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Al-Nb-Ti (Aluminum-Niobium-Titanium)

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The previous review of this system by [1993Gam] presented a liquidus projection, experimental isothermal sections at 1200, 1100, and 1000 °C, computed isothermal sections from [1992Kat] at 1400, 1200, 1100, and 700 °C, and a vertical section along the $NbAl_3$-$TiAl_3$ join. The thermodynamic assessment of this system by [1992Kat] presented a computed liquidus projection, computed isothermal sections at 1400, 1200, 1100, and 700 °C, and compared these with the available experimental data. The compilation of [1995Vil] gave a liquidus projection, a solidus projection, isothermal sections at 1200, 900, 600, and 20 °C, and vertical sections at 40, 50, and 60 wt.% Ti and along the Ti_3Al-Nb join. A large number of new publications have since appeared on the phase equilibria of this system, resulting in significant refinement of the data.

Binary Systems

The Al-Nb phase diagram [Massalski2] shows three intermediate phases: $NbAl_3$ ($D0_{22}$, $TiAl_3$-type tetragonal); σ ($D8_b$, σCrFe-type tetragonal, also denoted Nb_2Al); and Nb_3Al ($A15$, Cr_3Si-type cubic, denoted δ). The updated version of the Al-Ti phase diagram [2005Rag] depicts a number of intermediate phases. $TiAl_3$ has two crystal modifications. $TiAl_3$ [high temperature (HT)] ($D0_{22}$-type tetragonal) forms peritectically at 1387 °C and decomposes eutectoidally at 735 °C. $TiAl_3$ [low temperature (LT)] (tetragonal) forms at 950 °C and is stable at low temperatures. Ti_5Al_{11} is a superstructure based on the AuCu-type tetragonal phase. It forms peritectically at 1416 °C and decomposes eutectoidally at 995 °C to $TiAl_2$ and $TiAl_3$ (HT). $TiAl_2$ ($HfGa_2$-type tetragonal) forms congruently at 1215 °C from Ti_5Al_{11} and is stable at low temperatures. $Ti_{1-x}Al_{1+x}$ (AuCu-type tetragonal) is stable between 1445 and 1170 °C. Ti_3Al_5 is a LT phase that is stable below 810 °C. TiAl, often designated γ, has the $L1_0$, AuCu-type tetragonal structure and forms peritectically at 1460 °C. (βTi) [body-centered cubic (bcc), also denoted β] and liquid undergo a peritectic reaction at 1490 °C to yield (αTi) (close-packed hexagonal, also denoted α). Ti_3Al, commonly called α_2, has the $D0_{19}$, Ni_3Sn-type hexagonal structure and forms congruently from (αTi) at 1176 °C. There are no intermediate phases in the Nb-Ti system. A continuous bcc solid solution between βTi and Nb exists over a wide range of temperatures.

Ternary Phases

An NaHg-type orthorhombic phase ($oC16$, $Cmcm$, denoted O), first reported by [1988Ban], occurs at a composition of approximately Ti_2NbAl, with the lattice parameters of $a = 0.60893$ nm, $b = 0.95694$ nm, and $c = 0.46666$ nm [1990Moz]. A number of later reports [1991Ben, 1992Hsi, 1993Mur, 1993Row, 1994Ben, 1994Hou, 1996Vas, 1997Ban, 2001Ser, 2002Wo, 2003Hu] confirm the O phase, and discuss the mechanism and kinetics of its formation. In a Ti_2AlNb alloy, the O phase forms directly from the ordered bcc phase $B2$ at ~1000 °C [1991Ben] and is in a two-phase equilibrium with $B2$ down to ~800 °C. An apparent equilibrium phase forms at the composition Ti_4Al_3Nb after prolonged annealing at 700 °C [1990Ben]. It has the $B8_2$, Ni_2In-type hexagonal structure. [1994Wan] and [1996Che] reported a ternary phase around the composition $TiAl_3Nb$ labeled γ_1, as a derivative of the γ phase, with a and c axes equal to $\sqrt{2}$ and 2 times, respectively, of the values of the tetragonal parameters of γ. However, no evidence about the existence of this phase was found in other work [1989Kal, 1990Per, 1998Hel, 2002Leo]. See also the discussion on this phase by [1997Jew], [1998Che], [1998Din1], and [1998Hel].

