Al-Ni-Si (Aluminum-Nickel-Silicon)

V. Raghavan

The previous collations of data on this ternary system are by [1993Beu] and [1995Vil]. The compilation of [1995Vil] includes liquidus and solidus projections for Al-rich alloys, isothermal sections at 1100, 600, and 500 °C, and vertical sections at 2, 2.5, 4, 7.5, and 12.5 wt.% Ni, and at 2, 6, and 14 wt.% Si, respectively. Recently, in a series of articles, Richter and colleagues [2003Ric, 2004Ric1, 2004Ric2, 2004Cha] made a comprehensive study of the entire composition range, and presented a liquidus projection, a reaction sequence, and several isothermal sections.

Binary Systems

The Al-Ni phase diagram [1993Oka] shows five intermediate phases: $NiAl_3$ (Fe_3C-type orthorhombic); Ni_2Al_3 ($D5_{13}$-type hexagonal); $NiAl$ (CsCl-type cubic); Ni_5Al_3 (Ga_3Pt_5-type orthorhombic); and Ni_3Al ($L1_2$, $AuCu_3$-type cubic; also denoted γ'). The temperatures of the peritectic formation of Ni_3Al (1362 °C) and the eutectic solidification of (NiAl + Ni_3Al) (1360 °C) are tentative. Recently, the liquidus and solidus in the (Ni) region were redetermined by [2001Miu]. The solidus temperatures in the NiAl region were determined by [2002Bit]. The phase boundary between (Ni) and (Ni) + Ni_3Al was determined between 600 and 1200 °C by [2003Ma]. The Al-Si system is a simple eutectic diagram with the eutectic temperature and composition occurring at 577 °C and 12.2 at.% Si [Massalski2]. The Ni-Si phase diagram was recently investigated experimentally and calculated by thermodynamic optimization [1999Du]. There are a number of intermediate phases in this system. Around the composition Ni_3Si, three crystal modifications are known: β_1 is the low-temperature phase with an $L1_2$, $AuCu_3$-type cubic structure. β_2 and β_3 have the $GePt_3$-type monoclinic structure. The hexagonal γ phase is stoichiometric at $Ni_{31}Si_{12}$. δ-Ni_2Si (33.3 at.% Si) is a Co_2Si-type orthorhombic phase, and θ-Ni_2Si (33.4 to 41 at.% Si) is a Ni_2In-type (?) hexagonal phase. [2004Ric1] reinvestigated the region of stability of θ-Ni_2Si and found it to be in good agreement with the results of [1999Du]. However, no clear conclusion could be drawn regarding its structure. Ni_3Si_2 (ε) is orthorhombic. NiSi is an MnP-type orthorhombic structure. $NiSi_2$ has the CaF_2-type cubic structure.

Ternary Compounds

Four established ternary compounds are known in this system [2002Ric, 2003Ric, 2004Ric1]. $Al_{13}Ni_{67}Si_{20}$ (originally designated τ_1) is actually a solid solution based on the binary orthorhombic compound δ-Ni_2Si [1995Vil, 2004Ric1]. $AlNi_2Si$ (τ_2) has the FeSi-type cubic struc-

ture. Al_6Ni_3Si (τ_3) has the Ge_7Ir_3-type cubic structure. $Al_ySi_{9-y}Ni_{13\pm x}$ (τ_4) was earlier believed to be a superstructure based on the hexagonal structure of θ-Ni_2Si. Its structure is $Ga_3Ge_6Ni_{13}$-type hexagonal [2002Ric]. However, the structural similarities between τ_4 and θ, and the quenching problems make a clear demarcation between these phases difficult. They are clubbed together as θ (τ_4) in the diagrams below. A new compound, $AlNi_{16}Si_9$ (τ_5), was reported to be stable at temperatures below 783 °C and to occur in the isothermal section at 550 °C [2002Ric, 2004Ric1, 2004Ric2]. The structural details of the above compounds are summarized in Table 1 [2004Ric1]. [2003Jai] found a new Si-rich compound at the composition $AlNiSi_4$, which was reported to form through a ternary peritectoid reaction among (Al), (Si), and $NiAl_3$ at temperatures between 565 and 550 °C. The crystal structure is not known.

