

# Aluminium - Nickel - Titanium

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## Introduction

The first detailed investigation of Ni-rich alloys containing more than 50 at.% Ni in the Al-Ni-Ti system was made by [52Tay]. 99.99 mass% pure Al, electrolytic Ni (99.96 mass%) and Ti sponge (99.95 mass%) were used as the initial materials. The alloys were synthesized in an arc furnace with special attention paid to the heat treatment which was conducted in vacuum. The alloys were homogenized at 1200°C for 4 d. They were annealed after homogenization at 1150°C for 2 h, at 1000°C for 1 d, at 850°C for 10 d and at 750°C for three weeks.

The existence of extended solid solutions based on pure Ni ( $\gamma$  phase),  $\text{Ni}_3\text{Al}$  ( $\gamma'$  phase) and  $\text{TiNi}_3$  ( $\eta$  phase) was found in the system. A brittle ternary phase  $\text{TiNi}_2\text{Al}$ ,  $\tau_4$ , was found in the alloys containing 50 at.% Ni; it has a structure of the  $\text{MnCu}_2\text{Al}$  type. The existence of  $\tau_4$  was confirmed by [62Hei] (Table 1). The  $\gamma'$  phase has an ordered fcc structure of  $\text{AuCu}_3$  type; a noticeable amount of both transition metals and silicon may be dissolved in it [59Gua]. The effect of elements dissolved on the  $\gamma'$  lattice parameter was studied by [63Arb, 66Arb, 84Och, 85Mis]. The interaction of the intermetallic compounds  $\text{Ni}_3\text{Al}$  and  $\text{TiNi}_3$  was investigated by [66Vuc, 67Min]. The  $\eta$  phase exists only at its stoichiometric composition and has no homogeneity field; it has a hexagonal structure of its own type. The vertical section  $\text{Ni}_3\text{Al}$  ( $\gamma'$ ) -  $\text{TiNi}_3$  ( $\eta$ ) appears not to be pseudobinary.

The Ti-rich portion of the phase diagram (the sum of Ni and Al contents is lower than 35 mass%) was investigated by [62Wu]. Four isothermal sections were constructed at 900, 800, 700 and 550°C. Two vertical sections were also constructed, one of which was at a Ni:Al ratio of 1:1 (in at.%); the other was constructed at the sum of Ni and Al contents equal to 10 mass%. The existence of  $\text{Ti}_3\text{Al}$  ( $\alpha_2$ ), however, was not taken into account during the analysis of this phase equilibria.

[61Kam] investigated the Al-rich part of the system up to 1% Ti and 8% Ni. 40 alloys were arc melted or prepared by adding to master alloys containing 10% Ni and Ti, respectively. Starting materials were 99.99% pure aluminium, 99.95% pure electrolytic nickel containing 0.3% cobalt and 99.8% pure titanium sponge. The liquidus surface of the Al corner was established from the results of differential thermal analysis, X-ray diffraction and microscopy. Small discrepancies exist regarding the exact location of  $e_3$ , which is given at 6 mass% Ni in [Mas2] but observed at 5.7 mass% Ni by [61Kam].

The partial Ni-NiTi-NiAl system was studied by [92Yan] who combined modelling according to the CALPHAD method with experimental determinations (electron microscopy) of the three-phase equilibrium  $\text{NiAl}$ - $\tau_4$ - $\text{Ni}_3\text{Al}$  at 900°C. An isothermal section at that temperature, the liquidus surface and a vertical section  $\text{Ni}_3\text{Al}$ - $\text{Ni}_3\text{Ti}$  were calculated. Calculations of the  $\gamma$ - $\gamma'$  equilibria are also due to [89Cer].

Using X-ray diffraction analysis of both as-cast alloys and alloys annealed at 800°C for a week, three more ternary phases were found by [65Ram] besides  $\tau_4$ ; these are  $\text{TiNiAl}$  ( $\tau_3$ ),  $\text{TiNiAl}_2$  ( $\tau_2$ ) and  $\text{Ti}_2\text{Ni}_1\text{Al}_{5+}$  ( $\tau_1$ ). The data after [65Ram] on the formation of these ternary phases were later confirmed by [73Mar]. The structure and properties of directional solidified eutectic  $\text{Ni}_3\text{Al}(\gamma') + \text{TiNi}_2\text{Al}(\tau_4) + \text{TiNi}_3(\eta)$  were investigated by [69Tho]. The ternary eutectic point  $\gamma' + \tau_4 + \eta$  was found to lie at 21.4 at.% Ti, 11.2 at.% Al and 67.4 at.% Ni; the eutectic temperature is 1304°C.

[83Sri] studied the quaternary system Ti-Ni-Al-C and determined lattice parameters of binary and ternary phases, among them  $\tau_4$  ( $\text{TiNi}_2\text{Al}$ ). A schematic isothermal space at 1100°C which contains the section Al-Ni-Ti is given. Samples were prepared by sintering powder mixtures

by arc melting and annealing. [89Fie] studied several alloys along the join NiAl and TiNi<sub>2</sub>Al. Six alloys were prepared from 99.9% pure elements by arc melting under argon and drop casting into Cu molds. Solidus and liquidus temperatures were determined by DTA. Due to temperature limitations of the equipment the liquidus determination in a 5% Ti specimen was not possible. Segregation data were obtained from electron microprobe analysis.

Various portions of the phase diagram were investigated by [85Nas1, 85Nas2, 85Oma1, 85Oma2, 86Sei]. Alloys which were arc melted from high purity components (better than 99.99 mass%), homogenized at temperatures close to their melting points for 3 h, annealed in vacuum at 900°C for a week and water quenched, were investigated by [85Nas2] using metallographic analysis and X-ray diffraction. Phase equilibria in these alloys were established as well as the homogeneity field of ternary phases together with the limit solubility of the third component in the binary phases. The possible constitution of liquidus surfaces was proposed by [85Nas2] for a portion of the phase diagram with Al contents less than 50 at. %.

Al-rich alloys (from pure Al to the section NiAl-TiAl, i.e., up to the sum of Ti and Ni contents of 70 mass%) were studied by [85Oma1, 85Oma2, 86Sei]. The alloys were arc melted from high purity components and remelted for 4 to 5 times; then they were annealed at 1150, 1000, 800 and 600°C for 50 h depending on their composition and water quenched. The alloys were investigated by DTA, metallographic analysis and X-ray diffraction. Both the liquidus surface and four isothermal sections at 1150, 1000, 800 and 600°C were constructed. The specific features of the phase diagram constitution and the formation of ternary compounds were considered in reviews [82Nas, 90Kum, 91Lee]. The heat of formation for a wide range of alloys was determined by [58Kub]; thermodynamic calculations of phase equilibria in the system were made by [74Kau, 78Ans].

## **Binary Systems**

The generalized version of the Ti-Al phase diagram, as presented in the Al-Nb-Ti system report of this work, including the results after [89Kal, 89McC, 90Sch], was accepted to analyze the phase equilibria in the ternary system. A thermodynamic calculation of the Ti-Al phase diagram is given in [88Mur]. The binary system Ni-Al is essentially based on [Mas2], however, according to [87Hil, 88Bre, 91Ver], the  $\gamma'$  phase (Ni<sub>3</sub>Al) in the Ni-Al system is formed by a reaction  $L + \gamma(\text{Ni}) \rightleftharpoons \gamma'(\text{Ni}_3\text{Al})$  at 1372°C and the binary eutectic  $\gamma'(\text{Ni}_3\text{Al}) + \beta_1(\text{NiAl})$  solidifies at 1369°C. The Ti-Ni binary phase diagram is taken from [Mas2].

