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Al-Mn-Ti (Aluminum-Manganese-Titanium)

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The ASM compilation [1995Vil] of data on this system is based on the following studies. [1955Dom] determined the phase equilibria in the Ti-TiAl-Mn_2Ti region between 1200 and 700 °C and presented six isothermal sections at 1200, 1100, 1000, 900, 800, and 750 °C, and six vertical sections at 60, 70, 80, and 90 wt.% Ti and at 5 and 10 wt.%, Mn respectively. [1977Cha] found that Mn_2Ti dissolves as much as 30 at.% Al at a constant Ti content. [1989Mab] determined an isothermal section for Al-rich alloys at 1000 °C. This section shows an $L1_2$-type cubic compound at the composition $Ti_{25}Mn_9Al_{66}$ and an $Mn_{23}Th_6$-type cubic phase at $TiMnAl_2$.

Recently, Butler and coworkers [1997But, 1998But, 1999But] presented new experimental data on alloys containing up to 30 at.% Mn, and computed a number of isothermal sections and a liquidus projection for this system.

Binary Systems

The Al-Mn phase diagram [1997Oka] shows a number of intermediate phases: $Al_{12}Mn$ ($Al_{12}W$-type cubic); Al_6Mn ($D2h$-type orthorhombic); Al_4Mn (hexagonal); $Al_{11}Mn_4$ (high-temperature orthorhombic and low-temperature triclinic); γ-AlMn (34.5 to 51.3 at.% Mn; body-centered cubic [bcc]); γ_1 (30 to 38.2 at.% Mn) and γ_2 (31.4 to 47 at.% Mn; $D8_{10}$, Al_8Cr_5-type rhombohedral); and ε-Al_2Mn_3 (53.2 to 60 at.% Mn; close-packed hexagonal [cph]). For a thermodynamic evaluation of the Al-Mn system, see [1999Liu]. 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; and $TiAl_3$ (low temperature [LT]) (tetragonal) forms at ~950 °C and is stable at low temperatures (LT). 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 low-temperature 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) (bcc; also denoted β), and the liquid under-