Liquidus Projection

A comprehensive study of the phase equilibria of this system was reported recently by Richter and coworkers. They studied the system in three parts: alloys with 0 to 33.3 at.% Ni [2003Ric]; alloys with 33.3 to 66.7 at.% Ni [2004Ric1]; and alloys with 66.7 to 100 at.% Ni [2004Cha]. With starting metals with a purity of 99.999% Al, 99.99% Ni, and 99.9999% Si, [2003Ric] melted 36 alloys in the Ni range of 0 to 33.3 at.% in an arc furnace under Ar atm. [2004Ric1] and [2004Cha] melted about 50 and 20 alloys, respectively, in the Ni range of 33.3 to 66.7 at.% and 66.7 to 100 at.%, respectively. The phase equilibria were studied by means of differential thermal analysis at a cooling/heating rate of 5 °C per min, x-ray powder diffraction, optical microscopy, and electron probe microanalysis.

The liquidus projection from the results of [2003Ric, 2004Ric1, 2004Cha] is redrawn in Fig. 1 to agree with the accepted binary data. The fields of primary crystallization are marked. NiAl and (Si) have dominant areas of primary crystallization. In Fig. 1, the critical maxima are denoted, for example, by C_1 and C_2. The U-type transition reactions are numbered sequentially in order of decreasing temperature; this order may not tally with the numbering sequence adopted by Richter and coworkers. The ternary compound τ_4 originates from the upper critical point C_1 at a temperature of 1280 °C. The primary fields of separation of τ_4 and the binary compound θ are not delineated separately in Fig. 1. The ternary compounds τ_2 and τ_3 form through the ternary peritectic reactions P_1 and P_2. The final solidification is at the Al-corner at E_2. The temperature and composition of E_2 given by [2004Ric1] (565 °C and 2 at.% Ni-11 at.% Si) agree with those given by [1990Kuz] (569 °C and 2 at.% Ni-11 at.% Si).

[2003Jai] prepared liquid-solid diffusion couples between Ni and an Al-Si eutectic alloy, which were given
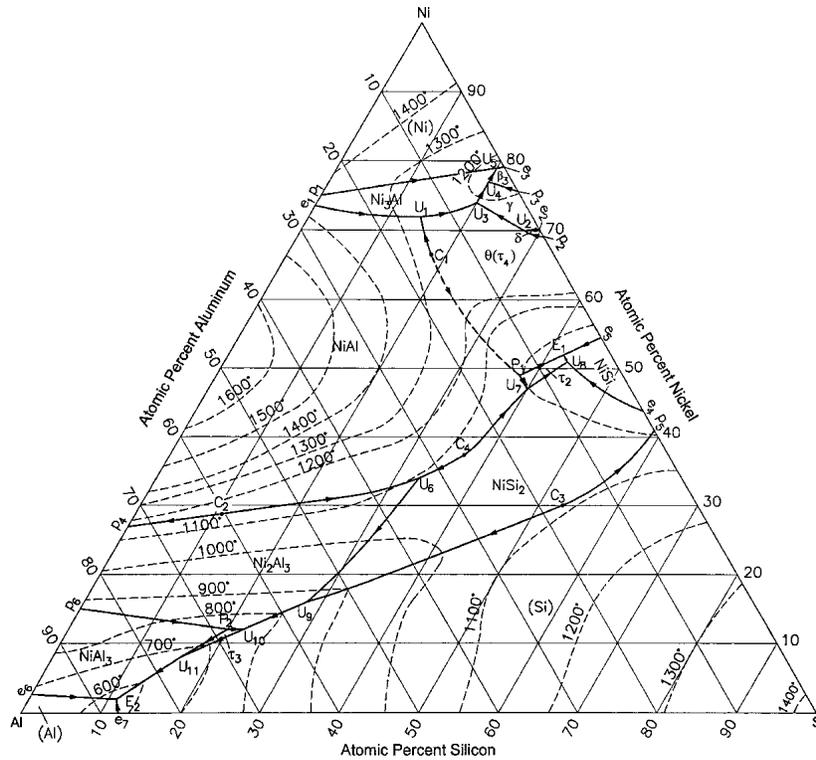
Fig. 1   Al-Ni-Si liquidus projection [2004Ric1, 2004Cha]