## **Solid Phases**

In spite of the general agreement among the various authors on the formation of the four ternary compounds  $\tau_1$  to  $\tau_4$ , some controversies exist concerning the ranges of existence with respect to composition and temperature and there is practically no direct evidence on the mode of formation of these compounds (see section "Invariant Equilibria"). The crystallographic data on the solid phases observed in the system Ti-Ni-Al are listed in Table 1. The data on the position of the  $\tau_3$  homogeneity field obtained by [73Mar] and [85Nas2] vary significantly. The  $\tau_4$  phase (TiNi<sub>2</sub>Al) is formed directly from a melt and has a significant homogeneity range.

## **Invariant Equilibria**

The data on the invariant equilibria involving the liquid phase are given in Table 2 according to [82Nas, 85Nas2, 91Lee] ( $U_1$ ); [69Tho, 82Nas, 85Nas2, 91Lee] ( $E_1$ ) and [85Oma2, 86Sei, 91Lee] ( $U_4, U_7, U_{11}, U_{12}$ ). Detailed discussions can be found in the reviews by [82Nas, 91Lee] and will not be repeated here. There are no established data on the invariant equilibria  $U_2, U_3, U_5, U_6, U_8, U_9$  and  $U_{10}$ . A reaction scheme of the invariant equilibria involving the liquid phase is given in Fig. 1 where all the approximately established reactions ( $U_2, U_3, U_5, U_6, U_8, U_9$  and

$U_{10}$ ) are shown by dashed lines [88Bre, 89Kal, 89McC, 90Sch, 91Lee]. A more extended but rather speculative reaction scheme has been presented by [82Nas]; however, due to the controversies on the mode of formation of the ternary compounds  $\tau_1$  to  $\tau_3$ , it is not reproduced here. Whereas [82Nas, 91Lee] assumed a peritectoid mode of formation for the  $\tau_1$  phase ( $Ti_{2.5}NiAl_{6.5}$ ), the phase richest in Al at  $\sim 997^\circ C$  ( $TiAl + TiAl_3 + Ni_2Al_3 \rightleftharpoons Ti_{2.5}NiAl_{6.5}$ ), precise investigations by [89Maz], however, revealed the presence of  $\tau_1$  in alloys annealed at  $1200^\circ C$  for 500 h in equilibrium with the liquid phase. On the other hand, the data of [85Oma2, 86Sei, 91Lee] testify that  $\tau_1$  has no field of primary crystallization on the liquidus surface.

The  $\tau_2$  phase ( $TiNiAl_2$ ) also appears to form in the solid state but the mode of its formation has not yet been established [82Nas]. Based on the experimental solid state equilibria [82Nas, 91Lee] speculated on the  $\tau_3$  phase ( $TiNiAl$ ) at  $\sim 992^\circ C$  according to the reaction  $TiNiAl_2 + TiNi_2Al + Ti_3Al \rightleftharpoons TiNiAl$ . According to a recent reinvestigation of the Ti-Al binary by [90Sch], it should be furthermore noted that the ternary diagram near the Ti-Al edge must be refined in the range from 23 to 45 at.% Ti. Thus the total amount of invariant reactions where the liquid phase is involved will undoubtedly be larger than that presented in Fig. 1 and Fig. 2. Additional reactions will involve equilibria existing in the Ti-Al binary ( $p_3$ ,  $p_4$  and  $p_5$ ).

## Liquidus Surface

The projection of the liquidus surface, as shown in Fig. 2, has been constructed using the data of [82Nas, 85Nas2, 85Oma1, 86Sei, 86Wil1, 87Hil, 88Bre, 89Kal, 89McC, 90Sch, 91Lee]. It should be noted that not all regions of the liquidus surface are investigated with sufficient accuracy; only the crystallization of Al- and Ni-rich alloys was studied in detail. The  $\tau_4$  phase has a significant field of primary crystallization; a number of invariant reactions takes place on its boards. Data on the experimentally studied reactions is given in Table 2. For additional reactions referring to the Ti-Al region between 23 to 45 at.% Ti see section 'Invariant Equilibria'.

## Isothermal Sections

Isothermal sections based on the reaction scheme and on the available experimental results [65Ram, 73Mar, 82Nas, 85Nas2, 85Oma1, 86Sei, 89Maz, 90Sch, 91Lee] are presented in Figs. 3, 4, 5. At  $1150^\circ C$ , the liquid phase is widely expanded from the Ti-Ni edge into the ternary up to 33 to 34 at.% Al, (Fig. 3). By this, the liquid is in equilibrium with  $\beta$ (Ti),  $\alpha_2$ ( $Ti_3Al$ ),  $\kappa$ ( $TiAl$ ),  $\beta_1$ ( $NiAl$ ) and  $\beta_2$ ( $TiNi$ ). The results of [89Maz] on the  $\tau_1$  homogeneity range were also included in Fig. 3; this phase is in equilibrium with  $TiAl$ ,  $TiAl_2(r)$ ,  $Ti_2Al_5$ ,  $TiAl_3$  and the Al-rich liquid.

The liquid fields get significantly narrower with decreasing temperature down to  $1050^\circ C$ ; one field displaces towards Ti-rich alloys and the other, towards pure Al. At  $800^\circ C$ , a liquid field remains only in the vicinity of the Al corner. Under these conditions, all four ternary phases which have homogeneity fields take part in most of the two- and three-phase equilibria. According to the isothermal sections constructed by [85Oma1, 85Oma2, 86Sei], the  $\tau_1$  phase with an approximate composition of 29 at.% Ti, 10 at.% Ni and 61 at.% Al, formerly designated by [65Ram] as  $Ti_2Ni_1Al_{5+}$ , whose composition was suggested by [73Mar] at  $Ti_{2.5}NiAl_{6.5}$ , exists only at 800 and  $600^\circ C$ ; it was shown to be absent in the sections constructed at 1150 and  $1000^\circ C$  [85Oma1]. In contrast to [85Oma1] the  $\tau_1$  phase was reported to exist in alloys annealed at  $1200^\circ C$  for 500 h with 22 to 30 at.% Ti, 4 to 16 at.% Ni and 58 to 68 at.% Al [89Maz]. Whereas [65Ram, 73Mar] considered  $\tau_2$  ( $TiNiAl_2$ ) at  $800^\circ C$  to be stoichiometric, [85Nas1, 85Nas2] reported a homogeneous region at  $900^\circ C$  extending at 22 at.% Ni from 25 to 27 at.% Ti. The data on the structure and mechanical properties of this phase are given in [89Tur]. According to [73Mar],  $\tau_3$ ( $TiNiAl$ ) at  $800^\circ C$  has a significant homogeneity range extending from 41 to 51 at.% Al along the isoconcentrate line at 33.3 at.% Ti. It does not, however, include the stoichiometric composition  $TiNiAl$ . In a later investigation by [85Nas2] the homogeneity field of the ternary phase the  $\tau_3$ ( $TiNiAl$ ) at  $900^\circ C$  lies close to the