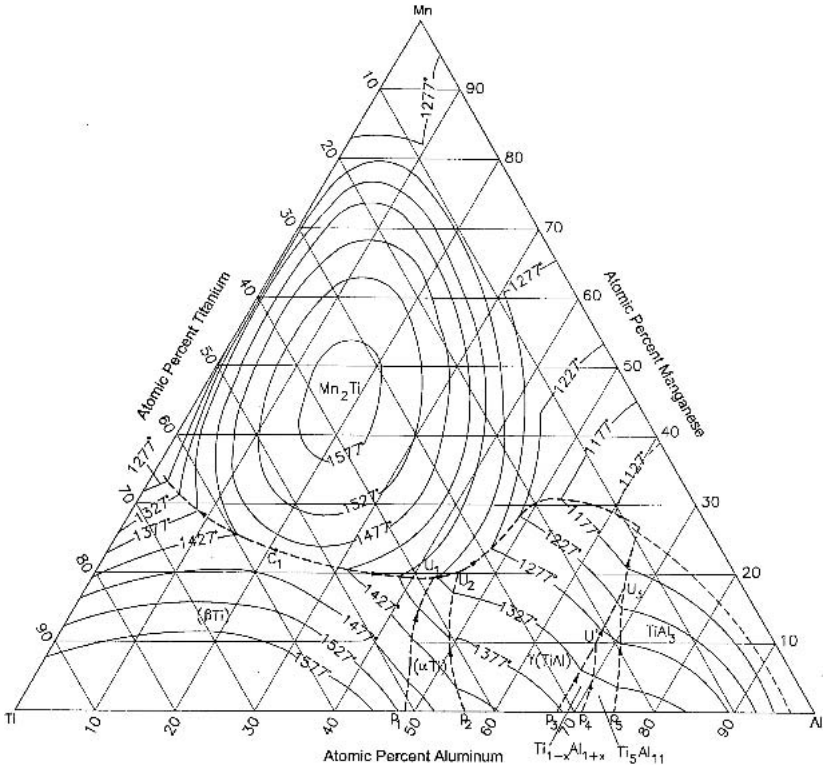
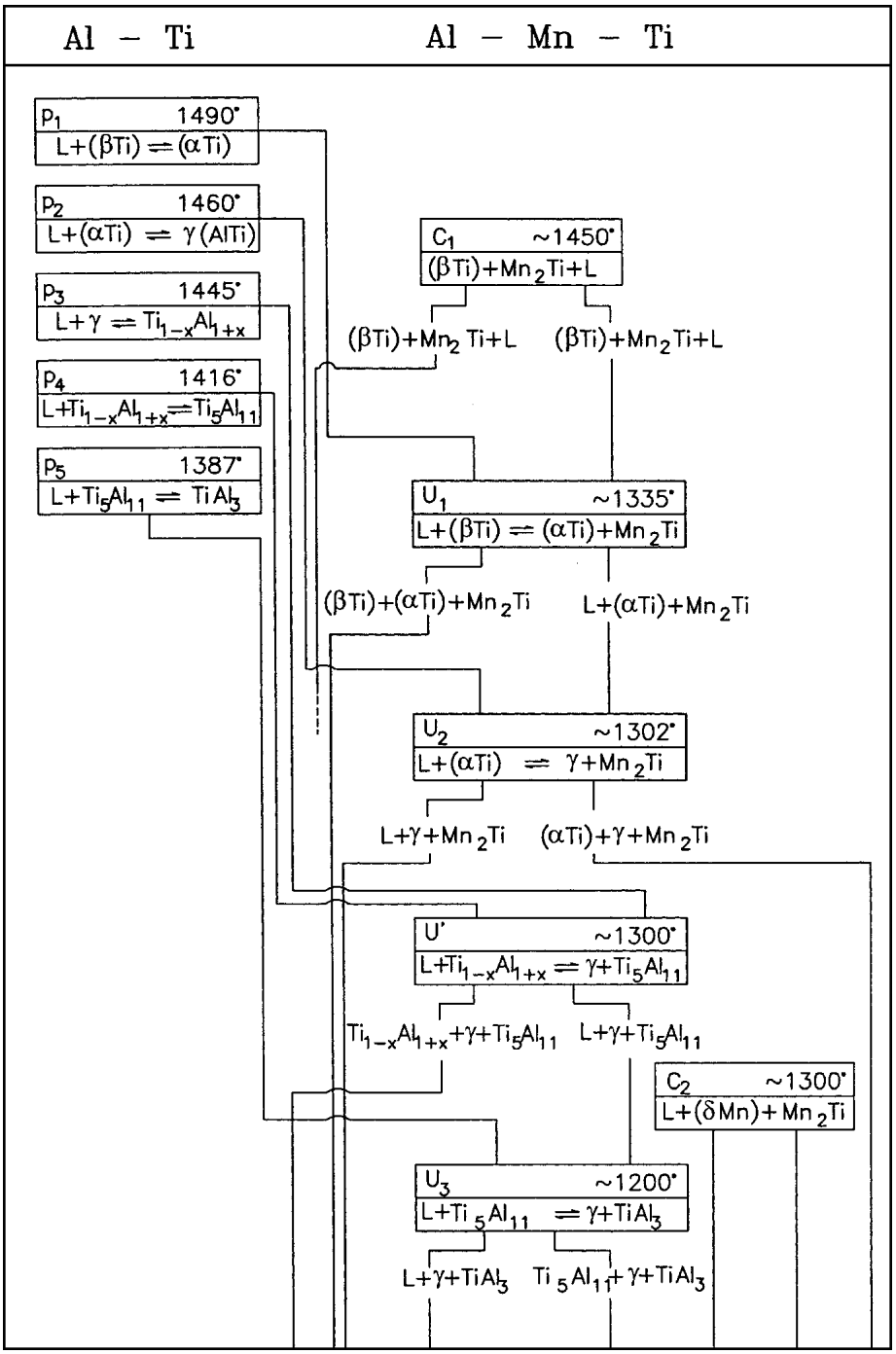


Fig. 1 Al-Mn-Ti computed partial liquidus projection [1997But]

Table 1 Al-Mn-Ti partial reaction sequence during solidification



goes a peritectic reaction at 1490 °C to yield (αTi) (cph, 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. The Mn-Ti phase diagram [Massalski2] has the following intermediate phases: αMnTi (tetragonal); βMnTi, Mn_2Ti (60 to 70 at.% Mn; *C*14, $MgZn_2$-type Laves phase); Mn_3Ti (orthorhombic); and Mn_4Ti (rhombohedral).

