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Al-N-Ti (Aluminum-Nitrogen-Titanium)

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[1984Sch] investigated this system and presented two isothermal sections at 1300 and 1000 °C, depicting three ternary compounds. Several computed and experimental phase diagrams and new data on crystal structures have since been reported.

Binary Systems

The Al-N system has one stoichiometric compound AlN (*B*4, ZnS-type hexagonal). The updated version of the Al-Ti phase diagram [2005Rag] depicts a number of intermediate phases: $TiAl_3$ ($D0_{22}$-type tetragonal), Ti_5Al_{11} (tetragonal), $TiAl_2$ ($HfGa_2$-type tetragonal), $Ti_{1-x}Al_{1+x}$ (AuCu-type tetragonal), Ti_3Al_5 (tetragonal), TiAl (γ) (AuCu-type tetragonal), and Ti_3Al (α_2) ($D0_{19}$, Ni_3Sn-type hexagonal). The Ti-N phase diagram [Massalski2] depicts a N-deficient mononitride TiN_{1-x} (δ) (*B*1, NaCl-type cubic) with a wide range of homogeneity, and two low-temperature phases Ti_2N (*C*4-type tetragonal) and δ′ ($ThSi_2$-type tetragonal). Nitrogen has a strong stabilizing effect on βTi and αTi, raising the upper temperature limit of their stability to 2020 and 2350 °C, respectively. For a thermodynamic assessment of the Ti-N system, see [1996Jon].

Ternary Phases

There are three ternary compounds in this system. Ti_3AlN_{1-x} (perovskite-type cubic, denoted τ_1 here) and Ti_2AlN (Cr_2AlC-type hexagonal, denoted τ_2 here) have been reported at temperatures between 1325 and 900 °C [1984Sch, 1995Wu, 1997Sch, 1997Zen, 1998Che, 1999Mag, 2004Han]. [1996Pie] reported a low-temperature modification (below 1200 °C) of Ti_3AlN_{1-x}, where the cubic perovskite structure transforms to a filled Re_3B-type orthorhombic structure, with $a \sim 0.3065$ nm, $b \sim 1.0748$ nm, and $c \sim 0.8455$ nm. [1997Dur] observed that Ti_2AlN (τ_2) has some nitrogen deficiency, with a suggested formula of $Ti_2AlN_{0.8}$. However, [1999Mag] reported the composition of τ_2 forming in the scales during nitriding as $Ti_{2.04}Al_{0.96}N_{1.09}$. There has been some controversy regarding the structure of the third compound τ_3 [1984Sch, 1997Lee, 1998Bar, 1998Lee]. [1999Bar, 2000Pro1] concluded that the stoichiometry of τ_3 is neither $Ti_3Al_2N_2$ as reported by [1984Sch] nor $Ti_3Al_{1-x}N_2$ as given by [1997Lee], but it is Ti_4AlN_{3-x} ($x = 0.1$) with hexagonal symmetry. It is stable only in a narrow temperature range between 1250 and 1400 °C [1997Lee, 2000Pro2]. [2000Pro2] proposed that this compound represents a family of layered carbides and nitrides with the general formula $M_{n+1}AX_n$, where n = 1-3, M is an early transition metal, A is a Group III-A or IV-A element and X is either C or N. This compound is relatively soft for a nitride and is machinable, in spite of its high stiffness (Young's modulus = 310 GPa) [2000Pro2]. Table 1 lists the crystal structure data on the above compounds.

Isothermal Sections

A number of experimental and computed isothermal sections have been determined for this system: [1984Sch] (1300 and 1000 °C, experimental); [1997Dur] (900 °C, experimental); [1997Sch] (1000 °C, computed); [1997Zen] (1300, 1200, and 900 °C, computed), [1998Che] (2500, 1900, 1600, 1580, 1400, 1300, 1200, 1000, and 900 °C, computed); [2000Pro1] (1325 °C, experimental); and [2004Han] (1000 °C, experimental). Among these, four selected isothermal sections are redrawn here to agree with the accepted binary data. As an example of the high-temperature equilibria, the computed section of [1998Che] at 1900 °C is redrawn in Fig. 1. It may be noted that there are no experimental points to validate this section. Only τ_2 is stable at this temperature (and at 1600 °C, not shown). Both τ_1 and τ_2, are stable in the computed sections at 1580 and 1400 °C. At 1300 °C, τ_1, τ_2, and τ_3 are stable. Between 1200 and 900 °C, τ_1 and τ_2 are stable [1998Che].