isoconcentrate line 26.5 at.% Ni in the range 23 to 33 at.% Al. The observed changes in  $c/a$  at 800°C also refer to a considerable homogeneous and relatively wide homogeneity field for which extension along the isoconcentrate line at 50 at.% Ni was reported at 800°C to vary from 18 to 35 at.% Al by [85Nas2], from 24 to 27 at.% Al at 800°C by [65Ram, 73Mar] and from 22 to 26 at.% Al at 1100°C by [83Sri]. According to [85Nas2], the maximum solubility of Ti in  $\gamma'$  is 17 at.% at 900°C and that in  $\beta_1$  (NiAl) is 11 at.%. Controversial reports exist on the solid solubility of Al in  $\text{TiNi}_3(\eta)$ ,  $\text{TiNi}_3$ , on the basis of EMP-analyses [85Nas2, 86Wil2, 89Ish], was shown to dissolve 3 to 9 at.% Al at  $\sim 900^\circ\text{C}$ , though little or no solubility was claimed from X-ray analyses by [51Tay, 52Tay, 65Ram, 67Min, 73Mar]. The schematic isothermal section at 1100°C of [83Sri] differs in the Al-Ti boundary system from the accepted one. The section contains the ternary phase  $\tau_4$ , in agreement with the isothermal sections at 1150 and 1025°C (Fig. 3 and Fig. 4), though  $\tau_1$  is missed.

The calculated and experimental Ni-TiNi-NiAl sections at 900°C [92Yan] is comparable to the 1025°C section (Fig. 4) and is in fair agreement.

## **Miscellaneous**

The analysis of isothermal sections and liquidus surfaces presented in Figs. 2, 3, 4, 5 allows us to affirm the existence of a pseudobinary section between congruently melting  $\tau_4$  and the binary  $\beta_1$  (NiAl). The intersection of its liquidus curve with the curve  $U_2$ - $U_3$  is marked in Fig. 2 by a small circle. The pseudobinary nature of the  $\beta_1$ - $\tau_4$  section has been corroborated by [89Fie] employing DTA, SEM and TEM analyses. The results of this investigation have at present been explained by [89Fie] in terms of a pseudobinary diagram involving a second order ordering reaction combined with a conditional spinodal ( $\beta_1$ ,  $\tau_4$ ) to form a tricritical point. Following this argumentation, the reaction at  $e_3$  in Fig. 1 would be a saddle point rather than a maximum eutectic reaction. Although further experiments are planned to resolve the true nature of the  $\tau_4$ - $\beta_1$  pseudobinary, first indications of segregation and disproportionation behavior suggest a melting point minimum at  $\sim 17.5$  at.% Ti, but a tricritical point at  $\sim 12.5$  at.% Ti [89Fie]. Thermodynamic information on the Ti-Ni-Al was provided by [58Kub] and enthalpies of formation have been presented in the form of an isoenthalpy diagram. Thermodynamic calculations of phase equilibria are due to [74Kau, 78Ans] and concern the isothermal sections at 1323, 1223, 1123, 1023, 900 and 750°C. Comparison with the observed phase relations at 800°C is fair. Free enthalpies of formation have been derived for  $\tau_2$ ,  $\tau_3$  and  $\tau_4$ . The phase  $\tau_1$  has not been considered [74Kau]. A calculated vertical section  $\text{Ni}_3\text{Al-TiNi}_3$  [92Yan] is given in Fig. 6.

The temperature dependence of the molar heat capacity of  $\text{Ni}_3(\text{Al},\text{Ti})$  was measured as well as the effect of titanium additions on the Ni self-diffusion coefficient and the sublimation rate at 1100°C [76Kov].

The kinetics of phase transformations and age hardening in the Ni-rich alloys containing up to 12.3 mass% Ti and 14.5 mass% Al in dependence of temperature and their composition was studied by [60Mih]. It was said [60Mih] that under nonequilibrium conditions,  $\text{Ni}_3\text{Al}$  and  $\text{TiNi}_3$  form a continuous solid solution. Age hardening is from coherent  $\gamma'$ ; the transformation of  $\gamma'$  to  $\text{TiNi}_3$  results in overaging [60Mih]. Investigations on the crystal structure and sequence of precipitation of phases corresponding to the Al-Ni-Ti system during the annealing at 750°C for 100 h were carried out by [65Hug] on ferritic and austenitic steels containing Ni, Ti, Al in addition to Mn, Si and Cr. The ferritic steels were alloyed by  $\sim 4$  mass% Ni, 0.33 to 2.97 mass% Ti and 0.35 to 1.97 mass% Al and the austenitic by  $\sim 25$  mass% Ni, 1.6 to 3.95 mass% Ti and 0.69 to 4.05 mass% Al. The sequence of precipitation obtained in the ferritic steels was  $\text{TiNi} \rightarrow \text{TiNi}_2\text{Al} \rightarrow \text{TiAl}$  whereas that for austenitic steels was  $\text{TiNi}_3 \rightarrow \text{Ni}_3\text{Al} \rightarrow \text{TiNi}_2\text{Al} \rightarrow \text{NiAl}$ .

The influence of Ti (in the range 4 to 12 at.%) on the dendritic crystallization of two-phase  $\gamma + \gamma'$  alloys was considered by [72Ham]. Hardening of  $\gamma'$  ( $\text{Ni}_3(\text{Al},\text{Ti})$ ) by precipitation of disordered  $\gamma$  during aging at 600, 700 and 800°C for  $10^6$  s was investigated by [86Tia]. The initial shape of  $\gamma$  precipitated from supersaturated  $\gamma'$  on aging is spherical or round cubic.  $\gamma$  precipitates

grow into platelets as aging proceeds and are completely coherent with the  $\gamma'$  matrix as long as they are platelets.

The influence of Al (in the range 0.5 to 2.5 mass%) on the structure and properties of the  $\beta_2$  phase, TiNi, was studied by [73Zwi] in the range 54.1 to 57.1 mass% Ni. A maximum creep resistance at 400°C was obtained in the alloy with 54.6 mass% Ni and 2.5 mass% Al. After testing for 250 h the plastic deformation of this alloy is virtually negligible. The temperature of direct and reverse thermoelastic martensite transformations for the alloy with 59.4 at.% Ti, 38.7 at.% Ni and 1.9 at.% Al was investigated by [86Edm]. The flow stress of polycrystalline Ni<sub>3</sub>Al has been determined in the temperature range - 196 to 1000°C in dependency of deviations from the stoichiometric composition and of titanium additions [70Lop]. Al-rich deviations from the stoichiometry as well as titanium additions result in strengthening.