Ternary Phase Equilibria

With starting metals of 99.8% Al, 99.95% Mn, and 99.95% Ti, Butler and coworkers [1997But, 1998But, 1999But] arc melted four alloys under an Ar atmosphere with a constant Ti-to-Al ratio of 1.14, and Mn contents of 5, 10, 20, and 30 at.% Mn, respectively. The phase equilibria were studied using optical microscopy, x-ray diffraction,

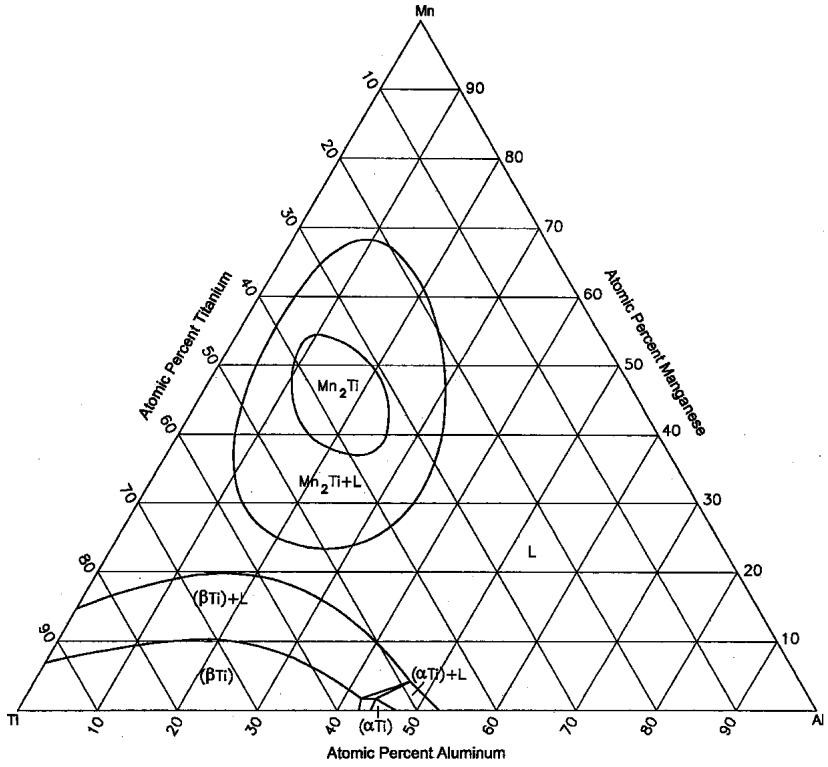


Fig. 2 Al-Mn-Ti computed isothermal section at 1477 °C [1997But]