Table 1 Al-N-Ti crystal structure and lattice parameter data

Phase	Composition, at.%	Pearson symbol	Space group	Prototype	Lattice parameter, nm
$Ti_3AlN_{0.56}$ (τ_1)	21.9 Al	*cP*5	$Pm\bar{3}m$	$CaTiO_3$	a = 0.41127
	12.3 N				
	65.8 Ti				
$Ti_2AlN_{0.82}$ (τ_2)	26.2 Al	*hP*8	$P6_3/mmc$	Cr_2AlC	a = 0.29869
	21.5 N				c = 1.3622
	52.3 Ti				
$Ti_4AlN_{2.9}$ (τ_3)	12.7 Al		$P6_3mc$		a = 0.29875
	36.7 N				c = 2.3350
	50.6 Ti				

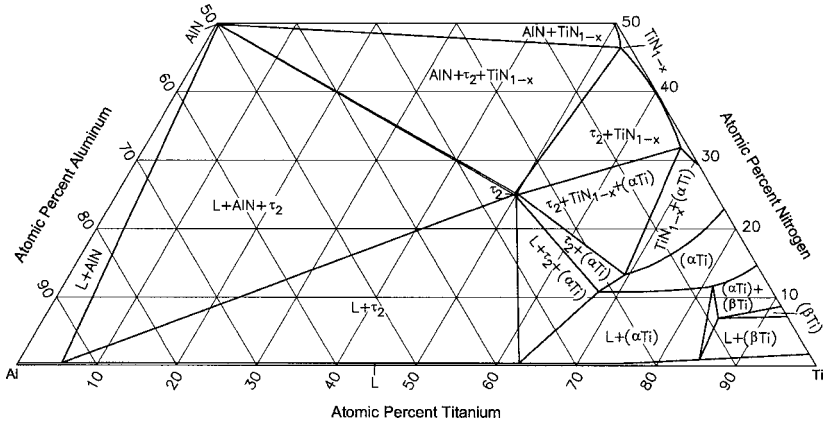

Fig. 1 Al-N-Ti computed isothermal section at 1900 °C [1998Che]

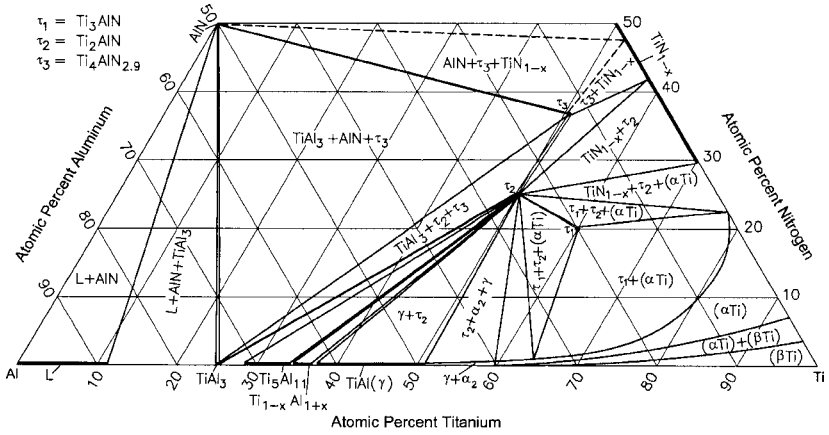

Fig. 2 Al-N-Ti isothermal section at 1325 °C [2000Pro1]

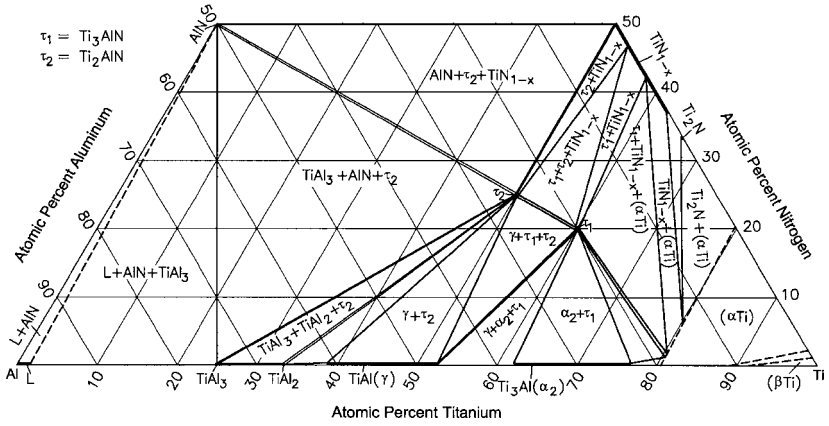

Fig. 3 Al-N-Ti isothermal section at 1000 °C [2004Han]

The section at 1325 °C determined by [2000Pro1] is redrawn in Fig. 2 to agree with the accepted binary data. It was obtained from samples prepared by hot isostatic pressing with a subsequent anneal for 168 h at 1325 °C. It depicts all the three ternary phases. The location of Ti_4AlN_{3-x} (τ_3) in Fig. 2 is significantly different from that of $Ti_3Al_2N_2$ in the section at 1300 °C by [1984Sch].