The Young's modulus and the tensile and creep rupture strength ( $\sigma_u^{\text{com}}$  and  $\sigma_{0.2}^{\text{com}}$ ), as determined at room temperature by compression tests on a directionally solidified eutectic Ni<sub>3</sub>Al + TiNiAl<sub>2</sub> + TiNi<sub>3</sub> at 21.4 at.% Ti, 67.4 at.% Ni, were reported to be 20.4, 1.62 and 1.27 GPa, respectively. The ultimate stress at tension  $\sigma_u$ , is 0.227 GPa at 1095°C; the corresponding value of relative elongation,  $\delta$ , is 30.7% [69Tho]. The oxidation rate of the uniaxially solidified eutectic alloy with 20 mass% Ti, 6 mass% Al and 74 mass% Ni is  $\sim 3.9 \cdot 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$  at 1105°C [78Hao].

The electron work function in the Ni-rich region (> 70 at.% Ni) was measured by [85Sav]. The highest value corresponds to pure Ni (4.11 eV); it additively decreases with increasing Ti and Al content, revealing a mapped outline of the phase equilibria.

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**Table 1: Solid Phases**

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
(Al) <660.45	cF4 Cu	a = 404.96	at 25°C [Mas2]
$\gamma$ , (Ni) <1455 $\text{Ni}_{1-x}\text{Al}_x$	cF4 Cu	a = 352.40  a = 353.8  a = 355.05	at 25°C [Mas2]  at 8 at.% Al, quenched from 1000°C, linear da/dx [85Mis] at 14 at.% Al, quenched from 1000°C, linear da/dx [52Tay]
$\text{Ti}_x\text{Ni}_{1-x}$		a = 355.5  a = 356.0	at 9.5 at.% Ti, quenched from 1000°C, linear da/dx [51Tay] quoted in [84Och] at 9 at.% Ti, quenched from 1000°C, linear da/dx [84Och, 85Mis]
( $\beta$ Ti)(h) 1670-882	cI2 W	a = 330.65	[Mas2]
( $\alpha$ Ti)(r) <882	hP2 Mg	a = 295.06 c = 468.35	at 25°C [Mas2]
$\epsilon$ , $\text{NiAl}_3$ <854	oP16 $\text{NiAl}_3$ ( $\text{Fe}_3\text{C}$ )	a = 661.14 b = 736.62 c = 481.12	58.5 to 61.2 at.% Al [V-C, Mas]
$\nu$ , $\text{Ni}_2\text{Al}_3$ <1133	hP5 $\text{Ni}_2\text{Al}_3$	a = 403.63 c = 490.05	59.5 to 63.2 at.% Al [Mas] at 40.8 mass% Al [L-B]
$\beta_1$ , NiAl <1638	cP2 CsCl	a = 287.04 a = 288.72 a = 287.26 a = 287.7	30.8 to 58 at.% Al [Mas] at 42.3 at.% Al at 50.4 at.% Al at 53.4 at.% Al [L-B] at 45 at.% Al [83Sri]
$\text{Ni}_5\text{Al}_3$ 700	oC16 $\text{Pt}_5\text{Ga}_3$	a = 744 b = 668 c = 372	32 to 36 at.% Al [Mas, V-C]

$\gamma'$ , Ni <sub>3</sub> Al <1372	cP4 AuCu <sub>3</sub>	1 + (Ni) <sup>O</sup> Ni <sub>3</sub> Al at 1372°C [87Hil, 91Ver] 24.5 to 26 at.% Al at 700°C
		[87Hil] 23.8 to 26.3 at.% Al at 1200°C [91Ver] at 25.1 at.% Al [L-B] at 26.4 at.% Al [L-B] [V-C]
		from a two phase alloy $\gamma+\gamma'$ (21 at.% Al) quenched from 1000°C [52Tay] from a two phase alloy $\gamma'+\beta_1$ (27.8 at.% Al) quenched
		from 1000°C [52Tay] quenched from 1000°C [85Mis, 59Gua] annealed 1000°C, powder ann. at 600°C [66Arb]
Ti <sub>x</sub> Ni <sub>3</sub> Al <sub>1-x</sub>		[63Arb] at 5 at.% Ti [66Arb] at 10 at.% Ti [63Arb] at 15 at.% Ti [52Tay]
		linear da/dx at 12.5 at.% Ti [59Gua]
		linear da/dx at 12 at.% Ti, quenched from 1000°C linear da/dx
(Ti <sub>x</sub> Ni <sub>1-x</sub> ) <sub>3</sub> (Ti <sub>y</sub> Al <sub>1-y</sub> )		[85Mis] 76.6 at.% Ni, 18.8 at.% Al, 1000°C [52Tay]
		76.6 at.% Ni, 13.4 at.% Al, 1000°C [52Tay]
		75.7 at.% Ni, 11.9 at.% Al, 800°C [52Tay]
		75.6 at.% Ni, 9.6 at.% Al, 1200°C [52Tay]
		75.6 at.% Ni, 9.6 at.% Al, 800°C [52Tay]
		from a two-phase alloy 20 at.% Ti, 75 at.% Al, ( $\gamma'+(\text{TiNi}_3)$ ), 900°C [85Nas2]
$\tau$ , TiAl <sub>3</sub> <1387	tI8 TiAl <sub>3</sub>	[90Sch]
		[83Sri]
		a = 384.88 c = 859.82 a = 384.6 c = 859.4

Ti <sub>2</sub> Al <sub>5</sub> ~1215-985	tI28 Ti <sub>2</sub> Al <sub>5</sub>	a = 390.53 c = 291.96	[90Sch]
Ti <sub>5</sub> Al <sub>11</sub> 1416-1206	tI16 ZrAl <sub>3</sub>	a = 392.30 to 393.81 c = 1653.49 to 1649.69 a = 392 c = 1662	29.1 to 31.5 at.% Ti [90Sch]  dissolves up to 4 at.% Ni from alloy 25 at.% Ti, 4 at.% Ni [64Sch]
TiAl <sub>2</sub> (h) 1433-1214	oC12 ZrGa <sub>2</sub>	a = 1208.84 b = 394.61 c = 402.95	33 to 34 at.% Ti [90Sch]
TiAl <sub>2</sub> (r) <1216	tI24 HfGa <sub>2</sub>	a = 396.7 c = 2429.68	[90Sch]
Ti <sub>1-x</sub> Al <sub>1+x</sub> ≈1445-1424	oP4	a = 402.62 b = 396.17 c = 402.62	at x = 0.28 [90Sch]
κ, TiAl <1460	tP4 AuCuI	a = 398.69 c = 405.39	38.5 to 52 at.% Ti [90Sch] at 38.5 at.% Ti, 1000°C
α <sub>2</sub> , Ti <sub>3</sub> Al <1180	hP8 Ni <sub>3</sub> Sn	a = 580.6 c = 465.5 a = 574.6 c = 462.4  a = 577.5 c = 459.3	at 78 at.% Ti [L-B] at 62 at.% Ti [L-B]  dissolves up to 5 at.% Al at 900°C from a 3-phase alloy: 55 at.% Ti, 25 at.% Ni (Ti <sub>3</sub> Al+τ <sub>3</sub> +TiNi <sub>2</sub> ) at 900°C [85Nas2] parameter a = 1155 pm given by [85Nas2]
δ, Ti <sub>2</sub> Ni <984	cF96 Ti <sub>2</sub> Ni	a = 1131.93(2) a = 1128  a = 1130.7	[87Mur] from a 3-phase alloy 50 at.% Ti, 30 at.% Ni (τ <sub>4</sub> +τ <sub>3</sub> +Ti <sub>2</sub> Ni), 900°C [85Nas2] [83Sri]
β <sub>2</sub> , TiNi <sup>a</sup> <1310	cP2 CsCl	a = 301.5	49.5 to 57 at.% Ni [V-C]