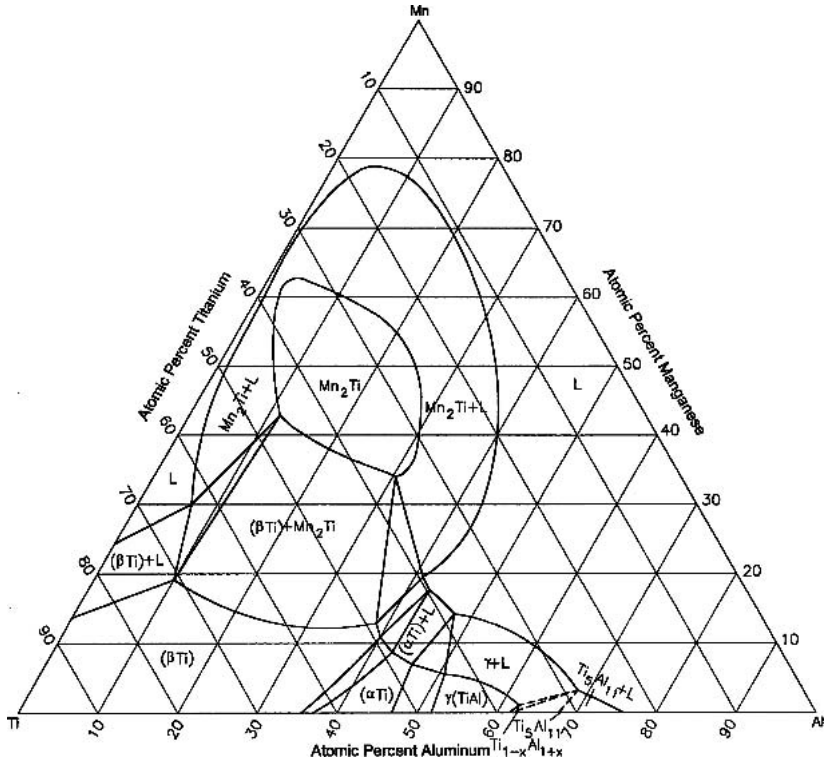


Fig. 3 Al-Mn-Ti computed isothermal section at 1352 °C [1997But]

and scanning electron microscopy, including energy dispersive x-ray analysis. Differential thermal analysis was performed at a heating rate of 10 °C/min.

In the CALPHAD calculations, the disordered solution phases (liquid and the allotropic forms of Ti and Mn), the ordered binary phases and their extension into the ternary

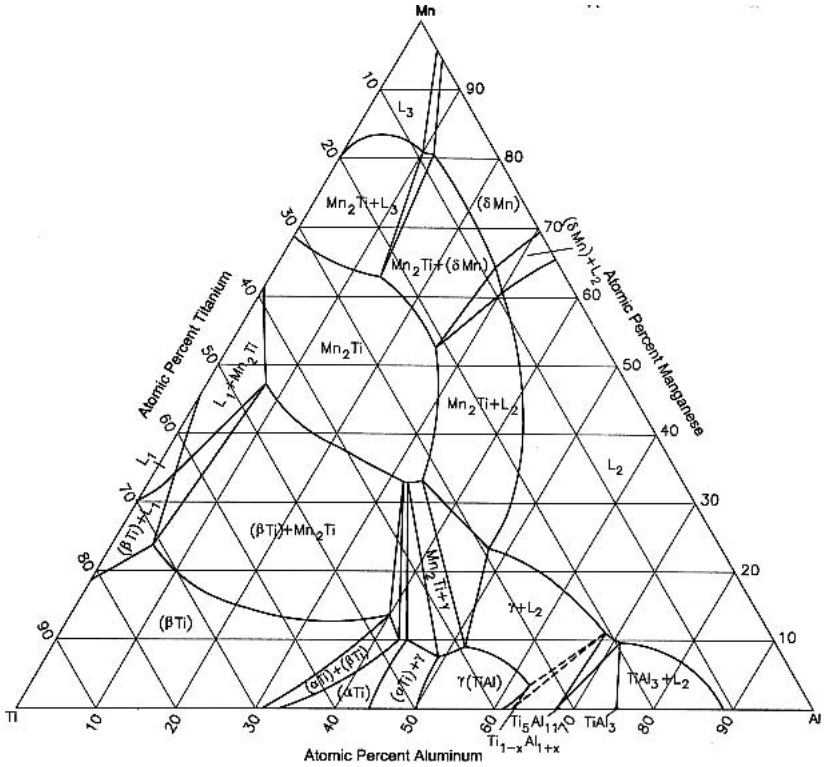


Fig. 4 Al-Mn-Ti computed isothermal section at 1277 °C [1997But]