With starting materials of 99.999% Al, 99.99% Ti, and 99% AlN, [2004Han] arc-melted alloys under Ar atm. The alloys were annealed at 1000 °C for 670 h. Diffusion couple

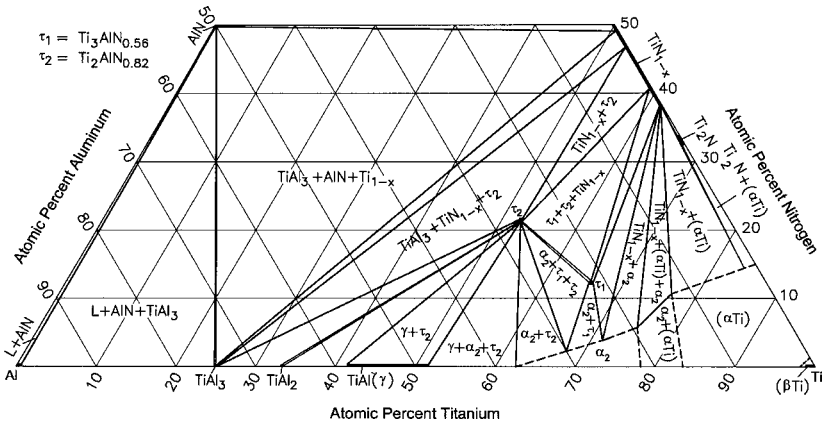

Fig. 4 Al-N-Ti isothermal section at 900 °C [1997Dur]

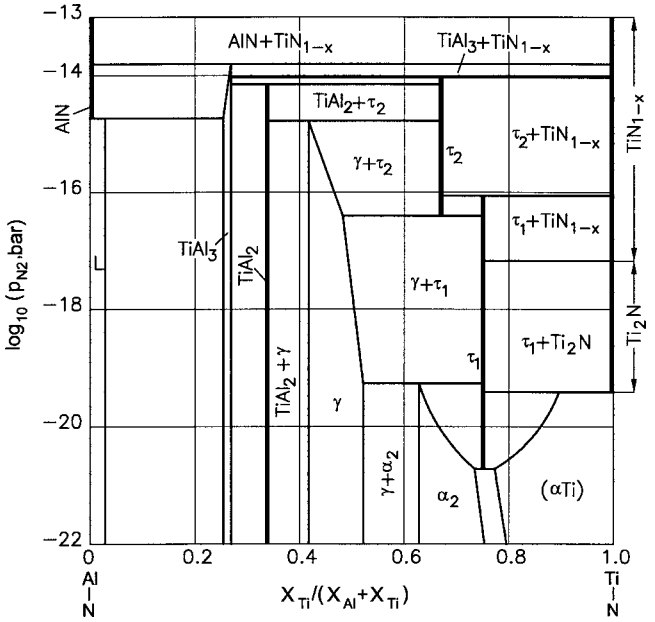

Fig. 5 Al-N-Ti computed stability diagram at 1000 °C. τ_1 = $Ti_3AlN_{0.56}$ and τ_2 = $Ti_2AlN_{0.82}$ [1997Sch]

experiments with AlN/Ti pair and nitriding from a gaseous phase were also adopted. The phase equilibria were studied with optical and scanning electron metallography, x-ray diffraction, and electron probe microanalysis. In Fig. 3, the isothermal section at 1000 °C constructed by [2004Han] is redrawn to agree with the accepted binary data. In Fig. 3, the three-phase equilibrium between AlN, $TiAl_3$, and Ti_2AlN (denoted τ_2 here and as τ_1 by [2004Han]) appear to be established. There are differences between [2004Han], [1998Che], and [1984Sch] in the triangulation of the 1000 °C isothermal section. In Fig. 4, an isothermal section at 900 °C constructed by [1997Dur] is redrawn. Comparing Fig. 3 and 4, a transition reaction AlN + $\tau_2 \leftrightarrow TiAl_3 + TiN_{1-x}$ is expected to occur between 1000 and 900 °C.

A stability diagram at 1000 °C computed by [1997Sch] is shown in Fig. 5, where the partial pressure of N_2 is plotted against the mole fraction $X_{Ti}/(X_{Ti} + X_{Al})$. At the left end, nitrogen remains dissolved in liquid Al at low pressures. As the pressure increases, AlN becomes stable. At the right end, nitrogen remains dissolved in (αTi) initially. As the nitrogen pressure increases, Ti_2N and TiN_{1-x} progressively become stable. The formation of τ_1 is very sluggish, and in real-time process applications, τ_1 may not form at all. To simulate this metastable condition, [1997Sch] computed an additional stability diagram at 1000 °C by suppressing the presence of τ_1 (not shown here).

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