Table 1   Al-Ni-Si crystal structure and lattice parameter data

Phase	Composition, at.%	Pearson symbol	Space group	Prototype	Lattice parameters, nm
$Al_{13}Ni_{67}Si_{20}$ (τ_1)(a)	0-21.3 Al 66.7 Ni 33.3-12 Si	$oP12$	$Pnma$	Co_2Si	$a = 0.5000\text{-}0.4958$ $b = 0.3733\text{-}0.3778$ $c = 0.7068\text{-}0.7257$
$AlNi_2Si$ (τ_2)	22-28 Al 50.0 Ni 22-28 Si	$cP8$	$P2_13$	FeSi	$a = 0.4551$(b)
Al_6Ni_3Si (τ_3)	61-58.6 Al 30.0 Ni 9-11.4 Si	$cI40$	$Im\bar{3}m$	Ge_7Ir_3	$a = 0.8316\text{-}0.8305$
$Al_ySi_{9-y}Ni_{13\pm x}$ (τ_4)	~13.6 Al ~59.1 Ni ~27.3 Si	$hP66$	$P3_121$	$Ga_3Ge_6Ni_{13}$	$a = 0.7653$ $c = 1.4665$
$AlNi_{16}Si_9$ (τ_5)	3.8 Al 61.5 Ni 34.6 Si	$oC104$	$Cmcm$	$AlNi_{16}Si_9$	$a = 1.2137$ $b = 1.1265$ $c = 0.8533$

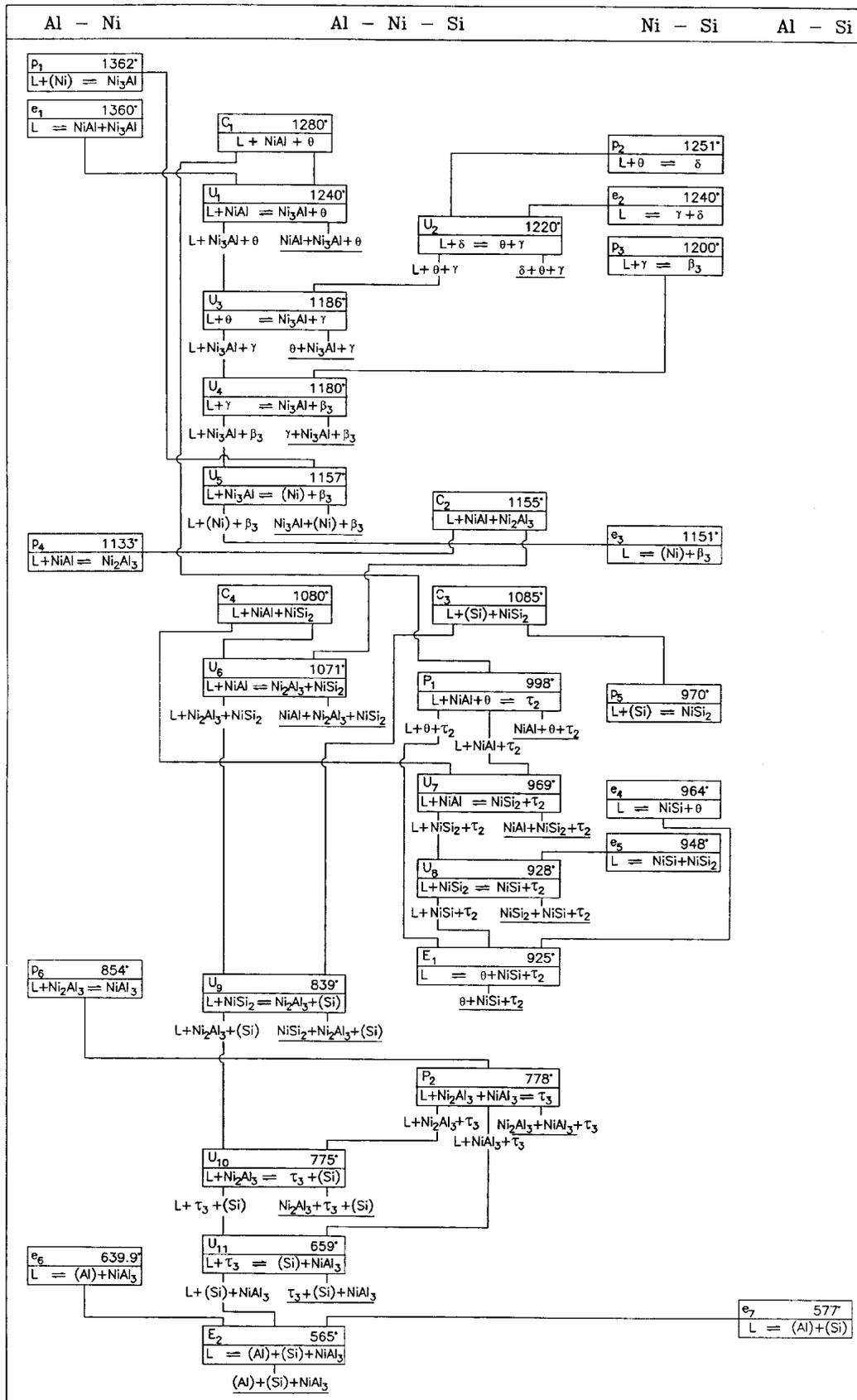(a) Solid solution-based δ-Ni_2Si. (b) For stoichiometric composition