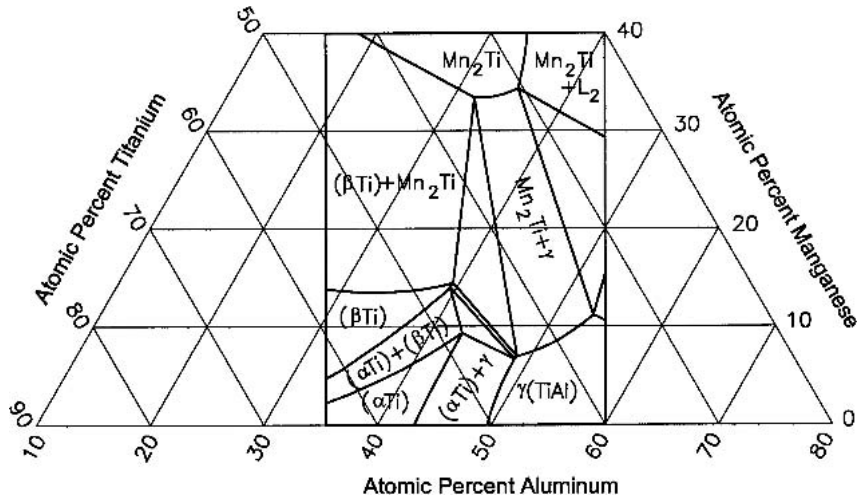


Fig. 5 Al-Mn-Ti computed partial isothermal section at 1235 °C [1999But]

system (α_2-Ti_3Al, γ-TiAl, Mn_2Ti, γ-AlMn, and ε-Al_2Mn_3), and the line compounds of the binary systems were considered. The ordered CsCl-type *B*2 structure was not modeled. The partial liquidus projection computed by [1997But] is redrawn in Fig. 1. The fields of primary crystallization are marked. Two transition reactions, U_1 and U_2, were identified by [1997But]. Two other reactions, U' and U_3 (postulated here), eliminate $TiAl_3$ and $Ti_{1-x}Al_{1+x}$ from the liquid-solid equilibria. Due to the lack of experimental data, the liquidus surface in Fig. 1 is incomplete. It may be noted that, due to the stabilizing effect of Al, Mn_2Ti nucleates in the ternary region, ~300 °C above its formation temperature in the Mn-Ti binary system. Table 1 lists the reaction sequence corresponding to the liquidus surface in Fig. 1. [1997But] computed five isothermal sections at 1477, 1427, 1352, 1320, and 1277 °C. Three of these, at 1477, 1352, and 1277 °C, respectively, are redrawn in Fig. 2 to 4. No attempt is made to modify the computed diagrams to fit the accepted binary data, except for the inclusion of the $Ti_{1-x}Al_{1+x}$ phase. With the coalescence of the L + Mn_2Ti and L + (βTi) fields,

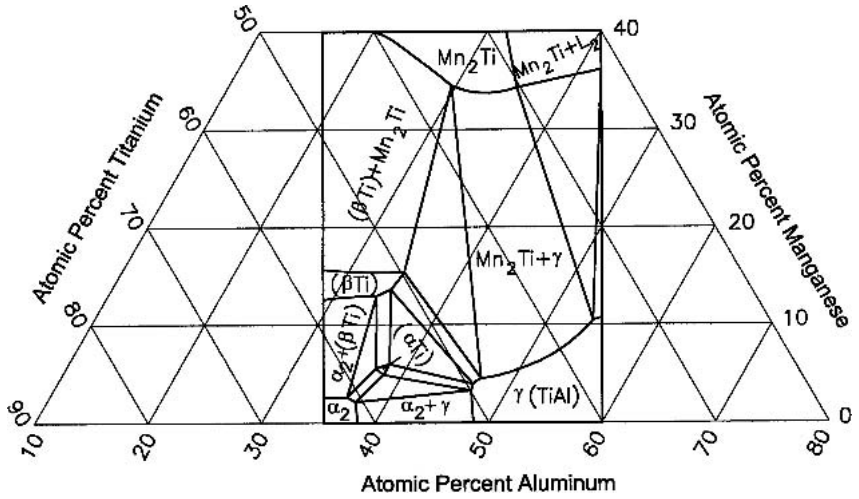
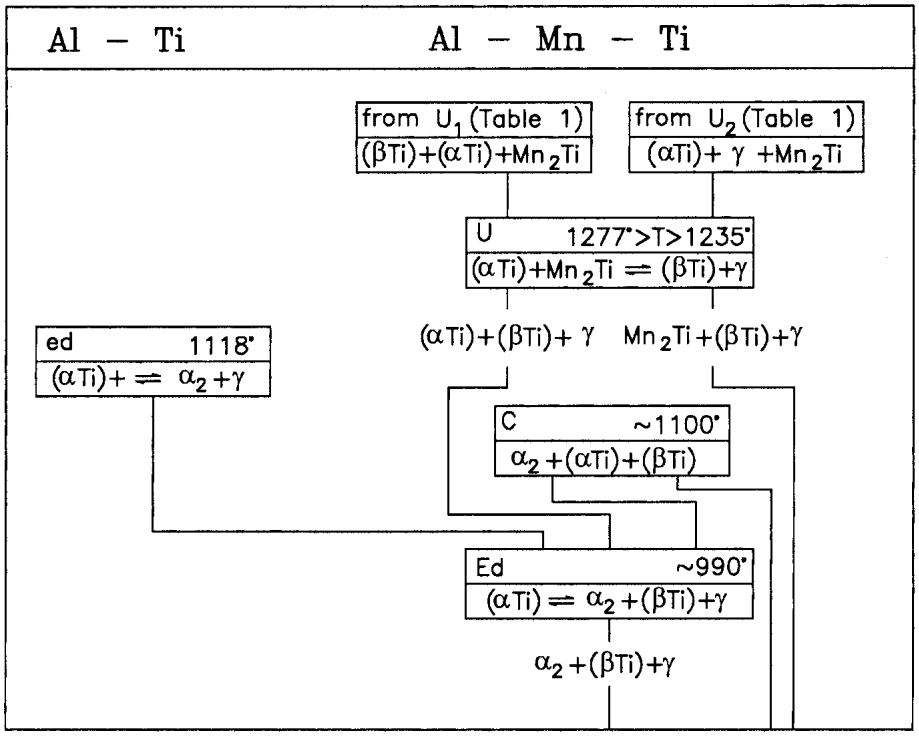


