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The ternary system Al–Ni–Ti Part II: Thermodynamic assessment and experimental investigation of polythermal phase equilibria

K. Zeng^a, R. Schmid-Fetzer^{a,*}, B. Huneau^{a,b,c}, P. Rogl^b, J. Bauer^c

^aAG Elektronische Materialien, Technische Universität Clausthal, Robert Koch Strasse 42, D-38678 Clausthal-Zellerfeld, Germany

^bInstitut für Physikalische Chemie der Universität Wien, Währingerstrasse 42, A-1090 Wien, Austria

^cLaboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6538, Université de Rennes I, Avenue du Général Leclerc, F-35042 Rennes Cedex, France

The Al–Ni–Ti phase diagram has been thermodynamically assessed and a consistent set of thermodynamic functions has been developed. The thermodynamic modeling is based on an experimental investigation of the phase equilibria in the composition range of $0.1 \leq x_{\text{Al}} \leq 0.7$. Alloys were prepared by argon-arc or vacuum-electron beam melting of elemental powder blends. X-ray powder diffraction, metallography, SEM and EMPA-techniques were employed to analyze the samples in the as-cast state as well as after annealing at 800, 900 and 1000°C. The existence of the four ternary compounds, τ_1 to τ_4 , has been confirmed, although homogeneity regions differ significantly from reports in the literature. The homogeneous phase, previously claimed at “Al₂₃Ni₂₆Ti₅₁”, is shown by high resolution microprobe and X-ray diffraction measurements to be an extremely fine-grained eutectic structure. The congruent melting behavior of $\tau_4 = \text{AlNi}_2\text{Ti}$ is confirmed, but, in contrast to earlier reports, primary crystallization and congruent melting have been observed for $\tau_1 = \text{Al}_{13}\text{Ni}_2\text{Ti}_5$ and $\tau_3 = \text{Al}_3\text{NiTi}_2$. In contrast to earlier assessments, τ_1 , τ_2 and τ_3 are experimentally found to be stable at 800, 900 and 1000°C. The thermodynamic modeling of the ternary phases τ_2 and τ_3 is done with simplified sublattice models, considering their crystal structure and homogeneity ranges. The sublattice model for τ_4 is taken from an earlier assessment of the nickel-rich ternary phase equilibria. The present assessment covers the entire composition range. An application to the solidification behavior of ternary alloys is also exemplified.

Keywords: A. Aluminides, miscellaneous; A. Laves phases; A. Titanium aluminides, based on Ti₃Al; B. Phase diagram; E. Phase diagram prediction

1. Introduction

The thermodynamic description of the Ti–Ni–Al phase diagram was recently optimized by Dupin [1]. Due to the lack of experimental data on the Ti–Al side of the phase diagram, however, the work focused on the Ni-rich region with more than 50 at% Ni. In order to cover the white spot of the system, experiments were designed to provide phase relation data in the Ni-poor region at 900°C [2]. The existence of the ternary compounds, τ_1 to τ_4 (see Table 1 below) was confirmed at that temperature, but, in contrast to earlier investigations and assessments [3,4,5] at significantly different compositions and with different shape of homogeneity regions. This is particularly true for the phase regions of

$\tau_3 = \text{Al}_3\text{NiTi}_2$ with the MgZn₂-type structure and for $\tau_2 = \text{Al}_2\text{NiTi}$. The complex atom-site substitution mechanism in τ_3 , changing from Ti/Al exchange at Al-poor compositions towards Ni/Al replacement for the Al-rich part, was monitored in detail by quantitative X-ray powder diffraction techniques (Rietveld analyses) [2].

As part of our systematic study of the phase equilibria and crystal structures of the phases within the quaternary system Al–N–Ni–Ti, the present paper reports a thermodynamic assessment of the Al–Ni–Ti ternary system incorporating the latest experimental results of the primary crystallization behavior of the ternary compounds in the composition range of $0.1 \leq x_{\text{Al}} \leq 0.7$, their crystal structures, as well as phase diagram data at 800 and 1000°C.

The thermodynamic descriptions of the ternary compounds $\tau_2 = \text{Al}_2\text{NiTi}$ and $\tau_3 = \text{Al}_3\text{NiTi}_2$ were reoptimized in accordance with the new experimental results. The

* Corresponding author.

Table 1
Notation of phases in the Al–Ni–Ti system

Phases	Symbols	Phases	Symbols
NiTi	β_2	Al ₁₁ Ti ₅	Al ₁₁ Ti ₅
Ni ₃ Ti	η	Al ₂ Ti	Al ₂ Ti
Ni Ti ₂	δ	Al ₃ Ti	θ
AlNi	β_1	AlTi	κ
AlNi ₃	γ'	AlTi ₃	α_2
Al ₃ Ni ₂	ν	(α Ti)	(α Ti)
Al ₃ Ni	ε	(β Ti)	(β Ti)
Al ₃ Ni ₅	Al ₃ Ni ₅	Al ₁₃ Ni ₂ Ti ₅	τ_1
(Ni)	(Ni)	Al ₂ NiTi	τ_2
(Al)	(Al)	Al ₃ NiTi ₂	τ_3
		AlNi ₂ Ti	τ_4

ternary compound richest in Al, $\tau_1 = \text{Al}_{13}\text{Ni}_2\text{Ti}_5$, was included. The thermodynamic descriptions optimized by Dupin [1] of the ternary solution phases and the ternary compound $\tau_4 = \text{AlNi}_2\text{Ti}$ were kept unchanged.

2. Experimental data

The literature data on the Al–Ni–Ti system have been critically reviewed in Refs. [3,4] to which readers are referred for details of the previous experimental phase diagrams. Here only a brief discussion of our recent experimental results is presented. Our techniques for sample preparation and heat treatment as well as the methods of characterization by X-ray diffraction (XRD), light optical microscopy (LOM), and electron microprobe analyses (EMPA) have been discussed in detail in our foregoing paper [2] and thus shall not be repeated here. The Greek notations of the phases employed in the review by Budberg [3] will be used throughout the paper (see Table 1).

2.1. Ternary compounds and liquidus surface

In the reviews of the Al–Ni–Ti system [3,4], the existence of four ternary compounds was accepted, i.e. $\tau_1 = \text{Al}_{13}\text{Ni}_2\text{Ti}_5$, $\tau_2 = \text{Al}_2\text{NiTi}$, $\tau_3 = \text{Al}_3\text{NiTi}_2$, and $\tau_4 = \text{AlNi}_2\text{Ti}$. Our recent experiments confirmed the existence of these four phases, but found significantly different composition ranges for τ_2 and τ_3 . According to the new results, τ_3 was given a formula Al_3NiTi_2 [2].

Crystallographic data from X-ray powder diffraction and the results of the EMPA are summarized in Table 2 for a selection of alloys revealing the presence of the ternary compounds τ_1 , τ_2 , τ_3 and τ_4 . Agreement exists on the formation of a pronounced field of primary crystallization of the congruent phase τ_4 [3,5]. The ternary compounds τ_1 to τ_3 were hitherto, however, described as incongruently melting phases with rather restricted thermal stability ranges [3]. In Dupin’s thermodynamic modeling

[1], τ_3 was considered as a congruent phase although its liquidus surface was very small and was located in the Ti-corner. Our LOM, SEM and EMPA analysis of alloys prepared at or close to the stoichiometric compositions of these compounds undoubtedly reveal a primary crystallization behavior resulting in congruent melting for τ_1 and τ_3 (see Figs. 1 and 2). Particularly τ_3 precipitated as the primary phase in a large composition area with less than 40 at% Ni. The evaluation of microstructures as a function of annealing treatment is shown for the $\tau_4 + \gamma' + \eta$ field (Fig. 3) as well as for the fine grained structures $\alpha_2 + \tau_3$ (Figs. 4 and 5).

2.2. Phase equilibria at 800, 900 and 1000°C

Phase relations in the ternary system Al–Ni–Ti at 900°C were experimentally re-established in detail in the composition range of $0.1 \leq x_{\text{Al}} \leq 0.7$ [2]. The results of this experimental investigation employing X-ray powder diffraction, metallography, SEM and EMPA-techniques on about 40 samples were at significant variation to the assessments and investigations hitherto presented [3,4,5]. Based on our experiments [2], the conclusions for 900°C (see Fig. 6) were as follows: (1) τ_3 is not stable below 30 at% Al and its banana-shaped homogeneity region bends towards the Al–Ti binary reaching almost 50 at% Al; (2) the low Al-end of τ_2 (as shown by Nash [5] actually belongs to τ_3 ; the Al-rich part of τ_2 (as suggested by Nash [5]) thus represents the true Al-poor end of τ_2 stretching now somewhat to higher Al-concentrations, and (3) there is no two-phase equilibrium $\kappa + \tau_2$. The three-phase equilibrium $\alpha_2 + \kappa + \tau_3$ has been recently confirmed at 900°C [6]. Heat treatments at 800 and 1000°C prove the stability of τ_1 , τ_2 and τ_3 at these temperatures in contrast to earlier assessments [3] (see Table 2 and Fig. 7). Lattice parameter and EMPA data show no significant variations in the extent and size of the homogeneous regions of the ternary compounds at 800, 900 or at 1000°C.