various annealing treatments. They measured the compositions of the coexisting phases by electron probe microanalysis. The formation of the binary and ternary intermetallics was inferred from microstructural characterization, composition measurements, and data from the literature on solidification reactions.

Reaction Schemes

A reaction sequence for the solidification reactions is shown in Table 2 [2004Ric1, 2004Cha]. The underlined three-phase equilibria in Table 2 do not take part further in the solidification process but may undergo solid-state reac-

Table 2   Al-Ni-Si reaction sequence during solidification [2004Ric1, 2004Cha]

Al $-$ Ni	Al $-$ Ni $-$ Si	Ni $-$ Si	Al $-$ Si

Al $-$ Ni

P_1 1362° — L+(Ni) ⇌ Ni$_3$Al

e_1 1360° — L ⇌ NiAl+Ni$_3$Al

P_4 1133° — L+NiAl ⇌ Ni$_2$Al$_3$

P_6 854° — L+Ni$_2$Al$_3$ ⇌ NiAl$_3$

e_6 639.9° — L ⇌ (Al)+NiAl$_3$

Al $-$ Ni $-$ Si

C_1 1280° — L + NiAl + θ

U_1 1240° — L+NiAl ⇌ Ni$_3$Al+θ
 L+Ni$_3$Al+θ   NiAl+Ni$_3$Al+θ

U_2 1220° — L+δ ⇌ θ+γ
 L+θ+γ   δ+θ+γ

U_3 1186° — L+θ ⇌ Ni$_3$Al+γ
 L+Ni$_3$Al+γ   θ+Ni$_3$Al+γ

U_4 1180° — L+γ ⇌ Ni$_3$Al+β$_3$
 L+Ni$_3$Al+β$_3$ γ+Ni$_3$Al+β$_3$

U_5 1157° — L+Ni$_3$Al ⇌ (Ni)+β$_3$
 L+(Ni)+β$_3$ Ni$_3$Al+(Ni)+β$_3$

C_2 1155° — L+NiAl+Ni$_2$Al$_3$

C_4 1080° — L+NiAl+NiSi$_2$

C_3 1085° — L+(Si)+NiSi$_2$

U_6 1071° — L+NiAl ⇌ Ni$_2$Al$_3$+NiSi$_2$
 L+Ni$_2$Al$_3$+NiSi$_2$ NiAl+Ni$_2$Al$_3$+NiSi$_2$

P_1 998° — L+NiAl+θ ⇌ τ$_2$
 L+θ+τ$_2$ NiAl+θ+τ$_2$
 L+NiAl+τ$_2$

U_7 969° — L+NiAl ⇌ NiSi$_2$+τ$_2$
 L+NiSi$_2$+τ$_2$ NiAl+NiSi$_2$+τ$_2$

U_8 928° — L+NiSi$_2$ ⇌ NiSi+τ$_2$
 L+NiSi+τ$_2$ NiSi$_2$+NiSi+τ$_2$

E_1 925° — L ⇌ θ+NiSi+τ$_2$
 θ+NiSi+τ$_2$

U_9 839° — L+NiSi$_2$ ⇌ Ni$_2$Al$_3$+(Si)
 L+Ni$_2$Al$_3$+(Si)   NiSi$_2$+Ni$_2$Al$_3$+(Si)