Fig. 6 Al-Mn-Ti computed partial isothermal section at 1000 °C [1999But]

Table 2 Al-Mn-Ti tentative partial reaction sequence in the solid state for Ti-rich alloys



two three-phase fields of L + (βTi) + Mn_2Ti come into existence between 1477 and 1427 °C. The transition reactions U_1 and U_2 occur at ~1335 and 1302 °C, respectively. The corresponding changes in the triangulation are seen in Fig. 4 (1277 °C). At about 1300 °C, the L + Mn_2Ti and L + (δMn) fields coalesce to form two three-phase fields of L + Mn_2Ti + (δMn) near the Mn corner (Fig. 4). The need for more experimental work in Mn-rich alloys to improve the thermodynamic description of the $(Mn,Al)_2Ti$ Laves phase was pointed out by Butler and coworkers.

[1998But] annealed the alloys with 5 and 10 at.% Mn in the temperature range of 1330 to 1090 °C for 24 to 336 h and quenched them in water. The same experimental techniques as described above were used. Using the CALPHAD approach, four isothermal sections were computed at 1330, 1285, 1235, and 1145 °C over a rectangular area resting on the Ti-Al side within the Gibbs triangle. [1999But] annealed the alloy with 20 at.% Mn in the temperature range of 1235 to 1000 °C for 72 to 336 h, and that was followed by water quenching. The same experimental techniques as listed

above were used to determine the phase equilibria. Using the CALPHAD method, additional isothermal sections were computed at 1090 and 1000 °C. Isothermal sections at 1235 and 1000 °C are redrawn in Fig. 5 and 6.

A tentative sequence for the solid-state reactions in Ti-rich alloys is shown in Table 2. Ti_3Al (α_2) forms congruently at 1176 °C. Below 1176 °C, the two-phase field of α_2 + (αTi) forms. At about 1100 °C, the α_2 + (αTi) field coalesces with the (αTi) + (βTi) field and generates two three-phase fields of α_2 + (αTi) + (βTi). A ternary eutectoid reaction (Ed): (αTi) → α_2 + (βTi) + γ is postulated here to occur just below 1000 °C.

Among other studies, [1988Has] reported a ternary phase at the composition $Mn_2Al_3Ti_3$, which was taken to be $(Mn,Al)_2Ti$ by [1999But]. [1990Zha] confirmed the existence of the $L1_2$-type cubic phase at the composition $Ti_{25}Mn_8Al_{67}$. [2001Kan] computed the boundaries between the (αTi), α_2, and γ-phases by the cluster-variation method.

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