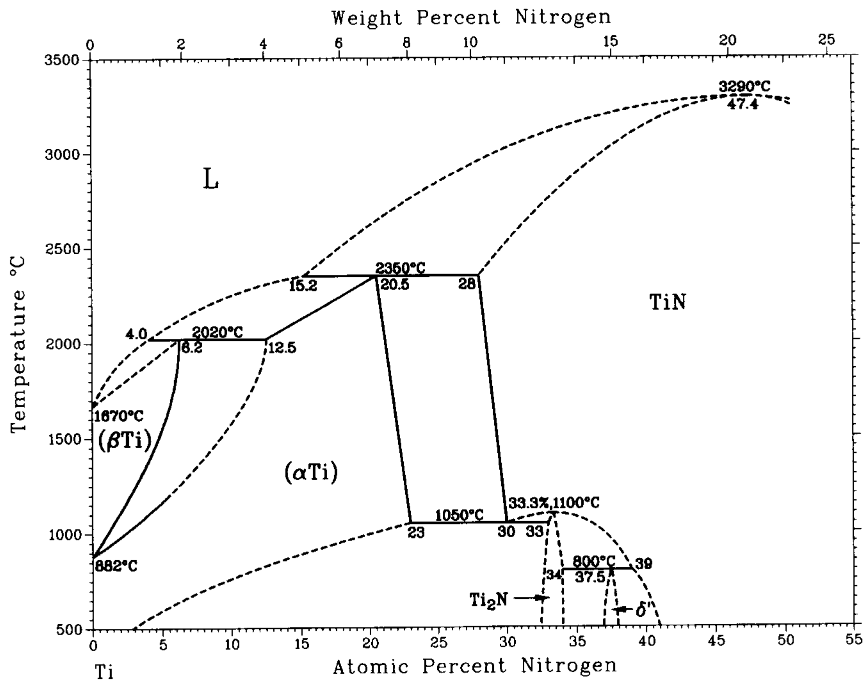

Fig. 2 N-Ti binary phase diagram. From [87Wri].

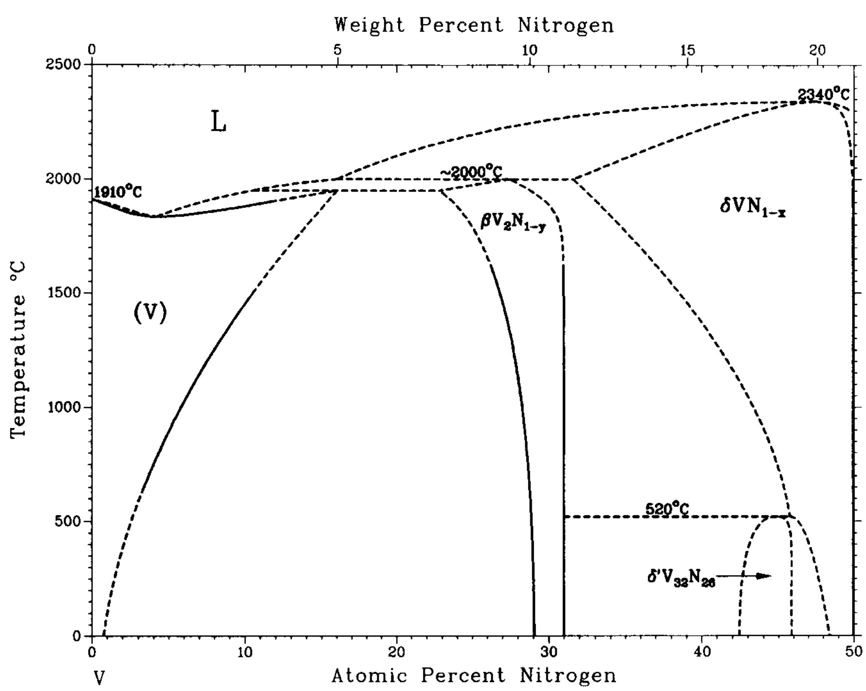

Fig. 3 N-V binary phase diagram. From [89Car].

Table 1 N-Ti-V Crystal Structure Data of Equilibrium Phases

Phase	Composition, at.%	Pearson symbol	Space group	Strukturbericht designation	Prototype
Terminal solid solution phases					
(αTi)	0 to ~3V, 0 to 23N	*hP*2	$P6_3/mmc$	*A*3	Mg
(βTi)	0 to 100V, 0 to 6.2N	*cI*2	$Im\bar{3}m$	*A*2	W
(V)(a)	0 to 100Ti, 0 to 17N	*cI*2	$Im\bar{3}m$	*A*2	W
Intermediate phases					
Ti_2N(b)	33N	*tP*6	$P4_2/mnm$	*C*4	Rutile
δTiN_{1-x}, δ(Ti, V)N	30 to 55N, 0 to 100V	*cF*8	$Fm\bar{3}m$	*B*1	NaCl
δVN_{1-x}(c)	~33 to 50N, 0 to 100Ti	*cF*8	$Fm\bar{3}m$	*B*1	NaCl
$\delta' Ti_2N$	38N	*tI*12	$I4_1/amd$	C_c	Si_2Th
βV_2N_{1-y}(b)	29 to 31N	*hP*9	$P3_1m$	...	εFe_2N
$\delta' VN_{1-x}$(b)	~43 to 46N	tetragonal (ordered)	$P4_2/nmc$	...	...