P_2 778° — L+Ni$_2$Al$_3$+NiAl$_3$ ⇌ τ$_3$
 L+Ni$_2$Al$_3$+τ$_3$ Ni$_2$Al$_3$+NiAl$_3$+τ$_3$
 L+NiAl$_3$+τ$_3$

U_{10} 775° — L+Ni$_2$Al$_3$ ⇌ τ$_3$+(Si)
 L+τ$_3$+(Si)   Ni$_2$Al$_3$+τ$_3$+(Si)

U_{11} 659° — L+τ$_3$ ⇌ (Si)+NiAl$_3$
 L+(Si)+NiAl$_3$ τ$_3$+(Si)+NiAl$_3$

E_2 565° — L ⇌ (Al)+(Si)+NiAl$_3$
 (Al)+(Si)+NiAl$_3$

Ni $-$ Si

P_2 1251° — L+θ ⇌ δ

e_2 1240° — L ⇌ γ+δ

P_3 1200° — L+γ ⇌ β$_3$

e_3 1151° — L ⇌ (Ni)+β$_3$

P_5 970° — L+(Si) ⇌ NiSi$_2$

e_4 964° — L ⇌ NiSi+θ

e_5 948° — L ⇌ NiSi+NiSi$_2$

Al $-$ Si

e_7 577° — L ⇌ (Al)+(Si)

tions at lower temperatures. For example, a U-type transition reaction, θ (τ_4) + Ni$_3$Al $\rightarrow$ δ + NiAl, is indicated by [2004Ric1] at 930 °C, which in turn is preceded by the transition reaction θ + γ $\rightarrow$ δ + Ni$_3$Al at 1040 °C [2004Cha]. τ_5 forms in the solid state through the ternary peritectoid reaction θ (τ_4) + δ + Ni$_3$Si$_2$ $\rightarrow$ τ_5 at 786 °C. The θ (τ_4) + δ + Ni$_3$Si$_2$ equilibrium in the above reaction originates from the eutectoid reaction in the Ni-Si binary system at 823 °C [2004Ric1]. τ_4 decomposes at 770 °C through the ternary eutectoid reaction τ_4 $\rightarrow$ τ_2 + Ni$_3$Si$_2$ + NiSi. A partial reaction scheme for the solid-state reactions is given by [2004Ric1].

Isothermal Sections

Using the same starting metals, sample preparation methods, and experimental techniques as given above, [2003Ric] annealed alloy compositions in the Ni range of 0 to 33.3 at.% at 550 °C for 3 to 6 weeks, followed by water quenching. An isothermal section up to 33.3 at.% Ni was constructed. Using the same experimental procedures, [2004Ric1] annealed alloy samples with Ni in the range of 33.3 to 66.7 at.%, at temperatures of 1000, 800, and 550 °C for 3 to 9 weeks and quenched them in water. Three isothermal sections were constructed. For the Ni range of 66.7 to 100 at.%, [2004Cha] constructed an isothermal section at 1000 °C.

The isothermal section at 1000 °C obtained from the results of [2004Ric1] and [2004Cha] is redrawn in Fig. 2 to agree with the accepted binary data. In Ni-rich alloys, the main feature is the formation of an $L1_2$-type continuous solid solution between Ni$_3$Al and Ni$_3$Si-β_1. No continuous solution was observed by [1960Gua] at 1100 °C, which is consistent with the result that β_1 forms through the peritectoid reaction (Ni) + β_2 $\rightarrow$ β_1 only at 1042 °C [1999Du]. The Ni$_3$Al and β_1-phase fields merge to form the continuous solid solution at a critical temperature that lies between 1042 and 1000 °C. At this critical temperature, the three-phase fields of (γ + Ni$_3$Al + β_1) and (Ni$_3$Al + (Ni) + β_1) should disappear. This continuous solid solution is denoted $L1_2$. In Fig. 2, the binary phase θ and the ternary compound τ_4 are shown as a single-phase field. δ-Ni$_2$Si dissolves ~15 at.% Al, and the lattice parameters of this orthorhombic phase were measured as a function of composition by [2004Ric1]. NiAl and Ni$_2$Al$_3$ dissolve about 20 at.% Si. NiSi$_2$ has a formation temperature of 993 °C in the Ni-Si binary system. Due to the stabilizing effect of Al, it is present in the ternary region at 1000 °C in Fig. 2.