A number of studies have reported the existence of the CsCl-type ordered bcc phase $B2$ in the ternary region [1989Ben, 1989Kes, 1990Per, 1993Nak, 1994Che, 1996Tak, 1997Hou, 1998Rho, 1999Cha, 2000Leo3]. [1991Ben] found the $B2$ phase in a Ti_2AlNb alloy at an annealing temperature of 1400 °C. [1996Vas] reported that the $B2$ phase persists at 1600 °C in a $Ti_{52}Al_{22}Nb_{26}$ alloy. [1993Nak] measured the composition at 1200 °C of $B2$ coexisting with (αTi) and γ as $Ti_{50}Nb_{12}Al_{38}$, with γ and σ as $Ti_{42}Nb_{19}Al_{39}$. The composition and temperature ranges of stability of the $B2$ phase versus the disordered bcc phase are not fully characterized in this system. A difficulty arises here, as the quenched specimens are in the ordered state, irrespective of their state at the annealing temperature. An indirect way of distinguishing between a disordered $A2$ phase and an ordered $B2$ phase at the annealing temperature is by analyzing the size of the antiphase domains in the quenched samples. A small size indicates that ordering occurred during quenching. The absence of antiphase boundaries in the $B2$ phase is taken to mean that ordering was present at the annealing temperature. In the diagrams given in this review, the region marked "bcc" can be partly $B2$.

Other metastable or transition phases such as ω and $L6_0$ are also known [1990Ben, 1992Sur, 1993Jac, 1993Li, 1995Lev, 1995Rui, 1997Sad, 1998Hel].

Pseudobinary Sections

Pseudobinary sections along the Ti_3Al-Nb, $NbAl_3$-Ti, and $NbAl_3$-$TiAl_3$ joins have been reported. [1990Per] used x-ray powder diffraction and differential thermal analysis to construct the section along the $NbAl_3$-$TiAl_3$ join, which is redrawn in Fig. 1. The system is pseudobinary, except at the $TiAl_3$ end, where $TiAl_3$ forms through a peritectic reaction. Below the solidus line, $TiAl_3$ and $NbAl_3$ form a continuous solid solution. [1990Per] suggested a congruently melting composition near the $NbAl_3$ end. The melting point of $NbAl_3$ from [Massalski2] is about 70 °C higher than that

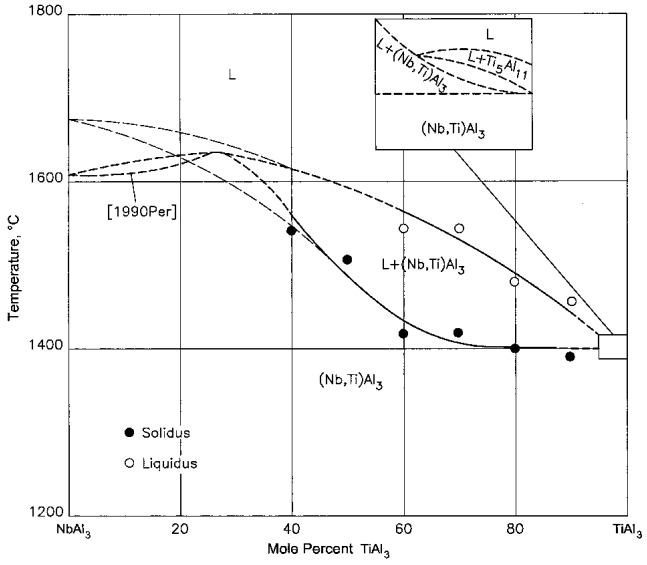


Fig. 1 Al-Nb-Ti pseudobinary section along the $NbAl_3$-$TiAl_3$ join [1990Per]

used by [1990Per], and this appears to rule out the possibility of congruent melting, as indicated schematically in Fig. 1.