3. Thermodynamic modeling

3.1. Phase stability of pure elements

The Gibbs energies of pure elements versus temperature $G_i^0(T) = G_i(T) - H_i^{\text{SER}}$ are represented by Eq. (1):

$$G_i^0(T) = a + bT + cT \ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \quad (1)$$

The $G_i^0(T)$ data are referred to the constant enthalpy value of the so-called Standard Element Reference, H_i^{SER} , at 298.15 K and 1 bar as recommended by SGTE (Scientific Group Thermodata Europe) [7]. These reference

Table 2
Crystallographic data and results of EMPA for ternary alloys Al–Ni–Ti

Nominal composition in at% Al–Ni–Ti	Heat treatment °C	Phase analysis	Space group	Pearson symbol	Structure type	Lattice parameters pm		Volume 10 ⁶ pm ³	Results of EMPA in at%		
						a	c		V	Al	Ni
10.7–33.3–56	arc	NiTi ₂	Fd $\bar{3}$ m	cF96	NiTi ₂	1124.82(8)		1423.1(2)			
		NiTi ₂	Fd $\bar{3}$ m	cF96	NiTi ₂	1125.30(6)		1425.0(2)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	590.84(4)		206.26(3)			
14.2–29–56.8	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.2(1)		27.32(2)			
		NiTi ₂	Fd $\bar{3}$ m	cF96	NiTi ₂	1124.4(1)		1421.7(3)			
	800	AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	578.8(2)		134.6(1)			
14.7–51–34.3	arc	NiTi ₂	Fd $\bar{3}$ m	cF96	NiTi ₂	1123.46(6)		1418.0(1)			
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	578.85(1)		134.56(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	591.63(5)		207.08(3)			
17.1–43–39.9	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs						
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	511.08(4)		188.54(4)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	590.16(5)		205.55(3)	19.3(3)	50.9(2)	29.8(3)
20–60–20	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	299.83(2)		26.95(1)			
		NiTi ₂	Fd $\bar{3}$ m	cF96	NiTi ₂	1124.5(1)		1422.0(3)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	591.50(6)		206.95(4)			
21–30–49	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs						
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.51(4)		188.72(5)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.77(3)		202.02(2)			
24–20–56	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.49(7)		46.46(2)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.12(8)		203.42(5)			
25–50–25	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)	22(2)	57(2)	21.5(8)
27–10–63	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	509.95(6)		187.24(4)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.12(8)		203.42(5)			
30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.12(8)		203.42(5)			
30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
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30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
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		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
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		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
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30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
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		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.12(8)		203.42(5)			
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		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
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30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
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		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
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	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
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		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.12(8)		203.42(5)			
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		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
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		Ni ₃ Ti	P6 ₃ /mmc	hP16	Ni ₃ Ti	510.3(1)		187.53(9)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	586.99(6)		202.25(4)			
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		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃	359.51(5)		46.47(1)			
	800	AlNi ₂ Ti (τ 4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.12(8)		203.42(5)			
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30–20–50	arc	NiTi	Pm $\bar{3}$ m	cP2	ClCs	301.3(1)		27.36(2)			
		Ni ₃ Al	Pm $\bar{3}$ m	cP4	AuCu ₃						

Table 2 (continued)

Nominal composition in at% Al-Ni-Ti	Heat treatment °C	Phase analysis	Space group	Pearson symbol	Structure type	Lattice parameters pm		Volume 10 ⁶ pm ³	Results of EMPA in at%			
						a	c		V	Al	Ni	Ti
31.3–28.7–40	1000	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.70(4)		205.06(3)				
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	579.67(9)	465.10(4)	135.34(4)				
		Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	500.62(2)	807.08(6)	175.16(2)				
	arc	800	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.97(3)		205.35(2)	24.2(2)	49.4(2)	26.4(2)
			AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn						
			AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.89(5)		205.26(3)			
40–12.5–47.5	1000	Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	500.29(7)	806.9(2)	174.90(6)				
		AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.93(7)		205.30(5)				
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	580.7(2)	465.1(2)	135.84(8)				
	arc	800	NiTi ₂	Fd $\bar{3}$ m	cF96	NiTi ₂	1124.44(5)		1421.7(1)			
			AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.92(4)		205.30(3)	23.8(1)	49.7(1)	26.4(1)
			Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	502.12(9)	814.1(3)	177.75(8)			
40–26.6–33.3	1000	AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	576.8(2)	463.5(2)	133.57(9)				
		Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12hP8	MgZn ₂	500.93(3)	809.19(8)	175.84(2)	41.5(2)	22.5(4)	36.0(5)	
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	578.4(1)	464.2(3)	134.49(8)	33.9(6)	1.6(5)	64.5(5)	
	arc	800	Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	501.16(5)	810.4(1)	176.27(3)	41.5(2)	21.6(2)	36.9(2)
			AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	577.51(4)	465.6(3)	134.46(7)	34.8(2)	1.0(4)	64.2(4)
			Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	498.78(3)	802.88(7)	172.98(2)			
43–17–40	1000	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	590.1(2)		205.5(2)				
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn							
		Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	499.77(5)	804.01(5)	173.91(3)	37.3(3)	26.4(2)	36.2(3)	
	arc	800	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.7(1)		205.12(9)	25.5(0)	48.6(0)	25.9(0)
			AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn						
			Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	499.70(2)	803.74(5)	173.80(2)	36.3(1)	26.8(2)	36.9(2)
49.5–23.5–27	1000	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	589.7(2)		205.1(1)	25.0(3)	48.6(3)	26.3(2)	
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn							
		Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	501.84(3)	816.54(8)	178.08(2)				
	arc	800	AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	576.25(7)	464.3(1)	133.51(4)			
			Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	500.91(2)	808.6(1)	175.71(3)	42.7(1)	22.2(3)	35.1(2)
			AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	578.38(4)	465.1(2)	134.74(6)			
50–37.5–12.5	1000	Al ₂ NiTi(τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆							
		Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	501.29(4)	812.86(5)	176.89(3)	43.1(1)	20.8(1)	36.1(1)	
		AlTi ₃	P6 ₃ /mmc	hP8	Ni ₃ Sn	578.3(1)	465.2(1)	134.72(6)	34.4(5)	2.0(3)	63.6(6)	
	arc	800	(αTi)	P6 ₃ /mmc	hP2	Mg	288.31(2)	4.5768(8)	32.947(6)			
			Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1188.9(1)		1680.6(4)			
			Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	501.00(8)	812.3(2)	176.57(6)			
55–10–35	1000	Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1189.49(7)		1683.0(2)	52.0(3)	24.9(2)	23.1(1)	
		Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	500.91(2)	808.18(8)	175.61(2)	44.0(4)	22.3(4)	33.7(2)	
		Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1190.68(4)		1688.1(2)	51.0(1)	24.8(1)	24.2(2)	
	arc	800	Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	500.31(4)	808.7(2)	175.29(4)	43.4(2)	23.0(2)	33.5(1)
			Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1188.91(8)		1680.6(2)			
			AlNi	Fm $\bar{3}$ m	cP2	CsCl	288.55(5)					
60–18–22	1000	Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂	500.03(4)	808.1(1)	174.98(4)				
		Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1189.36(7)		1682.4(2)				
		AlNi	Fm $\bar{3}$ m	cP2	CsCl	289.29(6)		24.21(1)				
	arc	800	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.2(1)		203.54(7)			
			Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1189.62(7)		1683.5(2)	50.8(1)	25.8(2)	23.7(3)
			AlNi	Fm $\bar{3}$ m	cP2	CsCl	289.23(4)		24.195(7)	47.7(2)	49.0(3)	3.3(1)
60–18–22	1000	AlNi ₂ Ti (τ4)	Fm $\bar{3}$ m	cF16	BiF ₃	588.72(6)		204.05(4)				
		AlTi	P4/mmm	tP4	AuCu	399.7(3)	406.2(3)	64.9(1)				
		AlTi	P4/mmm	tP4	AuCu	398.98(6)	408.72(1)	65.06(2)				
	arc	800	AlTi	P4/mmm	tP4	AuCu	398.25(4)	407.67(4)	64.66(1)	55.3(5)	0.7(1)	44.1(5)
			Al ₃ NiTi ₂ (τ3)	P6 ₃ /mmc	hP12	MgZn ₂				49.4(2)	16.1(2)	34.5(1)
			Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1188.78(7)		1680.0(2)			
1000	800	Al ₁₃ Ni ₂ Ti ₅ (τ1)	Pm $\bar{3}$ m	cP4	AuCu ₃	393.37(7)		60.87(2)				
		Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1189.97(8)		1685.0(3)				
		Al ₁₃ Ni ₂ Ti ₅ (τ1)	Pm $\bar{3}$ m	cP4	AuCu ₃	393.30(7)		60.84(2)				
1000	800	Al ₂ NiTi (τ2)	Fm $\bar{3}$ m	cF116	Mn ₂₃ Th ₆	1189.14(8)		1681.5(2)	55.3(2)	23.1(3)	21.4(2)	
		Al ₁₃ Ni ₂ Ti ₅ (τ1)	Pm $\bar{3}$ m	cP4	AuCu ₃	393.27(6)		60.82(2)	64.0(2)	9.7(1)	26.3(1)	