The isothermal section at 800 °C [2004Ric1] is redrawn in Fig. 3. The binary compound Ni$_3$Si$_2$ (ε) is stable at 800 °C, whereas θ-Ni$_2$Si (τ_4) is present only in the ternary region. The solubility of Al in δ-Ni$_2$Si is up to 22 at.%. The solubility of Si in NiAl and Ni$_2$Al$_3$ is the same as that at 1000 °C. The ternary compounds τ_2 and θ (τ_4) are present at 800 °C. At 550 °C (Fig. 4) [2003Ric, 2004Ric1], the ternary compounds τ_3 and τ_5 are present, in addition to τ_2. The binary compound Ni$_5$Al$_3$ [1993Oka] was not found at 550 °C by [2004Ric1]. The solubility of Si in NiAl and Ni$_2$Al$_3$ is about 12 at.%. The lattice parameter of NiAl varies linearly from 0.2890 nm at Ni$_{50}$Al$_{50}$ to 0.2848 nm at Ni$_{50}$Al$_{30}$Si$_{20}$, and from 0.2869 nm at Ni$_{45}$Al$_{55}$ to 0.2828 nm
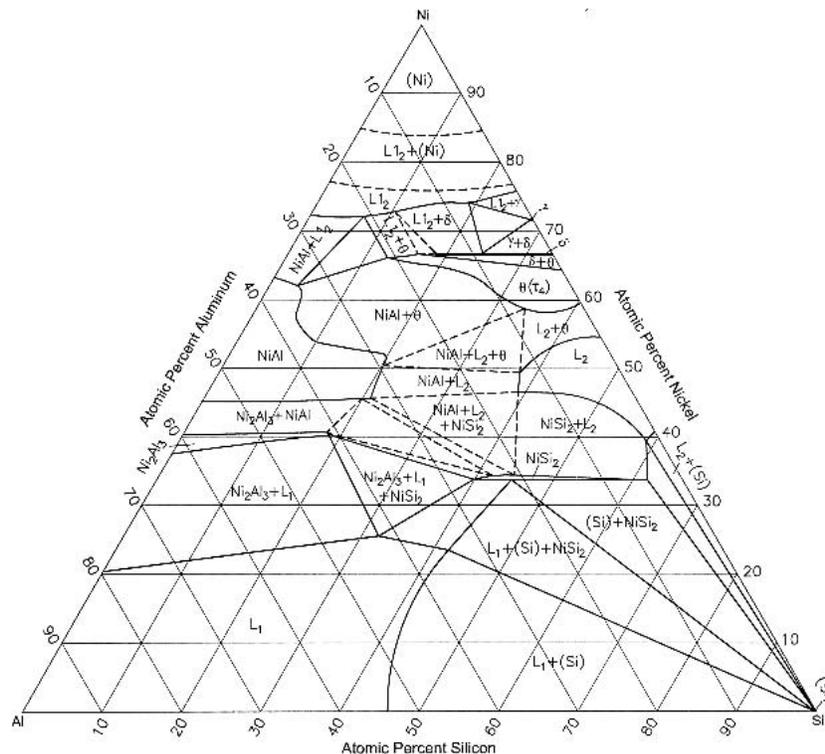
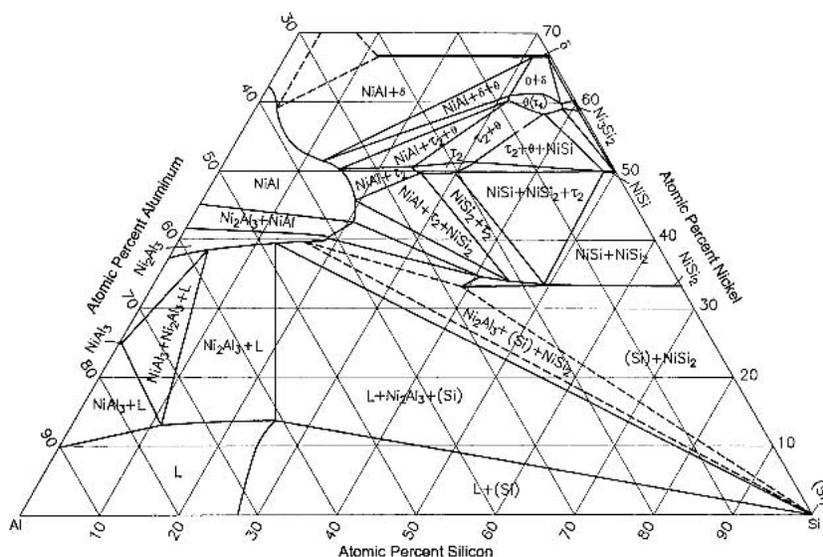**Fig. 2** Al-Ni-Si isothermal section at 1000 °C [2004Ric1, 2004Cha]