Liquidus Projection

A complete liquidus projection of this ternary system was reported by [1989Kal], followed by more experimental results by [1990Per], a computed projection by [1992Kat], a partial projection by [1992Pav1], and a reinvestigation by [1995Zdz] and [2000Leo1]. [1990Per] arc-melted alloys under an Ar atmosphere. The liquidus and solidus temperatures were determined by differential thermal analysis. The phase structures were characterized by optical and scanning electron microscopy, x-ray diffraction (XRD), and electron probe microanalysis (EPMA). [1995Zdz] induction-melted alloys under an Ar atmosphere. The melting temperatures of about 20 ternary alloys were determined by a specially calibrated optical pyrometer. The samples were characterized by scanning and transmission electron microscopy, XRD, and EPMA. The liquidus projection constructed by [1995Zdz] is redrawn in Fig. 2 to agree with the accepted binary data. The projection is similar to the one given by [1990Per] and [1992Kat]. The extension of the primary fields of Nb_3Al and σ to the higher Ti contents found by [1995Zdz] was not confirmed by [2000Leo1]. The more restricted boundaries of these fields suggested by [2000Leo1] are indicated in Fig. 2. [1990Per], [1995Zdz], and [2000Leo1] agree on the absence of a ternary eutectic reaction among σ, γ, and $D0_{22}$. The U-type reactions U_1 to U_4 on the liquidus surface (Fig. 2) are the same in [1990Per], [1995Zdz], and [2000Leo1]. The temperature of the U_2 reaction $L + D0_{22} \rightarrow \sigma + \gamma$ was measured as 1469 °C by [1990Per]. The liquidus surface appears to be extremely flat, on descending along $U_2 \rightarrow U_3 \rightarrow U_4 \rightarrow p_4$, with a drop of only 9 °C. Clearly, more experimental results in this region will be useful. The primary crystallization of $Ti_{1-x}Al_{1+x}$, and Ti_5Al_{11} is shown schematically in Fig. 2.

Isothermal Sections

A number of full or partial isothermal sections were determined or redetermined for this ternary system in the last 15 years. A typical list is: [1989Kal] (full at 1200 °C); [1990Per] (full at 1200 °C); [1991Smi] and [1992Smi] (Nb-rich at 1100, 900, and 800 °C); [1992Kat] (computed, full at 1400, 1200, 1100, and 700 °C); [1992Men] and [1996Men] (Nb-rich at 1650, 1200, and 1000 °C); [1992Pav1] (Nb-rich at 1200, 900 and 600 °C); [1992Pav2] (Nb-rich at 900 and 600 °C); [1992Zak] (Nb-rich at 1100 and 900 °C); [1993Gam] (full at 1400, 1200, 1100, 1000, and 700 °C); [1993Nak] (Nb-poor at 1200 °C); [1993Row] (around O phase at 900 °C); [1994Che] (Nb-poor at 1200 °C); [1994Kum] (Nb-poor at 1000 °C); [1995Zdz] (full at 1200 °C); [1996Che] (full at 1400, 1150, and 1000 °C); [1998Din2] (Nb-poor in the range 1300-1000 °C); [1998Hel] (full at 1200 and 1000 °C); [1998Wan] (full at 1400 °C); [2000Leo2] (partial at 1100 and 900 °C); and [2002Leo] (1100 °C).

With starting metals of 99.99% Al, 99.95% Nb, and 99.95% Ti, [1998Wan] arc-melted 22 ternary alloys. After annealing at 1400 °C for 4 to 6 h, the samples were quenched in water. The phase equilibria were studied by XRD, EPMA, and metallography. Diffusion couple studies, differential thermal analysis, and differential scanning calorimetry were also used. The isothermal section constructed by them at 1400 °C is redrawn in Fig. 3 to agree with the accepted binary data. A part of the γ region marked γ_1 by [1998Wan] is not shown separately from γ in Fig. 3 due to the nonconfirmation of the existence of γ_1 [1997Jew, 1998Hel, 2002Leo]. The triangulations seen in Fig. 3 are the same as those in the computed section of [1992Kat], but significant differences exist on the extent of the phase regions.

[1995Zdz] induction-melted 21 ternary alloys under an Ar atmosphere (the purity of the starting metals was not stated). The samples were annealed at 1200 °C for 2 weeks and quenched. The melting temperatures of the alloys were determined using a calibrated optical pyrometer. The phase structures were studied by scanning electron microscopy, XRD, and EPMA. The isothermal section at 1200 °C constructed by [1995Zdz] is redrawn in Fig. 4 to agree with the accepted binary data. It is in reasonable agreement with the section given by [1998Hel]. The triangulations seen in Fig. 4 are the same as those in the corresponding sections in [1992Kat] and [1990Per]. However, at 1200 °C, the island-like *B*2 phase found by [1990Per] centered around the composition 45Al10Nb45Ti was not found by [1995Zdz] or [1998Hel]. There are no other ternary phases at 1200 °C [1995Zdz, 1998Hel]. The equilibria involving $Ti_{1-x}Al_{1+x}$, $TiAl_2$, and Ti_5Al_{11} are shown schematically in Fig. 4. They do not match the tentative equilibria shown by [1998Hel] in this region, due to differences in the Al-Ti phase diagram that was used. Also, α_2 (Ti_3Al) indicated by [1998Hel] is not present at 1200 °C.