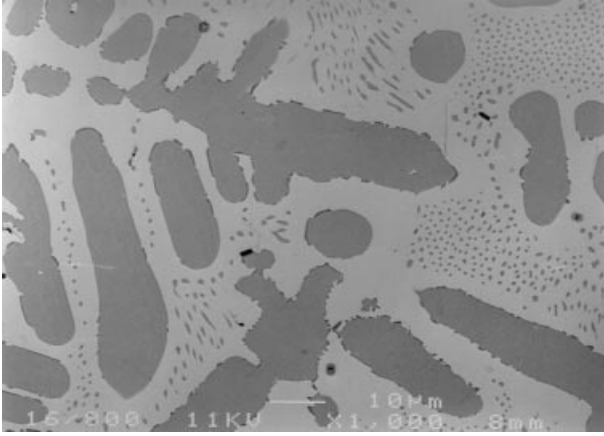


Fig. 1. SEM micrograph of the alloy 60Al-18Ni-22Ti (at%) annealed at 800°C and quenched (magnification 1000×). The large dark particles are $\tau_1 = \text{Al}_{13}\text{Ni}_2\text{Ti}_5$ ($\text{Al}_{64}\text{Ni}_{10}\text{Ti}_{26}$) and the white phase is $\tau_2 = \text{Al}_2\text{NiTi}$ ($\text{Al}_{55}\text{Ni}_{23.5}\text{Ti}_{21.4}$). Even after annealing the primary dendrites of τ_1 can be clearly seen.

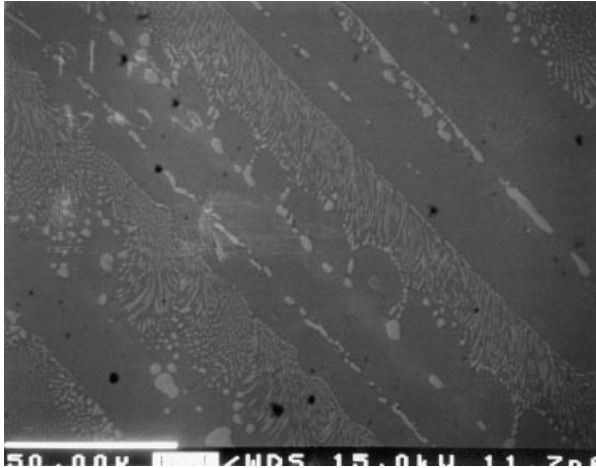


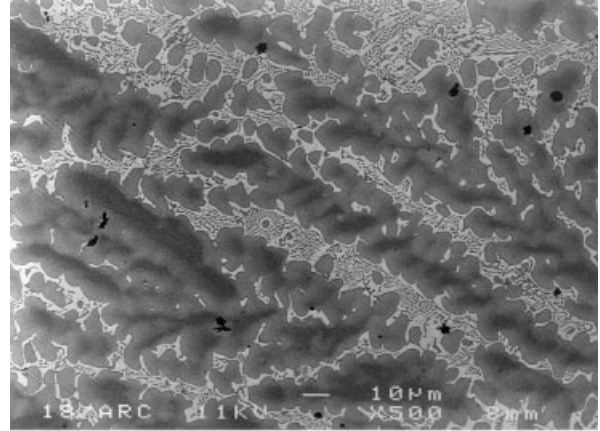
Fig. 2. SEM micrograph of the as-cast alloy 39Al-29.5Ni-31.5Ti (at%). The black primary phase is τ_3 with 27 at% Ni and 38.5 at% Al, and the bright particles are τ_4 with 48 at% Ni and 24.5 at% Al.

states are hcp-Ti, fcc-Ni, and fcc-Al. The $G_i^0(T)$ expressions may be given for several temperature ranges, where the coefficients $a, b, c, d, e, f, i, j,$ and k have different values. The $G_i^0(T)$ functions of the pure elements Al, Ni and Ti were taken from Ref. [7].

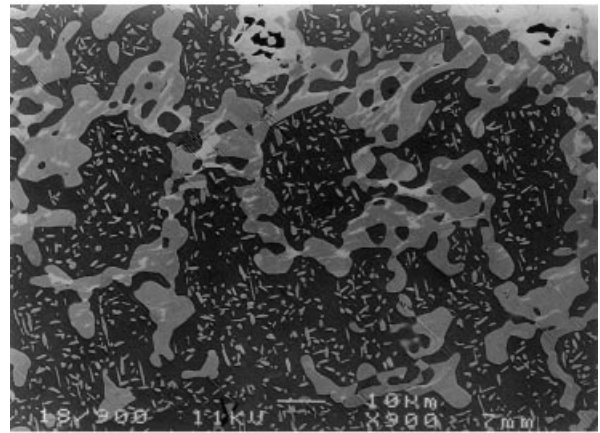
3.2. Summary of modeling of binary boundary systems

3.2.1. The Ni-Ti system

The modeling done by Saunders [8] in the framework of the COST-507 project is used. The phases $\beta_2 = \text{NiTi}$ and $\eta = \text{Ni}_3\text{Ti}$ were described by the two-sublattice model, while $\delta = \text{NiTi}_2$ was treated as a line compound. The phase diagram has been well characterized with good overall agreement among the phase diagram studies (Fig. 8). The thermodynamics of the system show some inconsistencies, though.



(a)



(b)

Fig. 3. SEM micrograph of the as-cast alloy 20Al-60Ni-20Ti (at%) (magnification 500×). The primary dendrites are $\tau_4 = \text{AlNi}_2\text{Ti}$, and the white phase is $\gamma' - \text{AlNi}_3$. Inset: SEM micrograph of the same alloy after annealing at 800°C. The black phase is $\tau_4 - \text{AlNi}_2\text{Ti}$, the grey phase is $\gamma' - \text{AlNi}_3$, and the white particles are $\eta - \text{Ni}_3\text{Ti}$.

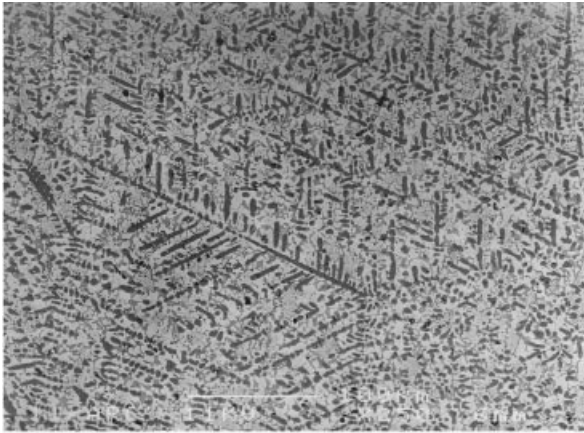
3.2.2. The Al-Ti system

This system was recently modeled four times [9–12]. Since the review of the Al-Ti system by Murray [13], further detailed experimental work has been added. These studies clearly indicated that (αTi) forms peritectically from the melt and (βTi) rather than peritectoidally from (βTi) and $\kappa - \text{AlTi}$ as concluded in Ref. [13]. Based on the experimental results in Refs. [14–16], Saunders [11] took this new feature into account and optimized this system from the then-up-to-date experimental data. The phases and their compositions were based on the experimental data by Kaltentbach et al. [17]. The solid solution phase (βTi) was predicted to have a congruent melting point at about 20 at% Al. Although some important experimental results were published since then, such as the Refs. [18–22] which have been incorporated into the later assessments [9,10] the data by Saunders [11] have been employed in the present work in order to keep consistency

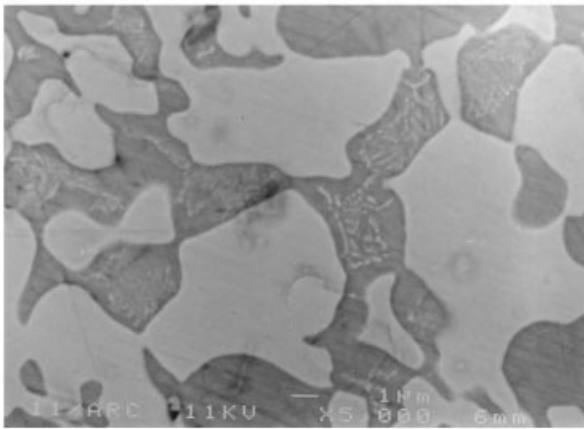
with the ternary work of Dupin [1] and the COST databank. The calculated phase diagram using Saunders' data is shown in Fig. 9.