(a) (V) forms a continuous bcc solid solution with (βTi). (b) No data on the solubility of Ti. (c) Isomorphous to TiC. From [66Str].

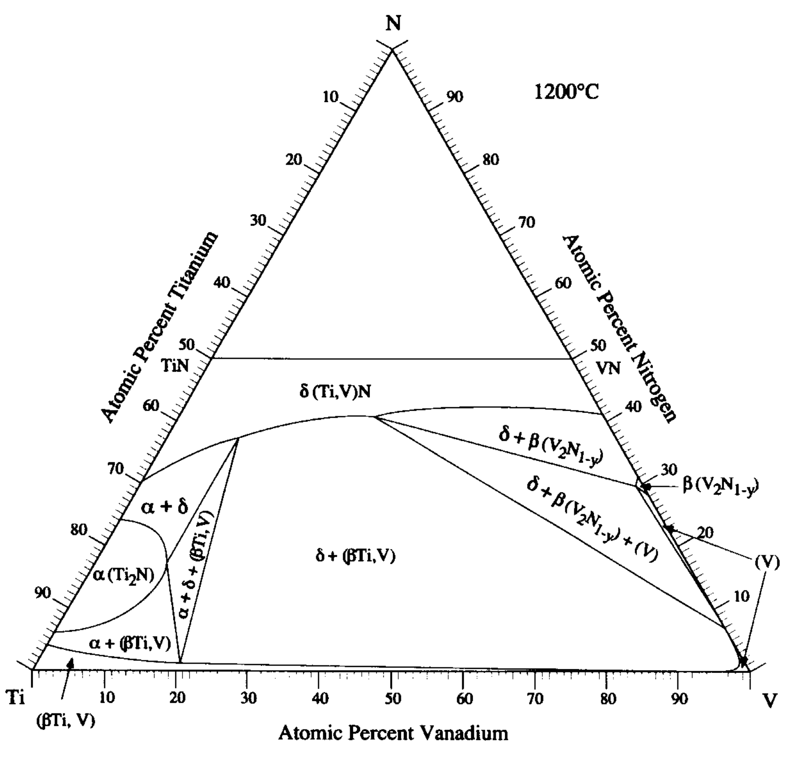

Fig. 4 Assessed isothermal N-Ti-V section at 1200 °C.

The N-V phase diagram (Fig. 3), from [89Car], is characterized for up to 50 at.% N. There is only one solid solution, (V), and three vanadium nitrides, βV_2N_{1-y}, $\delta' V_{32}N_{26}$, and δVN_{1-x}. The $\delta' V_{32}N_{26}$ phase is considered to be a nitrogen-ordered form of VN_{1-x} and has been reported at several other stoichiometric compositions. However, most of these compositions are believed to be metastable. The solubility of N in (V) and the homogeneity range of VN are also large. As in the N-Ti system, the majority of the phase boundaries are not well established.

Ternary System

Solid Phases

Table 1 provides the crystal structure data for the solid phases of the N-Ti-V system. (βTi) and (V) form a continuous bcc

Table 2 Lattice Parameter Data of N-Ti-V Intermediate Compounds

Phase	Lattice parameters, nm a	b	c	Comment	Reference
Ti_2N	0.4943	...	0.3036	...	[87Wri]
TiN	0.4241 ± 0.0002	...	...	...	[87Wri]
	0.419	...	...	~45 mol% VN	[66Str]
	0.417	...	...	~60 mol% VN	[66Str]
	0.4163	...	...	75 mol% VN	[72Kie]
	0.4192	...	...	50 mol% VN	[72Kie]
	0.4216	...	...	25 mol% VN	[72Kie]
δVN_{1-x}	0.4182	...	...	...	[89Car]
$\delta' Ti_2N$	0.4198	...	0.8591	...	[87Wri]
βV_2N_{1-y}	0.4920	...	0.4542	...	[89Car]
$\delta' VN_{1-x}$	~0.8190	...	...	...	[89Car]

solid solution. The solubility of nitrogen in the three terminal solid solution phases is large compared to that of carbon. The $B1$-type δTiN_{1-x} and δVN_{1-x} compounds are completely miscible [66Str]. No true ternary phases have been reported.

Table 2 lists the lattice parameter data of the N-Ti-V phases. The lattice parameter of δTiN_{1-x} decreases almost linearly with the increase of the mole percentage of VN.