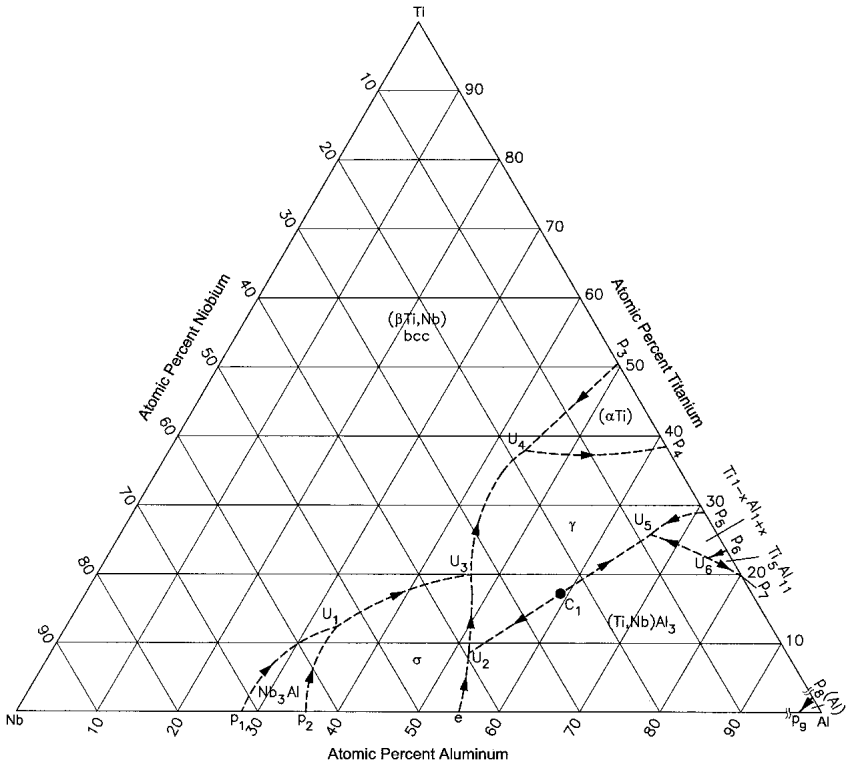


Fig. 2 Al-Nb-Ti tentative liquidus projection

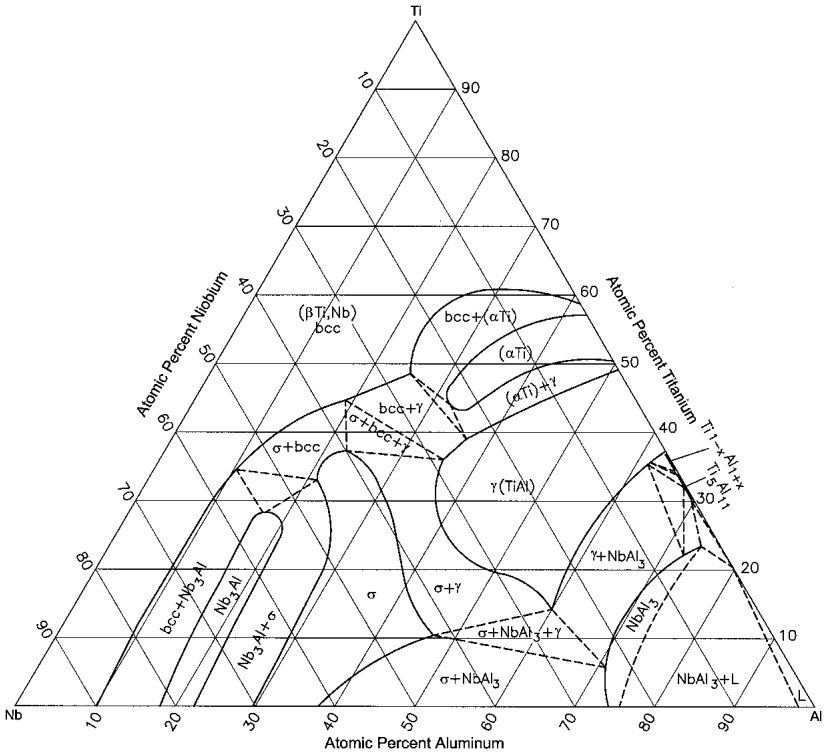


Fig. 3 Al-Nb-Ti isothermal section at 1400 °C [1998Che]