3.2.3. The Al-Ni system

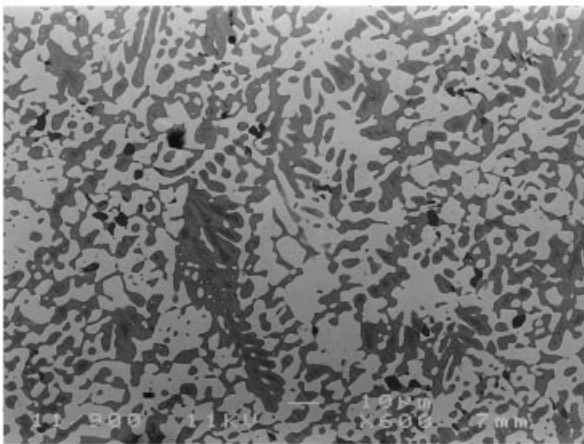
The sublattice model was used by Ansara et al. [23] to describe the thermodynamic behaviour of the Al-Ni binary ordered phases $\gamma' = \text{AlNi}_3$, $\beta_1 = \text{AlNi}$, and $\nu = \text{Al}_3\text{Ni}_2$. The calculated phase diagram and the thermodynamic



(a)

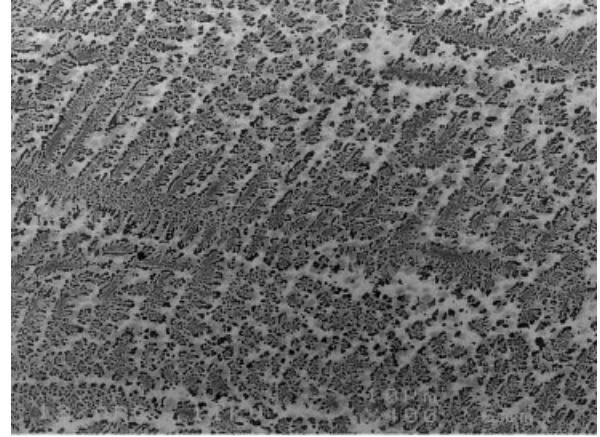


(b)

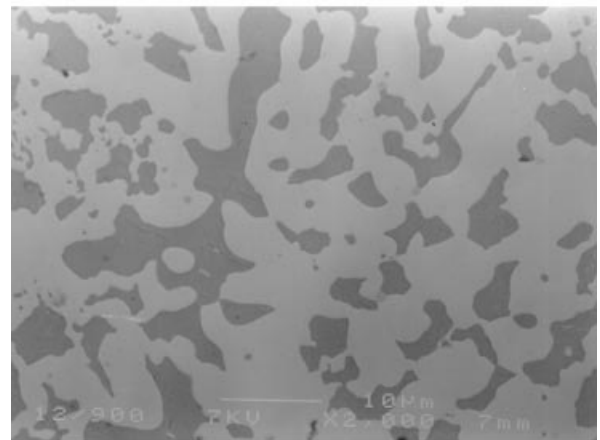


(c)

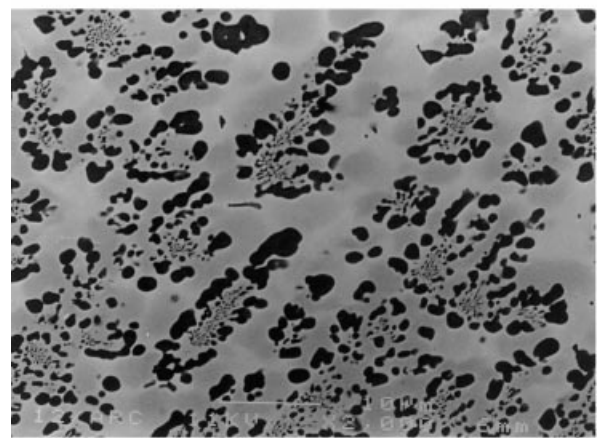
Fig. 4. SEM micrograph of the alloy 40Al-12.5Ni-47.5Ti (at%), (a) as-cast conditions (magnification 250 \times): the dark dendrites are α_2 -AlTi₃ and the white phase is τ_3 -phase. Inset: a more magnified micrograph of (a) with 5000 \times . (b) after annealing at 900°C (magnification 600 \times).



(a)



(b)



(c)

Fig. 5. SEM micrograph of the alloy 30Al-20Ni-50Ti (at%), (a) as-cast conditions (magnification 400 \times); the dark dendrites are τ_2 -AlTi₃ and the white phase is τ_3 -phase. Inset: a more magnified micrograph of (a) with 2000 \times . (b) after annealing at 900°C (magnification 2000 \times).

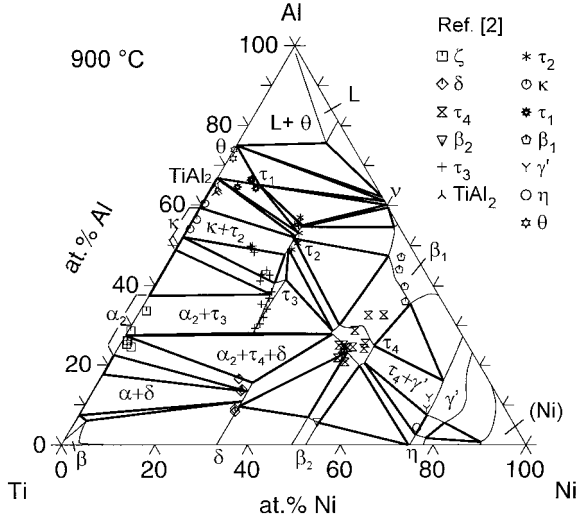


Fig. 6. Calculated isothermal section of the Al-Ni-Ti phase diagram at 900°C, compared with the experimental data by Huneau et al. [2].

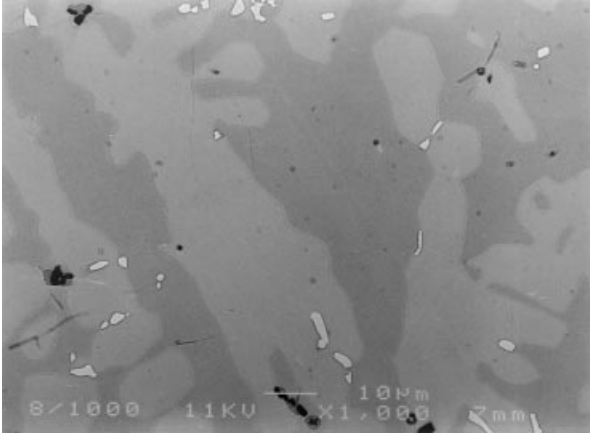


Fig. 7. SEM micrograph of the alloy 49.5Al-23.5Ni-27Ti (at%) annealed at 1000°C (magnification 1000×). The dark grey grains are τ_2 -Al₂NiTi (Al₅₁Ni₂₅Ti₂₄), the light grey phase is τ_3 -phase (Al_{43.5}Ni₂₃Ti_{33.5}), and the white particles are τ_4 -AlNi₂Ti.

properties are in very good agreement with the experimental information (Fig. 10).

3.3. Modeling of ternary phases

3.3.1. Solution phases

The solution phases, Φ = liquid, fcc, bcc, and hcp, have been described by a substitutional solution model, with a Gibbs energy as follows:

$$G_m^\Phi = x_{Ti}G_{Ti}^{0,\Phi} + x_{Ni}G_{Ni}^{0,\Phi} + x_{Al}G_{Al}^{0,\Phi} + RT(x_{Ti} \ln x_{Ti} + x_{Ni} \ln x_{Ni} + x_{Al} \ln x_{Al}) + G_m^{E,\Phi} \quad (2)$$

where x_i is the mole fraction of the element i , $G_{Ti}^{0,\Phi}$, $G_{Ni}^{0,\Phi}$, and $G_{Al}^{0,\Phi}$ are the molar Gibbs energy of Ti, Ni, and Al,

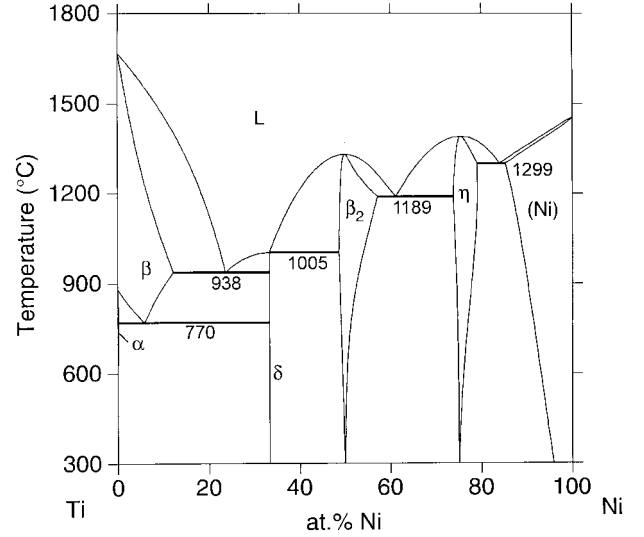


Fig. 8. Calculated Ni-Ti phase diagram using the data of Saunders [8].