$\eta$ , TiNi <sub>3</sub> <1380 Ti <sub>1-x</sub> Ni <sub>3</sub> Al <sub>x</sub>	hP16 TiNi <sub>3</sub>	a = 510.885(5) c = 831.874(5) a = 509.5 c = 830  a = 501.4 c = 829.8  a = 510.28 c = 827.19	[87Mur]  from as-cast alloy, x = 0.25 sample also contained $\gamma'$ , a = 359.5 [66Vuc] from a two-phase alloy 20 at.% Ti, 75 at.% Ni, ( $\gamma'$ +TiNi <sub>3</sub> ), 900°C [85Nas2] [83Sri]
* $\tau_1$ , Ti <sub>2.5</sub> NiAl <sub>6.5</sub>	cP4 AuCu <sub>3</sub>	a = 394  a = 393	at 25 at.% Ti, 8 at.% Ni, 800°C [73Mar, 64Sch] "Ti <sub>2</sub> Ni <sub>1-x</sub> Al <sub>5+x</sub> ", 800°C from a 3-phase alloy 25 at.% Ti, 6 at.% Ni, 700°C ( $\tau_1$ +NiAl <sub>3</sub> +TiNiAl <sub>6</sub> ) [65Ram]
* $\tau_2$ , Ti <sub>~1</sub> Ni <sub>~1</sub> Al <sub>~2</sub>	cF116 Cu <sub>16</sub> Mg <sub>6</sub> Si <sub>7</sub>	a = 1190	[64Sch, 65Ram, 85Nas2]
* $\tau_3$ , TiNi <sub>1-x</sub> Al <sub>1+x</sub>	hP12 MgZn <sub>2</sub>	a = 499.3 c = 804.9 a = 501.5 c = 823.2  a = 498 c = 812 a = 496.7 c = 804.4  a = 499.6 c = 805.2  a = 500.3 c = 804.1  a = 500.8 c = 807.1	0.23 ≤ x ≤ 0.53, 800°C [73Mar] at x = 0.23, 800°C [73Mar, 64Kri] at x = 0.53, linear da/dx scaled from diagram [73Mar] "Ti <sub>~2</sub> Ni <sub>~1</sub> Al <sub>~3</sub> " [64Sch]  from a 3-phase alloy 50 at.% Ti, 30 at.% Ni ( $\tau_3$ + $\tau_4$ +Ti <sub>2</sub> Ni), 900°C [85Nas2]  from a 3-phase alloy 25 at.% Ti, 40 at.% Ni ( $\tau_3$ + $\tau_2$ + $\tau_4$ ), 900°C [85Nas2]  from a 2-phase alloy 35 at.% Ti, 35 at.% Ni ( $\tau_3$ + $\tau_4$ ), 900°C [85Nas2]  from a 3-phase alloy 55 at.% Ti, 25 at.% Ni ( $\tau_3$ +Ti <sub>2</sub> Ni+Ti <sub>3</sub> Al), 900°C [85Nas2]

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* $\tau_4$ , TiNi <sub>2</sub> Al	cF16 BiF <sub>3</sub> or MnCu <sub>2</sub> Al	a = 589	from a 3-phase alloy 50 at.% Ti, 30 at.% Ni ( $\tau_3 + \tau_4 + \text{Ti}_2\text{Ni}$ ), 900°C [85Nas2]
		a = 592	from a 2-phase alloy 35 at.% Ti, 35 at.% Ni ( $\tau_3 + \tau_4$ ), 900°C [85Nas2]
		a = 586.5 to 588.6	variation of lattice parameter within the homogeneity range [83Sri] [52Tay] reports a = 293.6 pm for the CsCl-type subcell, [62Hei] reports a = 291.6 pm, CsCl

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a A detailed description of  
the crystal structure and  
lattice parameter

data of TiNi-martensite  
as well as of the  
martensitic transformation

temperatures can be  
obtained from [87Mur]

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**Table 2: Invariant Equilibria**

T (°C) Reaction	Type	Phase	Composition (at.%)			Comments
			Al	Ni	Ti	
$L + \gamma^O \rightarrow \gamma' + \eta$ 1302	U <sub>1</sub>	L	-	-	-	[91Lee]
$L^O \rightarrow \gamma' + \eta + \tau_4$ 1277 1304	E <sub>1</sub> E <sub>1</sub>	L L	- 11.2	- 21.4	- 67.4	[91Lee] [69Tho]
$L + \beta_1^O \rightarrow \kappa + \nu$ 1100	U <sub>4</sub>	L	-	-	-	[91Lee, 85Oma1, 86Sei]
$L + \kappa^O \rightarrow \vartheta + \nu$ 1050	U <sub>7</sub>	L	-	-	-	[91Lee, 85Oma1, 86Sei]
$L + \nu^O \rightarrow \varepsilon + \vartheta$ 820	U <sub>11</sub>	L	-	-	-	[91Lee, 85Oma1, 86Sei]
$L + \vartheta^O (Al) + \varepsilon$ 645 650	U <sub>12</sub> U <sub>12</sub>	L L	- -	- -	- -	[91Lee] [85Oma1, 86Sei]