[2002Leo] arc-melted 15 ternary alloys under Ar atmosphere. The samples were annealed at 1100 °C for 720 h and quenched in water. The phase equilibria were studied by metallography, XRD, and EPMA. [2002Leo] superimposed the tie-line and the tie-triangle compositions determined by them on the computed isothermal section

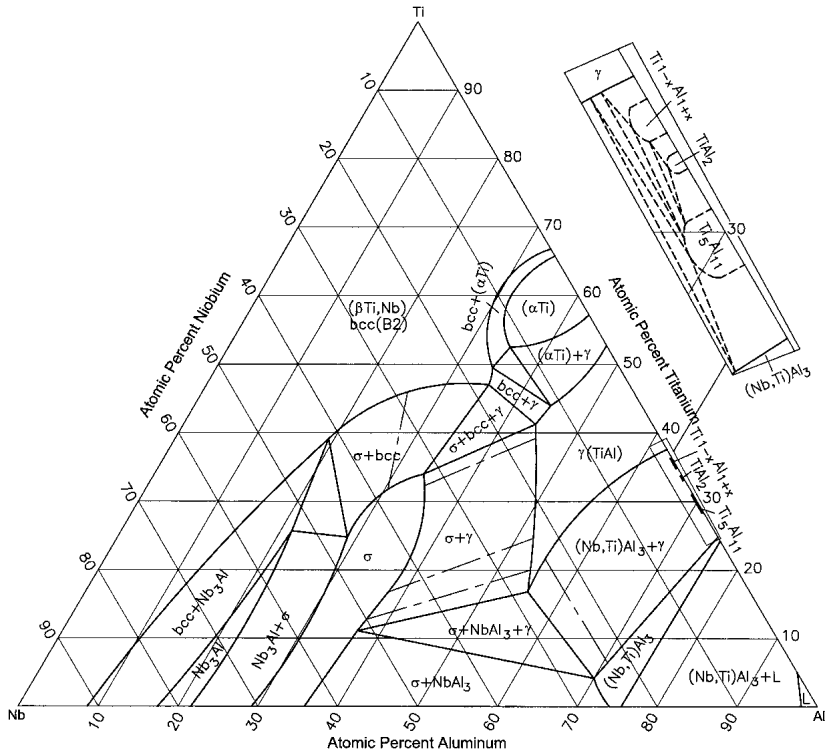


Fig. 4 Al-Nb-Ti isothermal section at 1200 °C [1995Zdz]

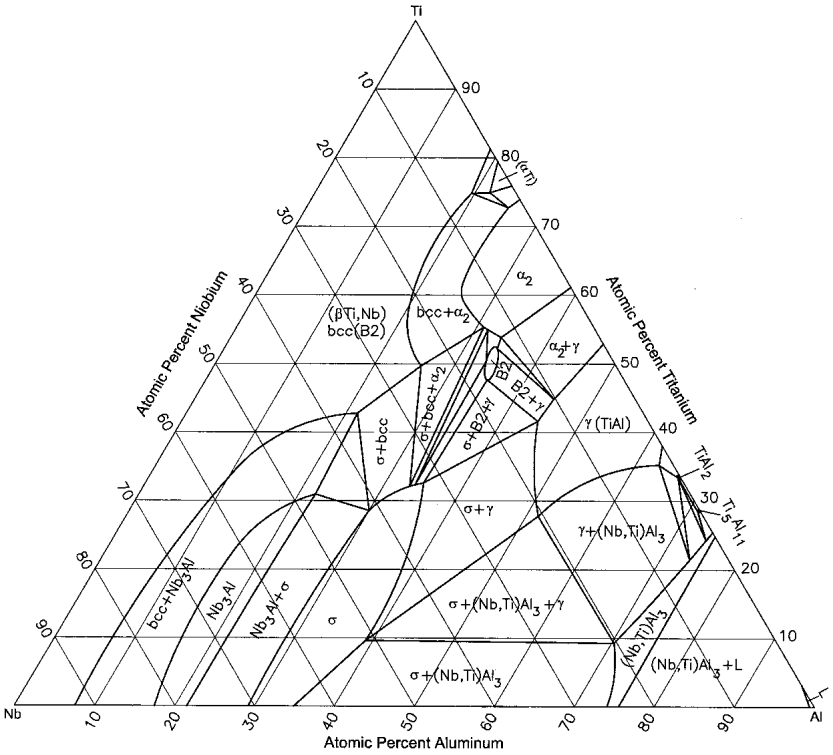


Fig. 5 Al-Nb-Ti isothermal section at 1100 °C [2002Leo, 1993Gam]

at 1100 °C determined by [1992Kat]. Figure 5 is redrawn with the (bcc + Nb_3Al), (Nb_3Al + σ), (σ + γ), (bcc + σ), and (bcc + Nb_3Al + σ) phase boundaries using the data of [2002Leo]. The upper part of the diagram is based on the section at 1100 °C reviewed by [1993Gam]. An island-like region of *B*2 is present around the composition 35at.%Al-