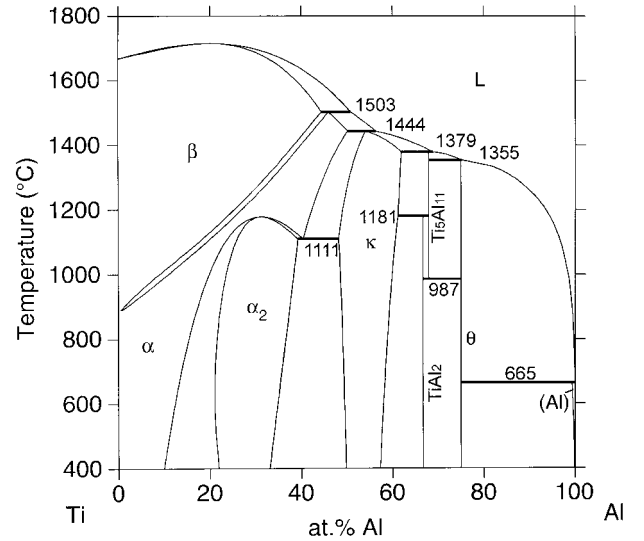


Fig. 9. Calculated Al-Ti phase diagram using the data of Saunders [11].

respectively, with the crystal structure of Φ and are defined by Eq. (1).

$G_m^{E,\Phi}$, the excess Gibbs energy, has been treated as follows:

$$G_m^{E,\Phi} = x_{Ti}x_{Ni}L_{Ti,Ni}^\Phi + x_{Ti}x_{Al}L_{Ti,Al}^\Phi + x_{Ni}x_{Al}L_{Ni,Al}^\Phi + x_{Ti}x_{Ni}x_{Al}L_{Ti,Ni,Al}^\Phi \quad (3)$$

where $L_{i,j}^\Phi$ are binary interaction parameters of the $i-j$ system, which are composition dependent according to the Redlich-Kister formalism [24]:

$$L_{i,j}^\Phi = \sum_{n=0}^m L_{i,j}^{n,\Phi} (x_i - x_j)^n \quad (4)$$

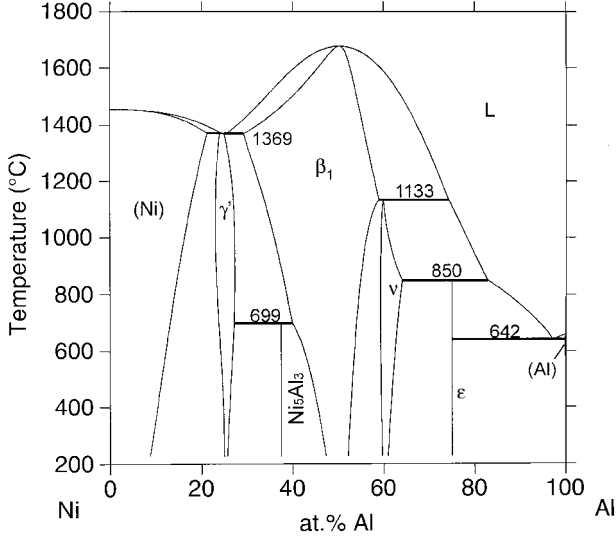


Fig. 10. Calculated Al-Ni phase diagram using the data of Ansara et al. [23].

They have been taken from previously assessed binary systems, i.e. Ni-Ti and Al-Ti by Saunders [8,11], and Al-Ni by Ansara et al. [23]. The parameter $L_{\text{Ti,Ni,Al}}^{\Phi}$ in Eq. (3) represents the ternary interaction, which is taken to be linearly composition dependent according to the expression:

$$L_{\text{Ti,Ni,Al}}^{\Phi} = x_{\text{Ti}}L_{\text{Ti,Ni,Al}}^{2,\Phi} + x_{\text{Ni}}L_{\text{Ti,Ni,Al}}^{1,\Phi} + x_{\text{Al}}L_{\text{Ti,Ni,Al}}^{0,\Phi} \quad (5)$$

3.3.2. Ternary compounds

3.3.2.1. $\tau_1(\text{Al}_{13}\text{Ni}_2\text{Ti}_5)$ and $\tau_4(\text{AlNi}_2\text{Ti})$. Although a sublattice model $(\text{Ti,Ni,Al})_3(\text{Ti,Ni,Al})_1$ could have been used for τ_1 because it essentially is an ordered fcc phase, it was modeled for simplicity as a stoichiometric phase at $\text{Al}_{13}\text{Ni}_2\text{Ti}_5$. For τ_4 , the sublattice model employed by Dupin [1] has been adopted.

3.3.2.2. $\tau_2(\text{Al}_2\text{NiTi})$. Dupin [1] suggested that τ_2 was of $\text{Cu}_{16}\text{Mg}_6\text{Si}_7$ -type and, correspondingly, we identified it as of the $\text{Mn}_{23}\text{Th}_6$ -parent type [2]. Dupin used the sublattice model $(\text{Ti,Al})_{16}(\text{Ni})_6(\text{Ti})_7$ to thermodynamically describe this phase as a line compound at 20.69 at% Ni, about 3.5 at% Ni less than the homogeneity range measured by us [2].

Model calculations for the crystal structure of τ_2 showed general consistency with the structure type of $\text{Mn}_{23}\text{Th}_6$ [2]. For comparison, the atom distributions in the sublattices of $\text{Mn}_{23}\text{Th}_6$ and τ_2 are listed in Table 3. For practical reasons, the number of sublattices can be decreased by putting the sublattices of the same or similar coordination numbers (CN) with the same occupation of atoms into one sublattice as shown in the last line of Table 3. Thus, we arrive at the sublattice formula $(\text{Al})_{16}(\text{Ti})_6(\text{Ni})_7$. In order to reproduce the

Table 3
Ideal distributions of atoms on the sublattices of $\text{Mn}_{23}\text{Th}_6$ and $\tau_2 = \text{Al}_2\text{NiTi}$

Phases	Sublattice with coordination number CN					Ref.
	CN8	CN12	CN17	CN13	CN12	
$\text{Mn}_{23}\text{Th}_6$	4Mn	24Mn	24Th	32Mn	32Mn	Pearson
$\tau_1 = \text{Al}_2\text{NiTi}$	4Ni	24Ni	24Ti	32Al	32Al	[2]
Sublattice	III	III	II	I	I	

homogeneity range observed by us [2], Ti must also be introduced into the first sublattice. Although the atom site occupation in τ_2 is slightly more complicated [2], the simple formula, $(\text{Ti,Al})_{16}(\text{Ti})_6(\text{Ni})_7$ has been employed to model τ_2 in the present work. This is still consistent with a line compound but with higher Ni-content than in Dupin's model.

A thermodynamic model for phases with several sublattices was used to describe the Gibbs energy for the individual phases [25]. For one mole of formula unit of the τ_2 phase $(\text{Ti,Al})_{16}(\text{Ti})_6(\text{Ni})_7$, this model yields the following expression for its Gibbs energy:

$$G_m^{\tau_2} = y_{\text{Ti}}G_{\text{Ti:Ti:Ni}}^{0,\tau_2} + y_{\text{Al}}G_{\text{Al:Ti:Ni}}^{0,\tau_2} + 16RT(y_{\text{Ti}} \ln y_{\text{Ti}} + y_{\text{Al}} \ln y_{\text{Al}}) + G_m^{E,\tau_2} \quad (6)$$

The term y_i represents the site fraction of component i on the first sublattice it occupies. The colons separate elements on different sublattices. The parameters $G_{\text{Ti:Ti:Ni}}^{0,\tau_2}$ and $G_{\text{Al:Ti:Ni}}^{0,\tau_2}$ represent the Gibbs energies of the hypothetical compounds $\text{Ni}_7\text{Ti}_{22}$ and $\text{Al}_{16}\text{Ti}_6\text{Ni}_7$ where the first sublattice is exclusively occupied by Ti and Al, respectively. They were referred to the standard state SER of the elements (see Section 3.1).

G_m^{E,τ_2} in Eq.(6) is the excess Gibbs energy which is represented by

$$G_m^{E,\tau_2} = y_{\text{Ti}}y_{\text{Al}}L_{\text{Ti,Al:Ti:Ni}}^{\tau_2} \quad (7)$$

where the parameter $L_{\text{Ti,Al:Ti:Ni}}^{\tau_2}$ represents the interaction energy between Ti and Al in the first sublattice, and the comma separates elements that interact on the same sublattice.

3.3.2.3. $\tau_3(\text{Al}_3\text{NiTi}_2)$. τ_3 was confirmed as of MgZn_2 -type in our experiments [2]. The sublattice formula used for this phase by Dupin [1] was $(\text{Ti,Ni,Al})_2(\text{Ti,Ni,Al})_1$, but the calculated homogeneity range is almost totally out of the experimental region measured by us [2], showing a much smaller Al-content.

The MgZn_2 -type Laves structure consists of 3 sublattices with coordination numbers (CN) of 12, 12, and

16, respectively, containing 12 atoms per unit cell. The larger Mg atoms occupy the sublattices of CN16, and the smaller Zn atoms occupy the sublattices of CN12 [31]. Consistent with the general conclusion that the percentage of the larger atoms on an atomic site increases with increasing coordination from nearly zero for CN12 to 100% for CN16, we would expect the smaller Ni as major atom filling the two sublattices of CN12 with 2- and 6-fold lattice sites, and the larger Ti or Al atoms to fill the 4-fold lattice sites with CN16. Experimental results, however, revealed that Ni was present in the CN16 sublattice and Al was the major occupier of the CN12 sublattice [2]. In addition, Ti also entered the CN12 sublattice. Therefore, the sublattice formula $(\text{Ti,Ni,Al})_2(\text{Ti,Ni})_1$ was used in the present work. The difference to Dupin's model is that it is simpler because Al does not enter the second sublattice.