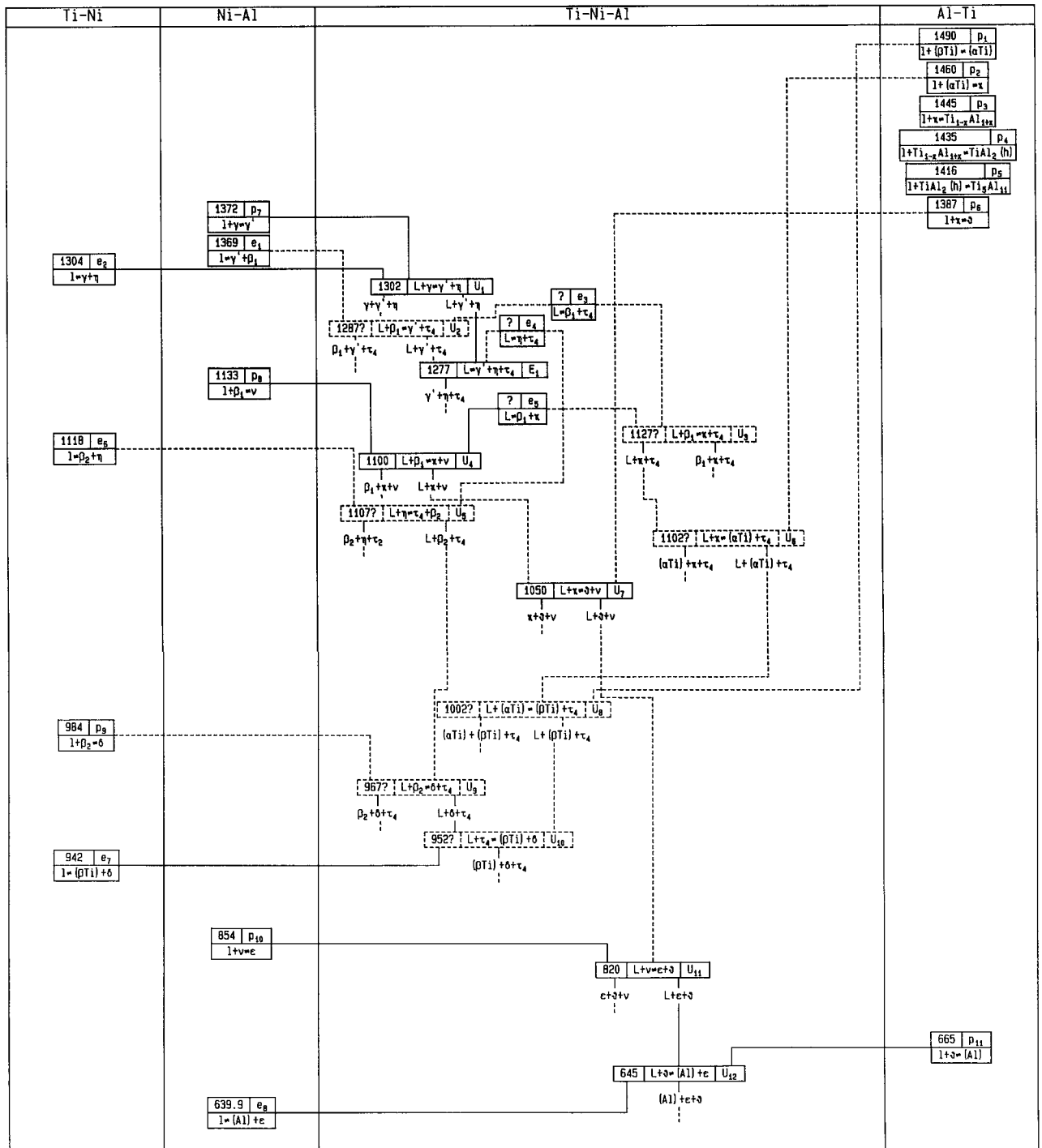


Fig. 1: Partial reaction scheme

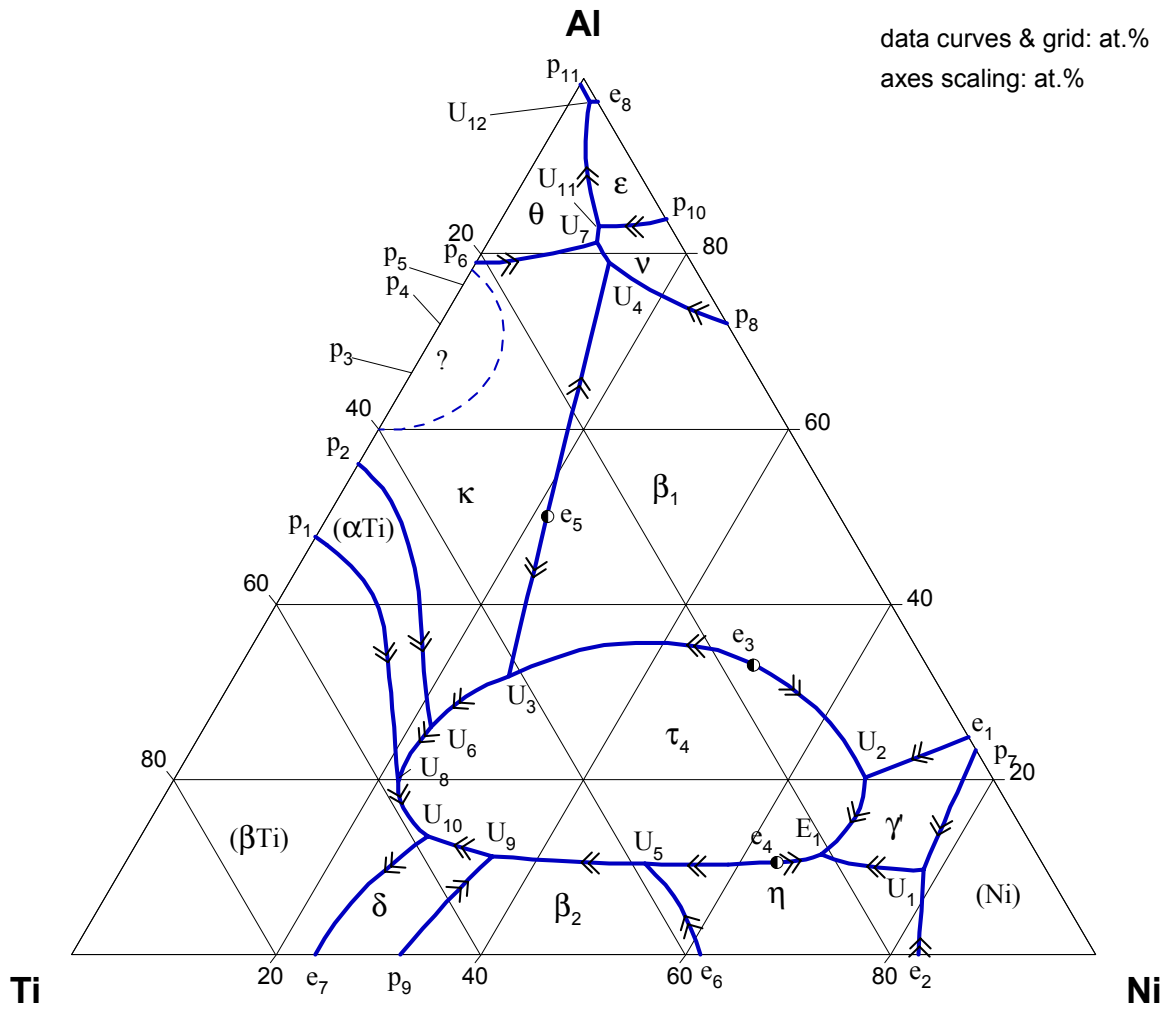


Fig. 2: Liquidus surface

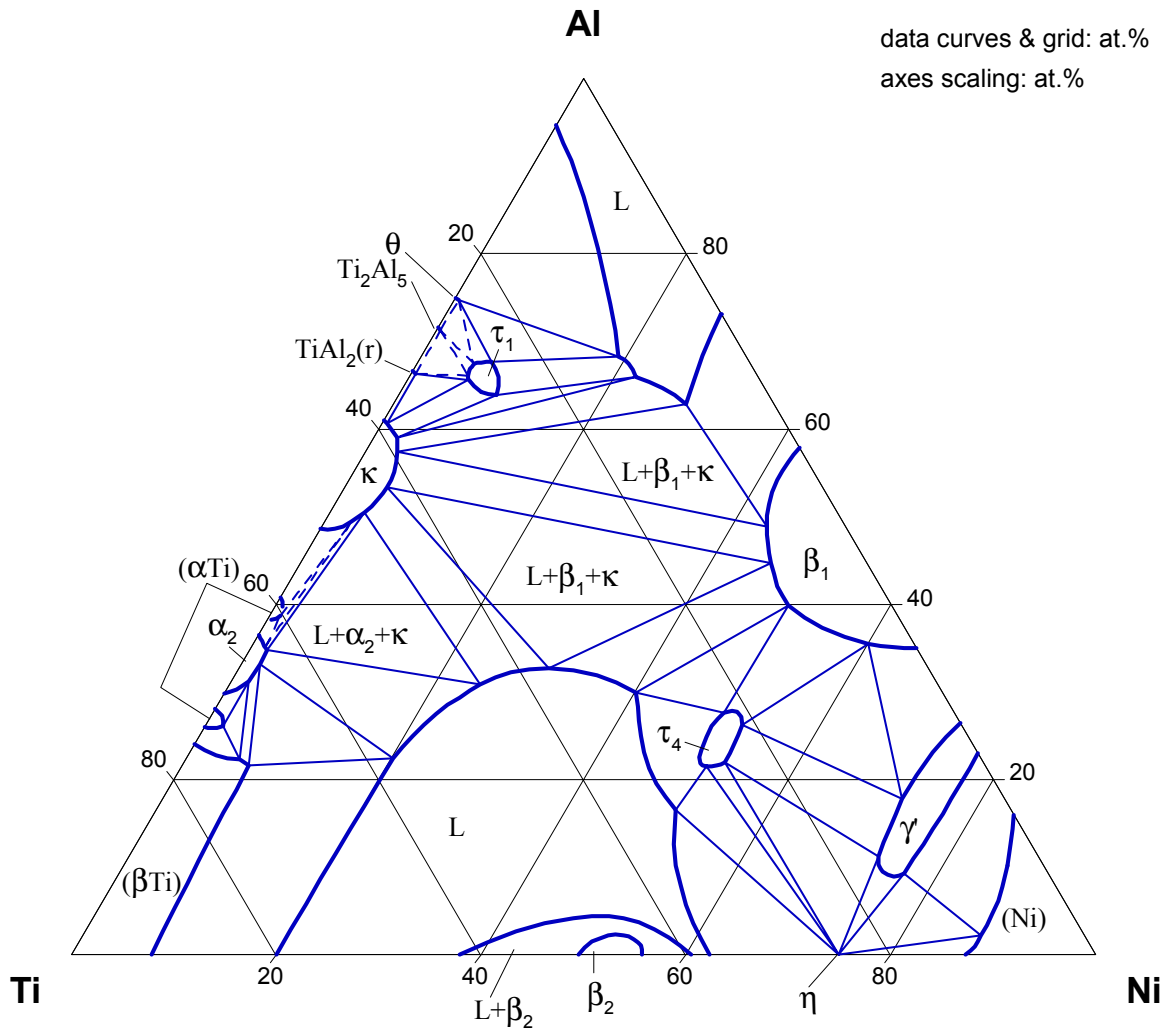