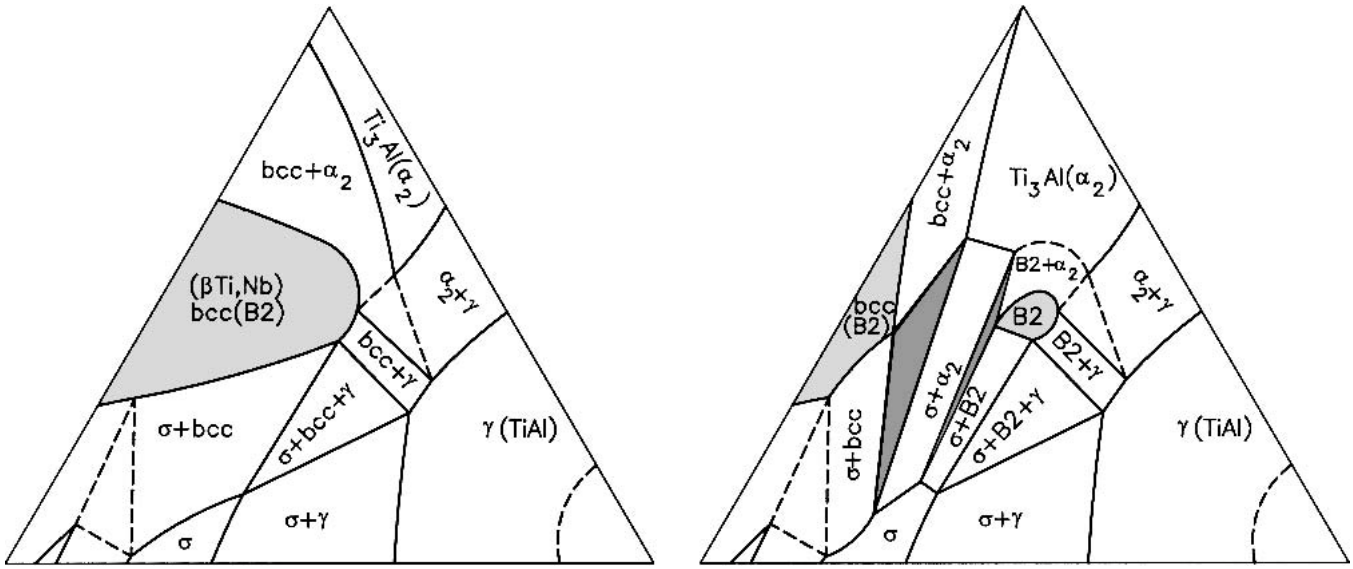


Fig. 6 Al-Nb-Ti formation of miscibility gap in the bcc (*B*2) phase between 1200 and 1100 °C (schematic)