Similar to Eq. (6), for 1 mol of formula unit of the τ_3 phase $(\text{Ti,Ni,Al})_2(\text{Ti,Ni})_1$, this model yields the following expression for its Gibbs energy:

$$\begin{aligned}
G_m^{\tau_3} = & y_{\text{Ti}}^I y_{\text{Ti}}^{II} G_{\text{Ti:Ti}}^{0,\tau_3} + y_{\text{Ti}}^I y_{\text{Ni}}^{II} G_{\text{Ti:Ni}}^{0,\tau_3} + y_{\text{Ni}}^I y_{\text{Ti}}^{II} G_{\text{Ni:Ti}}^{0,\tau_3} \\
& + y_{\text{Ni}}^I y_{\text{Ni}}^{II} G_{\text{Ni:Ni}}^{0,\tau_3} + y_{\text{Al}}^I y_{\text{Ti}}^{II} G_{\text{Al:Ti}}^{0,\tau_3} + y_{\text{Al}}^I y_{\text{Ni}}^{II} G_{\text{Al:Ni}}^{0,\tau_3} \\
& + 2RT(y_{\text{Ti}}^I \ln y_{\text{Ti}}^I + y_{\text{Ni}}^I \ln y_{\text{Ni}}^I + y_{\text{Al}}^I \ln y_{\text{Al}}^I) \\
& + RT(y_{\text{Ti}}^{II} \ln y_{\text{Ti}}^{II} + y_{\text{Ni}}^{II} \ln y_{\text{Ni}}^{II}) + G_m^{E,\tau_3} \quad (8)
\end{aligned}$$

The term y_i^n represents the site fraction of component i on the sublattice n it occupies. The parameters $G_{\text{Ti:Ti}}^{0,\tau_3}$ and $G_{\text{Ni:Ni}}^{0,\tau_3}$ are the Gibbs energy of the pure components Ti and Ni, respectively, with the same crystal structure of τ_3 , or G_i^{0,τ_3} (T), as described in Section 3.1; The other G^{0,τ_3} parameters represent the Gibbs energies of one mole of the hypothetical compounds NiTi_2 , Ni_2Ti , Al_2Ti , and Al_2Ni , respectively, formed by the two sublattices with the same crystal structure of τ_3 .

G_m^{E,τ_3} , the excess Gibbs energy, is represented by

$$\begin{aligned}
G_m^{E,\tau_3} = & y_{\text{Ti}}^I y_{\text{Ni}}^I (y_{\text{Ti}}^{II} L_{\text{Ti,Ni:Ti}}^{\tau_3} + y_{\text{Ni}}^{II} L_{\text{Ti,Ni:Ni}}^{\tau_3}) \\
& + y_{\text{Ni}}^I y_{\text{Al}}^I (y_{\text{Ti}}^{II} L_{\text{Ni,Al:Ti}}^{\tau_3} + y_{\text{Ni}}^{II} L_{\text{Ni,Al:Ni}}^{\tau_3}) \\
& + y_{\text{Ti}}^I y_{\text{Al}}^I (y_{\text{Ti}}^{II} L_{\text{Ti,Al:Ti}}^{\tau_3} + y_{\text{Ni}}^{II} L_{\text{Ti,Al:Ni}}^{\tau_3}) \\
& + y_{\text{Ti}}^{II} y_{\text{Ni}}^{II} (y_{\text{Ti}}^I L_{\text{Ti:Ti,Ni}}^{\tau_3} + y_{\text{Ni}}^I L_{\text{Ni:Ti,Ni}}^{\tau_3} + y_{\text{Al}}^I L_{\text{Al:Ti,Ni}}^{\tau_3}) \\
& + y_{\text{Ti}}^I y_{\text{Ni}}^I y_{\text{Al}}^I (y_{\text{Ti}}^{II} L_{\text{Ti,Ni,Al:Ti}}^{\tau_3} + y_{\text{Ni}}^{II} L_{\text{Ti,Ni,Al:Ni}}^{\tau_3}) \quad (9)
\end{aligned}$$

The L^{τ_3} parameters represent the interaction energies between components in the same sublattice dependent of the occupation of the components in the other one. Same to the expression of τ_2 , the comma here separates

elements that interact on the same sublattice, and the colon separate elements on different sublattices.

4. Results and discussion

The optimization procedure was started with the τ_3 phase at 900°C. The values of those parameters in Dupin's modeling, which correspond to the same occupations of sublattices, were used as starting values. After the experimental three-phase equilibria $\tau_3 + \alpha_2 + \tau_4$ and $\delta + \alpha_2 + \tau_4$ were calculated, the parameters of τ_2 and τ_1 were adjusted successively. Since our work focused on the phase relationships of the ternary compounds τ_1 , τ_2 , and τ_3 , the following discussion is limited to the region with less than 50 at% Ni.

4.1. Isothermal sections

4.1.1. 900°C section

The calculated isothermal section at 900°C is shown in Fig. 6. A narrow two-phase field $\alpha_2 + \tau_4$ has been calculated, and also the triangle $\alpha_2 + \tau_3 + \tau_4$ is very narrow. Because the binary Al–Ti parameters account for very well the experimental data in the Ti-rich region of the binary system, the only way to widen this triangle is to modify the τ_4 phase so as to reduce the Al-content of the vertex at τ_4 . But this is outside the scope of the present work because τ_4 is the key phase in the Ni-rich region that has been accepted from Dupin [1]. An attempt has been made to increase the Al-content of the lower limit of τ_2 and the upper limit of τ_3 in Fig. 6 by introducing a less negative interaction parameter between Al and Ti in the first sublattice of τ_2 , i.e. $L_{\text{Ti,Al:Ti,Ni}}^{\tau_2}$ in Eq. (7). It was successful not only for this purpose, but also to obtain the $\alpha_2 + \kappa + \tau_3$ equilibrium stable at 900°C which has been experimentally observed by Bauer et al. [6]. Although at that time only the region close to the $\alpha_2 + \kappa$ binary was investigated [6], small precipitates $\text{Al}_{40}\text{Ni}_{20}\text{Ti}_{40}$ were identified in equilibrium with $\alpha_2 + \kappa$, which at that time were speculated to be the “ τ_2 - Al_2NiTi ” phase cited by Budberg [3] and Nash [5]. From our subsequent reinvestigation of the isothermal section [2], however, it became obvious, that these precipitates crystallographically correspond to τ_3 rather than to τ_2 .

In our experiments, τ_3 was found to coexist with Al_2Ti [2]. This result has not been confirmed by the calculations which gave the competing equilibrium $\kappa(\text{AlTi}) + \tau_2$ and the adjoining equilibria $\kappa(\text{AlTi}) + \tau_3$ and $\text{Al}_2\text{Ti} + \tau_2$ instead. This may be due to an incorrect account of the substitution of Ti/Al by Ni/Al in τ_3 . In order to come closer to experimental data either τ_3 has to be rendered more stable or τ_2 less stable. There is, however, not much room for changes of the relative stabilities owing to the constraints imposed by the other

surrounding equilibria e.g. $\alpha_2 + \tau_4$. Further experimental and theoretical work is needed to solve this problem.

4.1.2. 1200°C section

With Dupin's parameters of the liquid phase as well as our parameters of τ_1 , τ_2 , and τ_3 , the liquid phase was calculated to be stable at 1200°C in the Ni-poor region around 15 at% Ni and 30–55 at% Al. The experiments by Mazdiyasi et al. [26] did not find evidence for liquid phase in the alloy with 7.4 at% Ni and 64 at% Al annealed at this temperature for 500 h. Thus, $L_{Ti,Ni,Al}^{0,L}$ and $L_{Ti,Ni,Al}^{2,L}$ in Eq. (5), which represent the contributions of Al and Ti, respectively, to the interaction energy in liquid, were changed from Dupin's modeling to prevent it from appearing in this region.

The resulting isothermal section at 1200°C is presented in Fig. 11. Five of the six phase equilibria suggested by Mazdiyasi et al. [26] were obtained (see the phase fields marked with star) while the other one, the $\tau_1 + \tau_3$ equilibrium, were not obtained. The τ_3 phase was identified by EMPA to be at 49Al–17Ni–34Ti (at%) in Ref. [26], but its crystal structure was not analyzed by means of X-ray diffraction techniques. Thus, no further attempt has been made to fit this data.