Fig. 3: Isothermal section at 1150°C

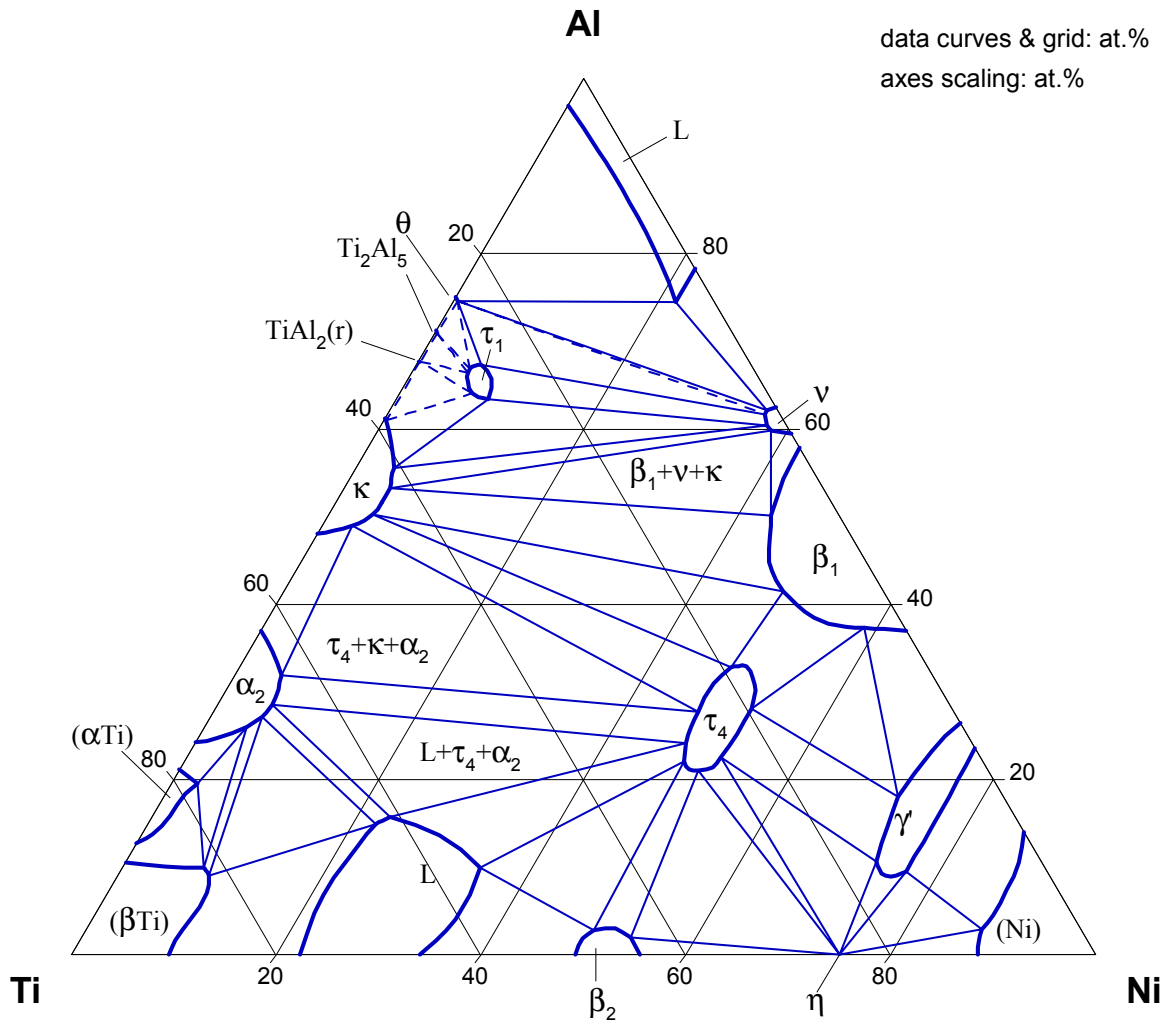


Fig. 4: Isothermal section at 1025°C

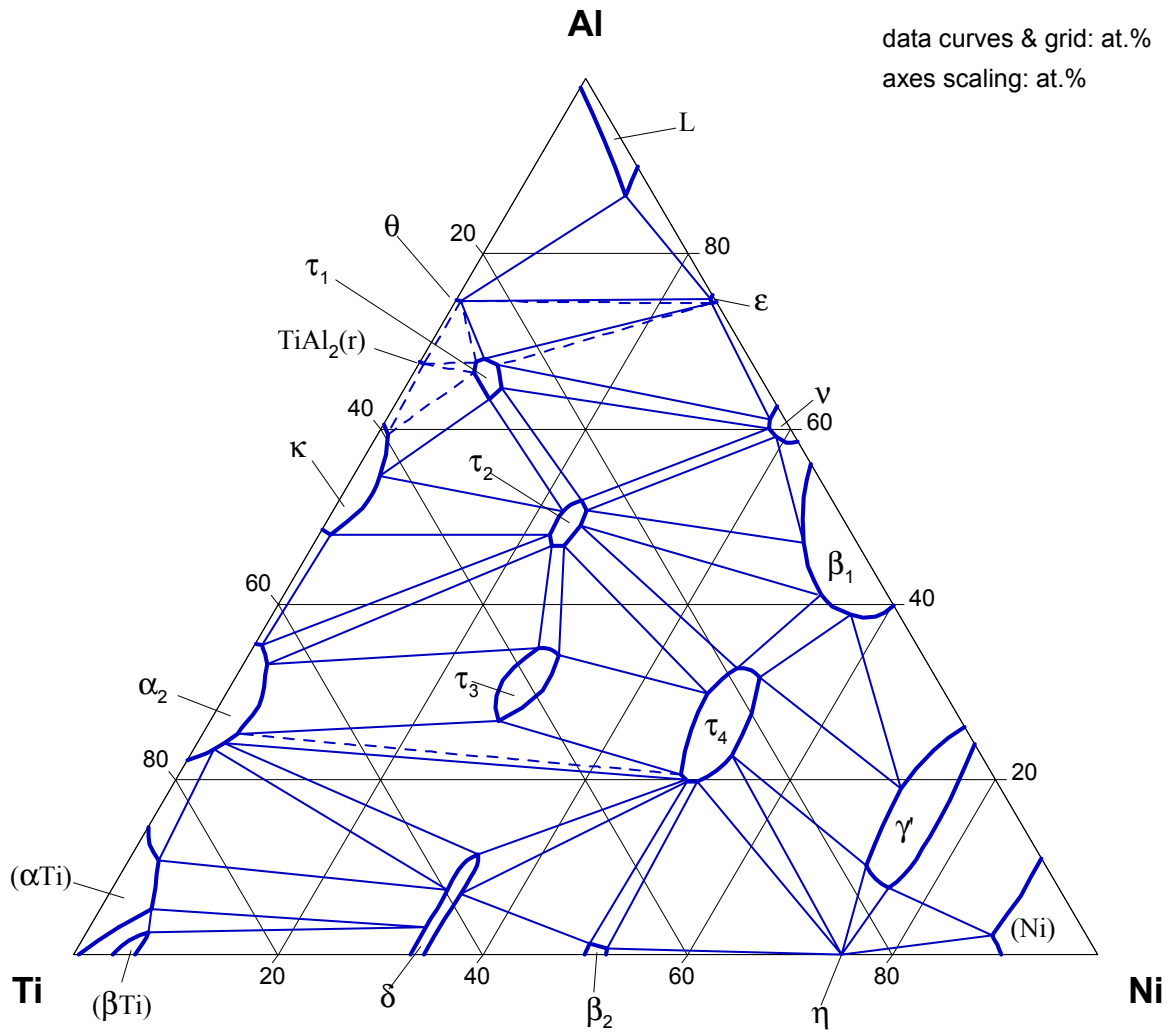