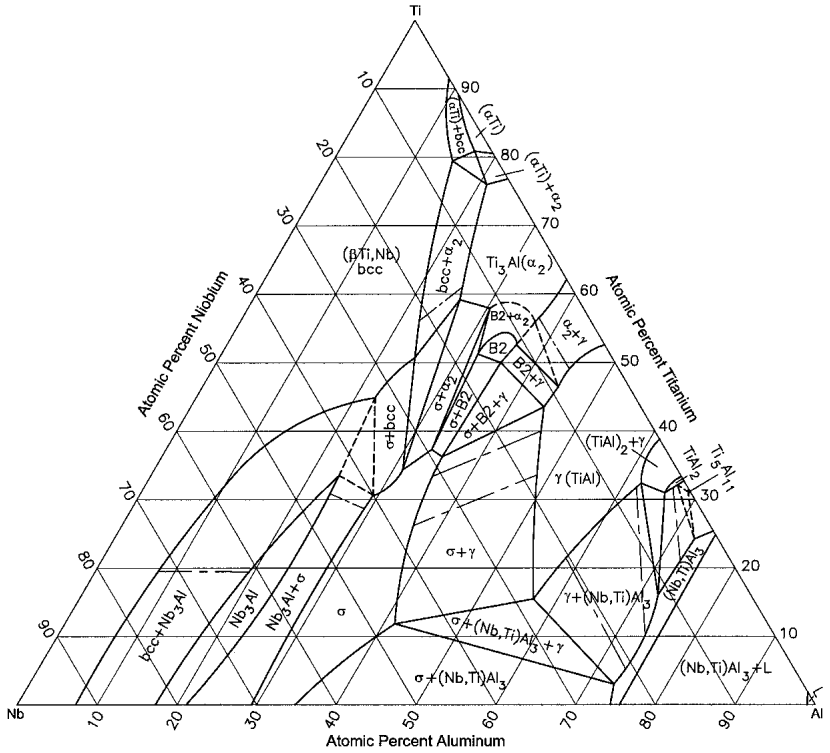


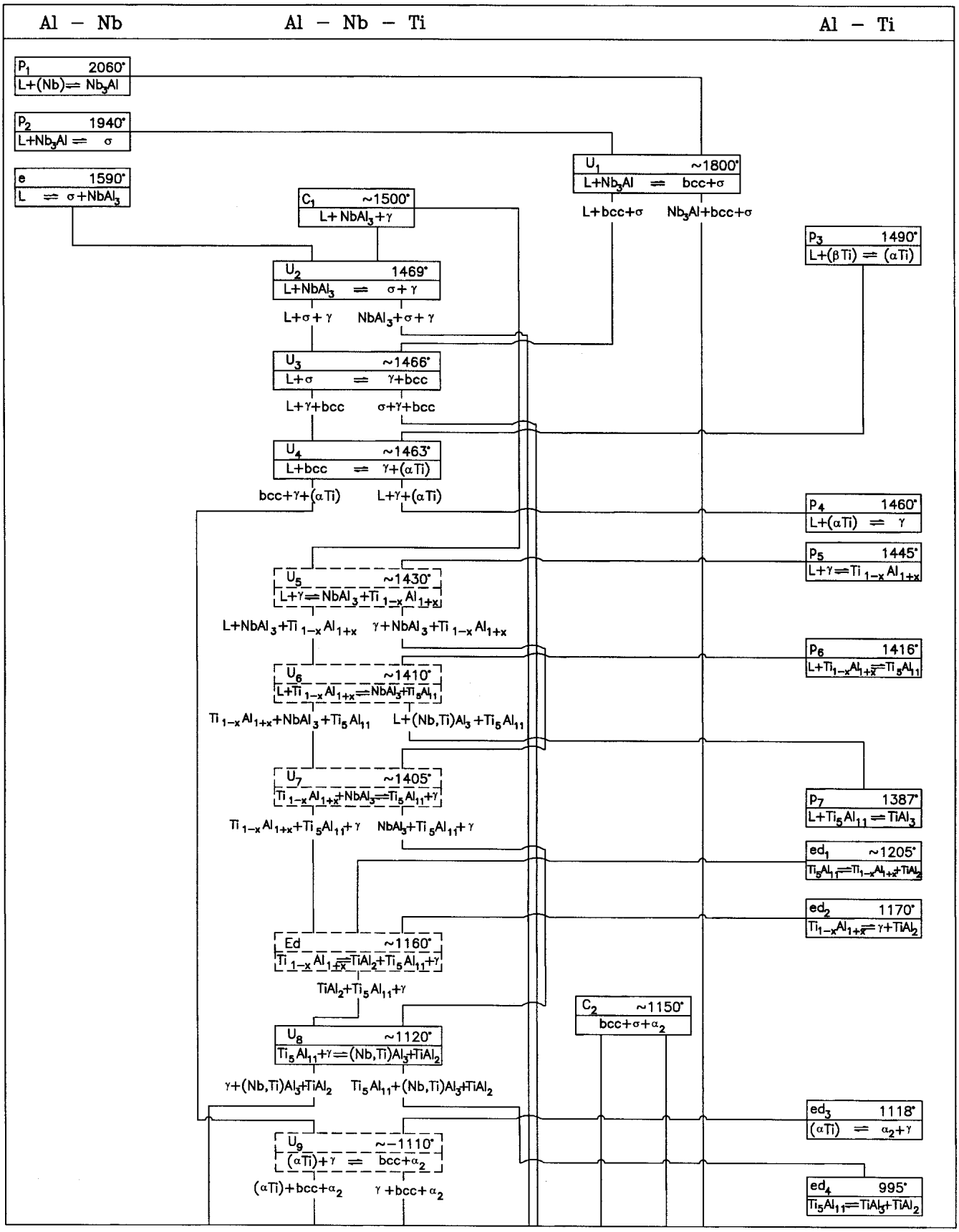
Fig. 7 Al-Nb-Ti isothermal section at 1000 °C [1998Hel]

15at.%Nb-50at.%Ti. It arises from a miscibility gap forming in the bcc (*B2*) region at a critical temperature C_2 between 1200 and 1100 °C, as illustrated schematically in Fig. 6.