4.1.3. 800°C section

The calculated phase relationships in the Al-corner at 800°C agree excellently with the experimental results by Omar et al. [27] (see the phase fields marked with star in Fig. 12). In contrast to Dupin's modeling [1], the τ_3 phase is predicted unstable at 800°C, which contradicts the experimental results [28,29]. We also observed τ_3 at 800°C, see Table 2, and no significant change in its phase amount was seen within 10 days. Long time heat

treatments to be sure of its stability have not yet been done. The calculated metastability at 800°C is because τ_3 has been made less stable at 900°C in order to have a stable $\alpha_2 + \tau_4$ tieline. In order to get τ_3 at 800°C, $L_{Ti,Al;Ni}^{\tau_3}$ in Eq. (9) must be more negative than at 900°C, or $-274606 + 50T$ (J/mole) considering the requirement of the phase equilibria at both temperatures. But with these coefficients, the calculated liquidus surface of τ_3 shrinks to the Ni–Ti side by about 50%, and the growing liquidus surface of τ_2 would cover most of the experimental data points for the primary phase τ_3 . The other equilibria determined in [28,29], which do not involve τ_3 , have been calculated (see the phase fields marked with circle and triangle, respectively, in Fig. 12).

4.2. Liquidus surfaces

The experimental data on the primary phases in different alloys are compared with the calculated projection of the liquidus surfaces in Fig. 13(a). Experimental results and calculations are in good agreement. As to those by Nash and Liang [5], however, the two alloys for τ_2 and three of the alloys for τ_4 were calculated to have τ_3 as the primary phase.

The calculated invariant reactions of the system related to the liquidus surfaces are summarized in Table 4 and Fig. 13(b).

5. Simulation of solidification processes

The present thermodynamic description of the Al–Ni–Ti system can be applied to simulate the solidification process of ternary alloys. As an example, the solidification

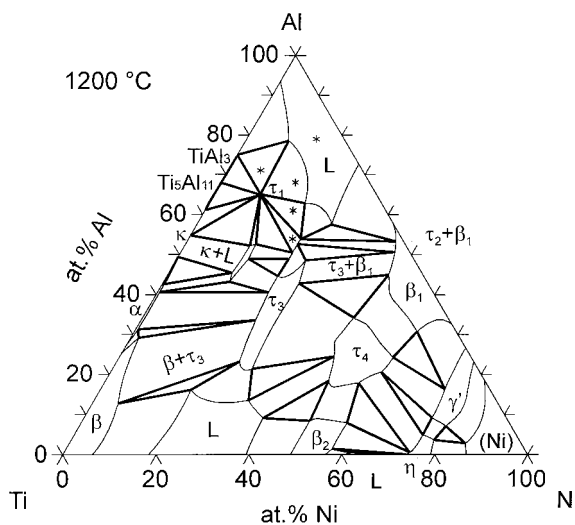


Fig. 11. Calculated isothermal section of the Al–Ni–Ti phase diagram at 1200°C. The phase fields marked with star “*” were suggested by Mazdiyasi et al. [26].

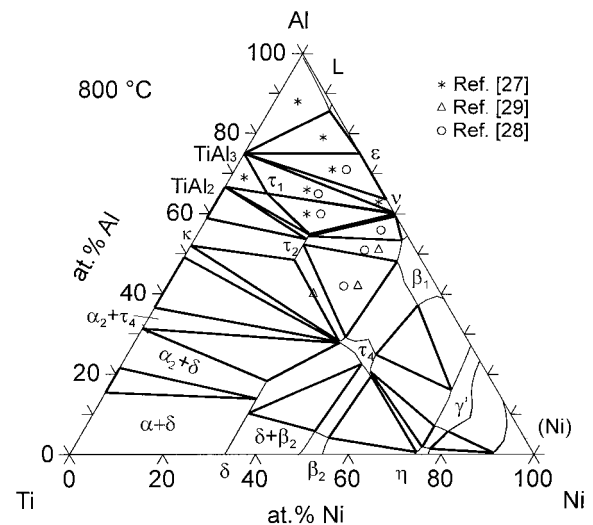


Fig. 12. Calculated isothermal section of the Al–Ni–Ti phase diagram at 800°C. The phase fields marked with symbols were experimentally observed.

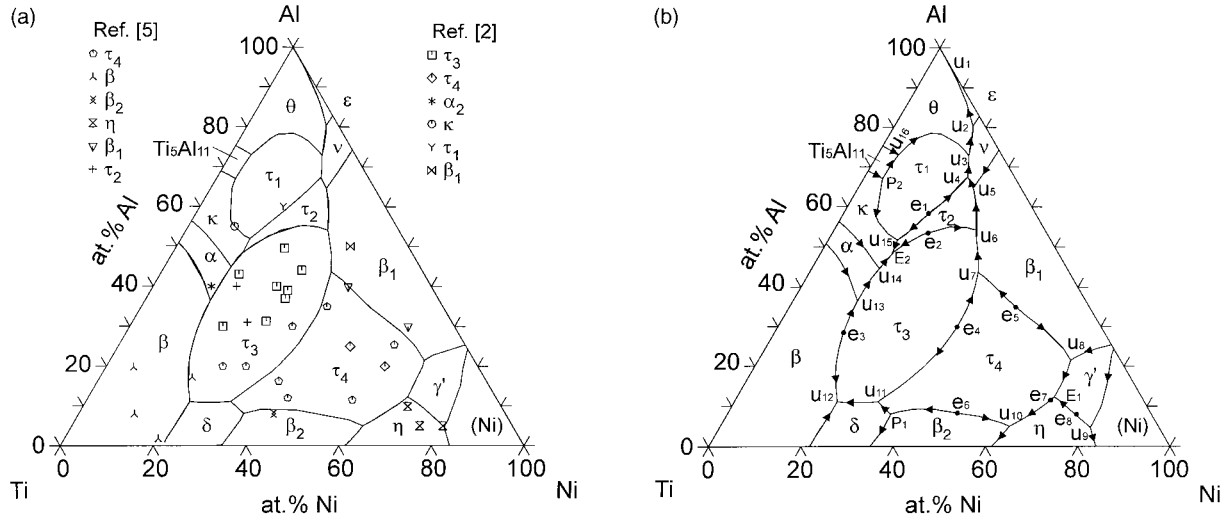


Fig. 13. Projection of the calculated liquidus surfaces. (a) Compared with the alloys whose primary phases have been experimentally determined (b) with the invariant equilibria which involve the liquid phase (see Table 4).

Table 4
Calculated invariant reactions of the Ti-Ni-Al system related to the liquidus surfaces

Types	Reactions	Liquid compositions		Temperature (C)
		at% Ni	at% Al	
U ₁	$L + \theta \leftrightarrow \varepsilon + (\text{Al})$	3.06	96.85	644.7
U ₂	$L + v \leftrightarrow \varepsilon + \theta$	16.96	80.41	838.8
U ₃	$L + \tau_1 \leftrightarrow \theta + v$	19.86	72.89	924
U ₄	$L + \tau_2 \leftrightarrow v + \tau_1$	22.41	67.34	995.7
U ₅	$L + \beta_1 \leftrightarrow v + \tau_2$	24.93	64.62	1068.3
U ₆	$L + \tau_3 \leftrightarrow \beta_1 + \tau_2$	30.51	54.09	1227
U ₇	$L + \tau_4 \leftrightarrow \tau_3 + \beta_1$	36.58	43.71	1334.8
U ₈	$L + \beta_1 \leftrightarrow \gamma' + \tau_4$	67.72	21.47	1312.7
E ₁	$L \leftrightarrow \gamma' + \eta + \tau_4$	68.77	12.27	1310.7
U ₉	$L + \gamma' \leftrightarrow (\text{Ni}) + \eta$	80.38	4.80	1335
U ₁₀	$L + \tau_4 \leftrightarrow \beta_2 + \eta$	62.71	5.03	1236.5
P ₁	$L + \beta_2 + \tau_4 \leftrightarrow \delta$	35.44	8.13	1116.4
U ₁₁	$L + \tau_4 \leftrightarrow \delta + \tau_3$	31.11	11.11	1110.5
U ₁₂	$L + \tau_3 \leftrightarrow (\beta\text{Ti}) + \delta$	22.30	11.17	1063.8
U ₁₃	$L + (\beta\text{Ti}) \leftrightarrow (\alpha\text{Ti}) + \tau_3$	13.99	36.51	1259.9
U ₁₄	$L + (\alpha\text{Ti}) \leftrightarrow \tau_3 + \kappa$	14.34	44.82	1178.6
U ₁₅	$L + \tau_1 \leftrightarrow \tau_2 + \kappa$	14.84	51.91	1179.5
E ₂	$L \leftrightarrow \kappa + \tau_2 + \tau_3$	15.05	48.31	1170.6
P ₂	$L + \text{Al}_{11}\text{Ti}_5 + \kappa \leftrightarrow \tau_1$	4.12	67.02	1337.3
U ₁₆	$L + \text{Al}_{11}\text{Ti}_5 \leftrightarrow \tau_1 + \theta$	4.48	73.01	1310.4
e ₁		17.6	56.85	1270.7
e ₂		20.42	54.04	1376.7
e ₃		15	28.5	1313
e ₄		38.89	29.96	1446.2
e ₅		49.1	34.96	1482
e ₆		49.8	8.35	1342
e ₇		68.4	11.5	1310.8
e ₈		75.8	8.01	1352

of the experimental alloy 39Al–29.5Ni–31.5Ti (at%) has been simulated under two extreme conditions: (1) back diffusion in the solid phases is complete (global equilibrium) and (2) no back diffusion in the solids (Scheil model). In both cases a uniform liquid composition and

local equilibrium at the solid–liquid interface has been assumed [30]. The calculated amount of the liquid phase varying with temperature during solidification is shown in Fig. 14. The solidification starts at the liquidus point 1896°C. Under equilibrium condition, the alloy is solidified as a single phase τ_3 , which means that only the primary solidification step occurs: $L \rightarrow \tau_3$. The liquid is consumed at 1530°C.