Fig. 3   Al-Ni-Si isothermal section at 800 °C [2004Ric1]

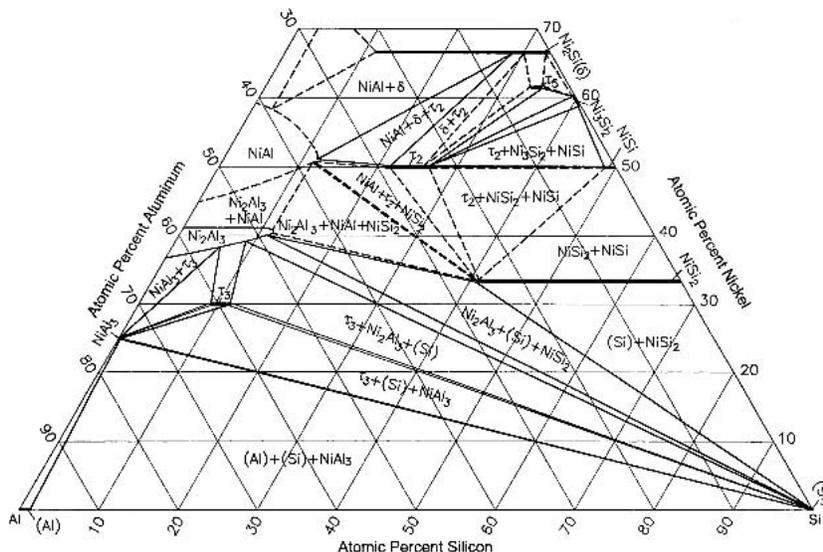**Fig. 4**   Al-Ni-Si isothermal section at 550 °C [2003Ric, 2004Ric1]

at $Ni_{45}Al_{35}Si_{20}$. At a constant Si content of 5 at.%, the lattice parameter varies in a complex manner from 0.28591 nm at $Al_{50}Ni_{45}Si_5$, to 0.28785 nm at $Al_{45}Ni_{50}Si_5$, to 0.28696 nm at $Al_{40}Ni_{55}Si_5$. The lattice parameters of Ni_2Al_3 vary from $a = 0.40365$ nm and $c = 0.49003$ nm at 0% Si to $a = 0.40151$ nm and $c = 0.48231$ nm at 11.5 at.% Si [2003Ric]. $NiSi_2$ dissolves 25.7 at.% Al. The lattice parameter of this cubic phase varies nonlinearly from 0.5406 nm at 0% Al to 0.5482 nm at 25.7 at.% Al [2003Ric].

[1997Mur] measured the lattice parameters of the $L1_2$ phase coexisting with (Ni) as a function of composition and from the known composition-lattice parameter relationship, [1997 Mur] derived the tie lines between (Ni) and $L1_2$ at 600 °C.

Vertical Sections

Twelve vertical sections at constant Ni contents were determined by Richter and coworkers, at 10, 20, and 30 at.% Ni [2003Ric], at 40, 45, 50, 55, 60, and 66.7 at.% Ni [2004Ric1], and at 70, 75, and 80 at.% Ni [2004Cha]. These vertical sections are consistent with the liquidus projection, the isothermal sections, and the reaction scheme in Table 2.

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