With starting metals of 99.99% Al, 99.8% Nb, and 99.7% Ti, [1998Hel] arc-melted 28 alloys under Ar atmosphere. The samples were annealed at 1000 °C for 96 h and quenched in an ice-water mixture. Also, eight diffusion couples were prepared and annealed at the desired temperatures and quenched. The composition of the coexisting phases was determined by EPMA. Optical/transmission electron microscopy and XRD were used to characterize the phase structures. The isothermal section constructed by [1998Hel] at 1000 °C is redrawn in Fig. 7 to agree with the accepted binary data. An island-like region of the ordered bcc phase *B*2 present in Fig. 5 (1100 °C) is also seen in Fig. 7 (100 °C).

The phase relationships below 1000 °C in the region

Table 1 Al–Nb–Ti tentative reaction sequence down to 1000 °C



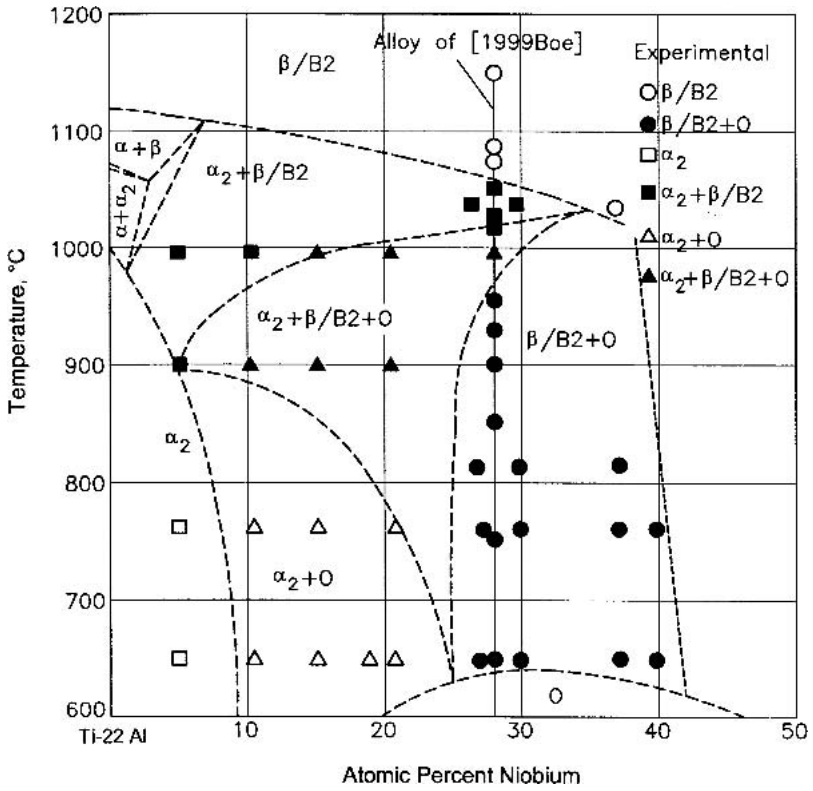


Fig. 8 Al-Nb-Ti vertical section at 22at.% A1 [1995Mir,1999Boe]

where the O phase is present are given by a vertical section of [1996Mir] (Fig. 8), with additional experimental points superposed from the work of [1999Boe] for a Ti-22 at.% Al-28 at.% Nb alloy.

Reaction Sequence

A tentative reaction sequence down to 1000 °C is written for this system in Table 1. Reactions U_1 through U_4 are those reported by [1990Per] and in a later work. The upper critical point C_1 is also suggested by [1990Per]. Reaction U_8 was suggested by [1989Kal] (labeled U_4 by them). The other reactions are postulated here. They are placed in broken boxes. The temperatures indicated for the postulated reactions are notional values. They merely indicate the likely sequence of the reactions with falling temperature. The miscibility gap in the bcc (*B*2) region occurs at C_2, generating two three-phase fields of [bcc (*B*2) + σ + α_2]. This reaction scheme is consistent with the liquidus projection in Fig. 2 and the isothermal sections in Fig. 3 to 7. The scheme does not include the equilibria involving the O phase, which is stable at and below 1000 °C [1991Ben, 1994Kum].

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