Under Scheil conditions, however, the contents of nickel and aluminum in liquid increase further with decreasing temperature and the solidification does not stop at 1530°C. After the primary crystallization of τ_3 , the composition path of the liquid phase reaches the valley line of the eutectic reaction $L \rightarrow \tau_3 + \tau_4$ at 1388°C (see Fig. 15). This three-phase reaction proceeds down to 1335°C, where the liquid survives the four-phase equilibrium $L + \tau_4 \rightarrow \tau_3 + \beta_1$ (U₇ in Fig. 15) and goes further all the way down until beyond U₂ in Fig. 13b. At 1230°C after U₇, however, the amount of residual liquid becomes virtually zero (0.1 mol%). Hence, the whole solidification process practically ends at 1230°C before reaching U₆. The amounts of liquid consumed in these four steps are 82.7, 10.8, 0.5, and 6.0 (mol%), successively. Under exact Scheil-conditions (step size < 1 K) the amount of liquid consumed in the transition type reaction U₇ (0.5 mol%) should even go to zero. As a result of the blocked solid state diffusion, in addition to the primary τ_3 and secondary eutectic $\tau_3 + \tau_4$, there is some eutectic $\tau_3 + \beta_1$ in the solidified microstructures.

The microstructures of the as-cast alloy of 39Al–29.5Ni–Ti (at%) are presented in Fig. 2. Although the solidification structures in Fig. 2 are not evenly distributed, it can still be seen that the black primary τ_3 dominates the picture. There are very fine eutectic structures of $\tau_3 + \tau_4$ in the micrograph, confirming the

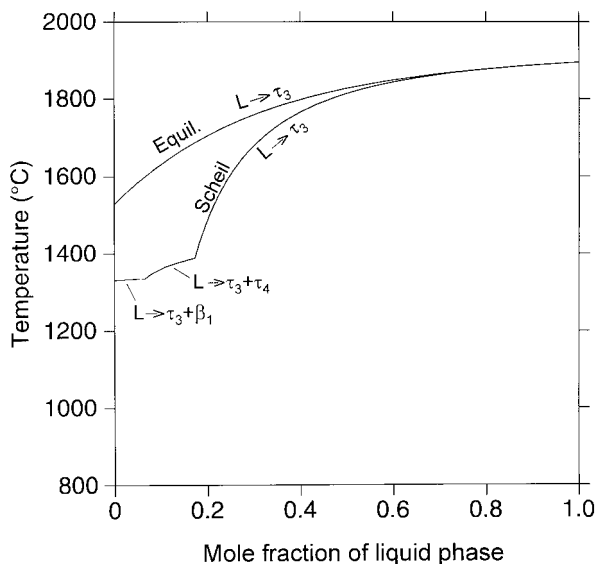


Fig. 14. Calculated molar fraction of the liquid phase versus temperature during solidification of the 39Al–29.5Ni–Ti (at%) alloy under equilibrium and Scheil model conditions.

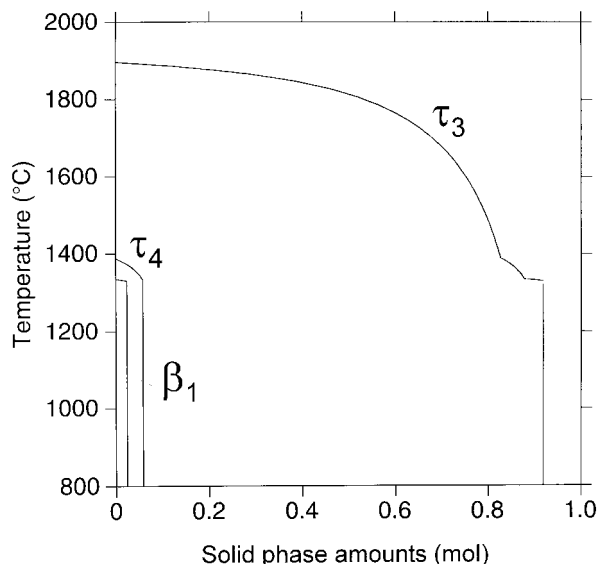


Fig. 16. Calculated molar fraction of the solid phases versus temperature during solidification of the 39Al–29.5Ni–Ti (at%) alloy under Scheil model conditions.

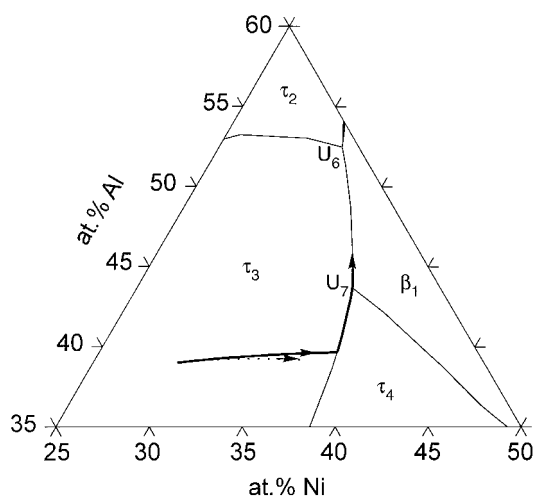


Fig. 15. Solidification path of the 39Al–29.5Ni–Ti (at%) alloy under equilibrium (dotted line) and Scheil model conditions (thick lines), imposed on the calculated projection of the liquidus surfaces (thin lines).

prediction of the reaction $L \rightarrow \tau_3 + \tau_4$ in Fig. 14. As to the predicted eutectic $L \rightarrow \tau_3 + \beta_1$, no corresponding microstructure is visible in Fig. 2. This result indicates that the experimental solidification was probably under a condition between equilibrium and Scheil, which means that a partial back diffusion has occurred in the solid phases. This is understandable because the solidification proceeds at high temperatures ($> 1330^\circ\text{C}$). Furthermore, the reaction $L \rightarrow \tau_3 + \beta_1$ is predicted by the Scheil model to happen within a very narrow temperature range from 1335 to 1230°C , compared to the temperature range of the entire solidification process ($1895\text{--}1230^\circ\text{C}$).

The calculated compositions of the primary phase τ_3 at the very beginning of solidification are 38.58Al–26.95Ni–34.48Ti (at%), almost the same as the experimental values 38.5Al–27Ni–34.5Ti (at%) determined by EMPA in the core of the primary phase. At the end of the primary solidification, the compositions of the finally precipitated τ_3 are predicted to be 39.37Al–30.23Ni–30.40Ti (at%). Fig. 16 presents the phase fractions in the solidified alloy versus temperature under Scheil condition. It can be seen that in the solidified alloy there are 91.8 at% τ_3 , 5.7 at% τ_4 , and 2.5 at% β_1 . Such data may be helpful in controlling the microstructures of the cast alloys by choosing an appropriate composition and cooling rate. The higher the cooling rate, the greater the volume fraction of the secondary τ_4 particles, or even some β_1 particles, in the τ_3 matrix. On the other hand, the β_1 particles, or even τ_4 , can be avoided by a slower cooling rate.

6. Conclusions

A complete and internally consistent picture of polythermal ternary Al–Ni–Ti phase equilibria has been developed by thermodynamic modeling. It enables a quantitative check and comparison of different — though interrelated — data on melting and solid state phase equilibria in a wide temperature range of the entire ternary system. New experimental data are presented on phase equilibria at 800 and 1000°C and with the liquid phase. They have been combined with available literature data, including the extensive study at 900°C presented in the companion paper, part I, to form the basis of our modeling. An application to the simulation of the solidification behavior of a ternary alloy is also demonstrated.

This may be useful in controlling the microstructure with reduced number of costly experiments, since this type of calculation can now be performed for any ternary alloy.

The limitations of the present modeling are partly due to conflicting experimental information and partly due to model simplifications. Especially the thermodynamic stability of τ_4 , which was fixed from a previous assessment of the Ni-rich equilibria [1], appears to be too low in comparison with the experimental Ni-poor equilibria. The model for τ_3 is not reproducing the exceptional banana-shaped homogeneity region of τ_3 at 900°C. The metastability of τ_3 at 800°C does not agree with experimental data. The calculated $\kappa + \tau_2$ equilibrium at 900°C is in conflict with the experimental $\text{Al}_2\text{Ti} + \tau_3$ equilibrium. These points show the area of specific future studies. The overall agreement with the vast majority of experimental data, however, indicates a reasonable reliability of the present assessment.

Acknowledgements

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