Fig. 5: Isothermal section at 800°C

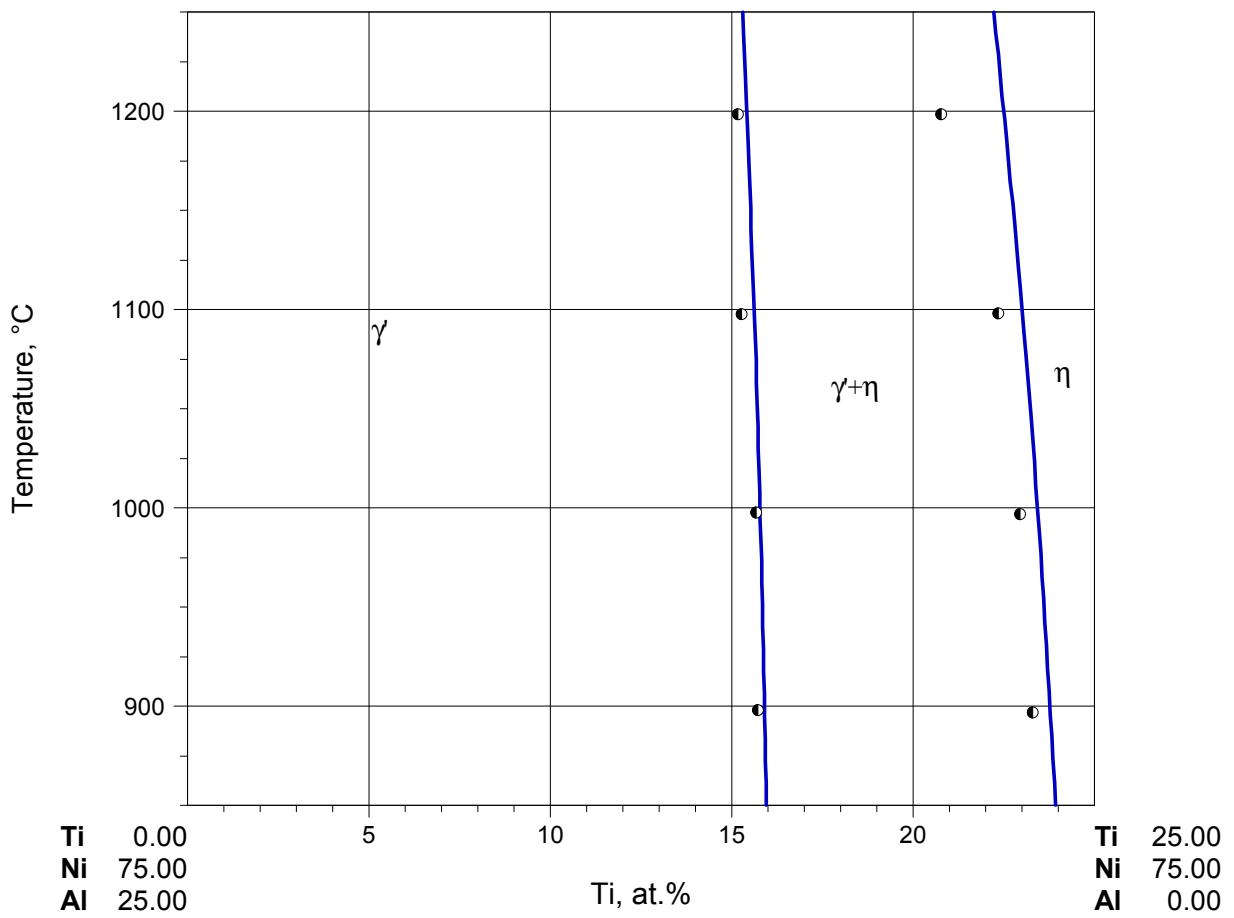


Fig. 6: Calculated vertical section Ni<sub>3</sub>Al-TiNi<sub>3</sub>, data points by [89Ish]