Isothermal Sections

A possible isothermal section at 1200 °C was constructed and illustrated in Fig. 4. Phase relationships near the V-N side are based on [71Shu] and the accepted binary phase diagram. [74Bar] determined the solubility of TiN in (V) at 1200, 1500, and 1800 °C. Using the thermodynamic relationship, [74Bar] derived Eq 1:

$$\ln X_N + \ln X_{Ti} = -\frac{309\,988}{RT} + \frac{100.52}{R} \qquad \text{(Eq 1)}$$

where T is the absolute temperature and R, the gas constant, is 8.314 J/K·mol. The curves calculated from Eq 1 (Fig. 5) show that the solubility of TiN in (V) is very small at 1200 °C (see the V corner in Fig. 4). The phase boundaries near the N-Ti side are highly speculative.

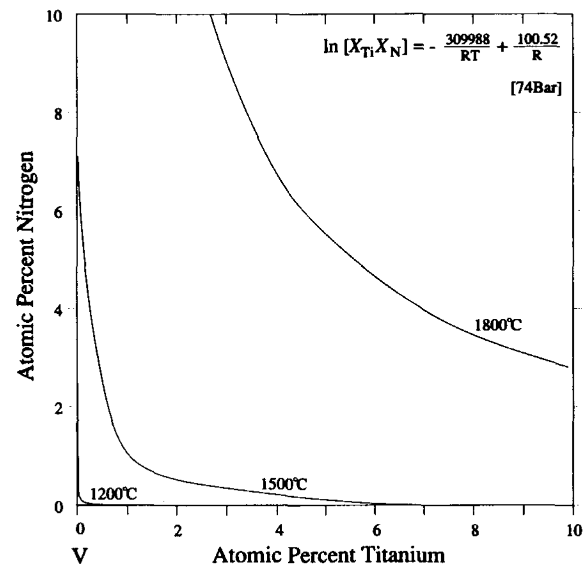

Fig. 5 TiN solubility curve in vanadium [74Bar].

Pseudobinary Systems

Figure 6 is an isopleth through TiN-V based on [71Shu]. From metallographic observation and DTA, [71Shu] concluded that a ternary eutectic reaction (the eutectic temperature is 1870 °C) exists as in the Zr-V-N and Hf-V-N systems. A few modifications were made in Fig. 6, for example, the melting temperatures of TiN and V and the (V)/[δ(Ti, N) + (V)] phase boundary. The latter should coincide with the solubility curve reported by [74Bar], namely,

$$\log\,[X_{TiN}] = -\frac{8106}{T} + 2.629 \qquad \text{(Eq 2)}$$

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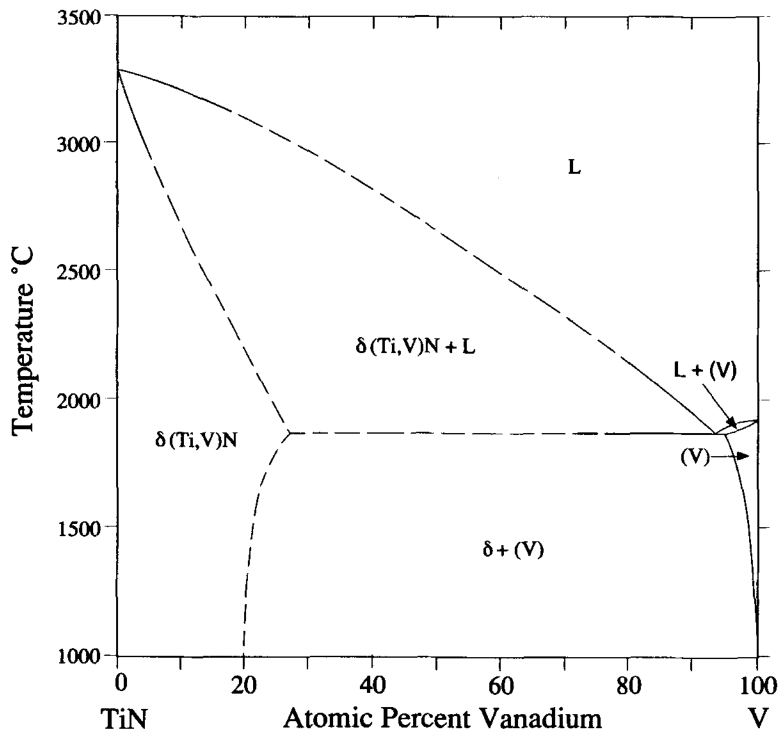

Fig. 6 Isopleth through TiN-V [71Shu].

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89Wei: F. Wei and H.M. Flower, "Phase Separation Reactions in Ti-50V Alloys," *Mater. Sci. Technol., 5,* 1172-1177 (1989). (Experimental)

*Indicates key paper.
#Indicates presence of a phase diagram.

N-Ti-V evaluation contributed by **M. Enomoto,** Department of Materials Science, Faculty of Engineering, Ibaraki University. Literature searched through 1989. Dr. Enomoto is the Alloy Phase Diagram Program Co-Category Editor for ternary titanium alloys.