

Liquidus Projection and Reaction Scheme of the Co-Al-Nb System

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By metallographic observation of the as-cast microstructures, determination of the liquidus temperatures and the temperatures of invariant reactions by differential thermal analysis, and measurement of the compositions of the primary phases and the eutectic residuals by electron probe microanalysis, a liquidus projection for the Co-Al-Nb system has been established for the first time. The binary Co-Nb intermetallic phases have a large solid solubility for Al and their melting temperatures increase markedly by the addition of Al. The only ternary compound, the Heusler phase NbCo₂Al, melts incongruently at about 1485 °C. By CALPHAD modelling the consistency of the experimental data has been checked. Calculated and experimentally determined temperatures of the invariant reactions are in good agreement and are summarised within a reaction scheme.

Keywords CALPHAD, differential thermal analysis (DTA), electron probe microanalysis (EPMA), liquidus surface, microstructure, ternary system

1. Introduction

The Co-Nb(-Al) system is of considerable interest for the basic understanding of the stability of the different polytypes of the Laves phase in dependence on temperature and composition, because all three polytypes of the Laves phase—hexagonal C14¹ and C36 and cubic C15—are stable within the binary Co-Nb system.^[1,2] A list of phases that are stable in the Co-Al-Nb system and the binary subsystems at the liquidus together with the invariant reactions involving the liquid is compiled in Table 1. Besides the binary phases a number of ternary compounds have been reported. The NbCo₂Al Heusler phase first reported by Markiv et al.^[4] exists between about 12–25 Nb (all compositions in at.% except where noted) and 25–35 Al^[5,6] and it is not known whether this phase melts congruently or incongruently. Hunt and Raman^[7] reported a phase at a composition of about 26 Co, 20 Al, 54 Nb whose structure they could not identify exactly but as the x-ray diffraction (XRD) pattern was closely related to that of Co₇Nb₆ (μ phase; Fe₇W₆-type) they termed the phase μ' . The phase was also reported by Burnashova et al.^[5]

¹Because all three Laves phases nominally have the same stoichiometry of AB₂, Strukturbericht designations are chosen to differentiate between these three polytypes.

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The hexagonal C14 Laves phase, which is only stable above about 1250 °C in the binary Co-Nb system,^[2] exists in the ternary system within an extended homogeneity range even at much lower temperatures, e.g., at 800 °C.^[5,6] Above 1250 °C the single-phase field of C14 extends from the binary system to an Al content of 55 at.%.^[6]

Unfortunately, only scarce information on phase equilibria within this system exists and neither a projection of the liquidus surface nor a reaction scheme has been published yet.^[8,9] Even the few information about phase equilibria involving the liquid is not unambiguous. Nesterovich et al.^[10] found that the eutectic α -Co(Al,Nb) + Co₂Nb (the structural variant of this Laves phase has not been specified) extends somewhat into the ternary system but this finding has explicitly not been accepted in the assessment by Neiva.^[8] However, also Haour et al.^[11] reported a eutectic at 77.3 Co, 7.3 Al, 15.4 Nb at 1240 °C which they assumed to be α -Co(Al,Nb) + Co₂Nb, though the phases have not been identified in their work. The only other information available is that Subramanian and Simmons^[12] observed a differential thermal analysis (DTA) signal at 1174 °C in the Al-rich corner of the system which they associated with the invariant reaction $L + \text{CoAl} \leftrightarrow \text{NbAl}_3 + \text{Co}_2\text{Al}_5$.

The current investigations were performed within the framework of the inter-institutional research project “The Nature of Laves Phases” (<http://Laves.mpie.de>) which focuses on the systems X-Al-Nb (X = Fe, Co, Cr). Because this investigation concentrates on the different polytypes of the Laves phase, the Nb- and Al-corner have not been considered in the present work. It is noted that for the Co-Al-Nb system also five isothermal sections between 800 and 1250 °C have been experimentally determined.^[6]

2. Experimental

Five binary Co-Al and 35 ternary alloys were produced from Co (99.95 wt.%), Al (99.999 wt.%), and Nb (99.9 wt.%) by crucible-free levitation melting. After melting, the alloys

Table 1 Crystallographic data, melting points and melting behaviour for binary and ternary phases of the Co-Al-Nb system

Phase/Reaction	Pearson symbol	Space group	Structure type	Strukturbericht designation	Melting behaviour	Temperature, °C	Composition Co-Al-Nb, at.%	References
αCo	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	Cu	<i>A1</i>	...	1495	...	[16]
$L \leftrightarrow (\text{Co}) + \text{CoAl}$	Eutectic	1400	L: 81.0-19.0-0	[16]
CoAl	<i>cP2</i>	<i>Pm$\bar{3}m$</i>	CsCl	<i>B2</i>	Congruent	1675	50-50-0	This work
Co ₂ Al ₅	<i>hP28</i>	<i>P6₃/mmc</i>	Co ₂ Al ₅	<i>D8₁₁</i>	Peritectic	1188	28.6-71.4-0	[3]
$L + \text{CoAl} \leftrightarrow \text{Co}_2\text{Al}_5$	Peritectic	1188	L: 24.4-75.6-0	[3]
NbAl ₃	<i>tI8</i>	<i>I4/mmm</i>	h-TiAl ₃	<i>D0₂₂</i>	Congruent	1714	0-25-75	[13]
$L \leftrightarrow \text{NbAl}_3 + \text{Nb}_2\text{Al}$	Eutectic	1571	0-56.2-43.8	[13]
Nb ₂ Al	<i>tP30</i>	<i>P4₂/mnm</i>	σ -CrFe	<i>D8_b</i>	Peritectic	1940	0-32-68	[17]
$L + \text{Nb}_3\text{Al} \leftrightarrow \text{Nb}_2\text{Al}$	Peritectic	1940	0~36~64	[17]
Nb ₃ Al	<i>cP8</i>	<i>Pm$\bar{3}n$</i>	Cr ₃ Si	<i>A15</i>	Peritectic	2060	0~22.5~77.5	[17]
$L + (\text{Nb}) \leftrightarrow \text{Nb}_3\text{Al}$	Peritectic	2060	0~28~72	[17]
(Nb)	<i>cI2</i>	<i>Im$\bar{3}m$</i>	W	<i>A2</i>	...	2469	...	[17]
$L \leftrightarrow (\text{Nb}) + \text{Co}_7\text{Nb}_6$	Eutectic	1364	36.7-0-63.3	[1]
Co ₇ Nb ₆ (μ)	<i>hR13</i>	<i>R$\bar{3}m$</i>	Fe ₇ W ₆	<i>D8₅</i>	Congruent	1424	48.2-0-51.8	[1]
$L \leftrightarrow \text{Co}_7\text{Nb}_6 + \text{C14}$	Eutectic	1379	45.1-0-54.9	[1,2]
$L + \text{C15} \leftrightarrow \text{C14}$	Peritectic	1424	58-0-42	[2]
NbCo ₂ (C14)	<i>hP12</i>	<i>P6₃/mmc</i>	MgZn ₂	<i>C14</i>	Peritectic	1424	63.5-0-36.5	[2]
NbCo ₂ (C15)	<i>cF24</i>	<i>Fd$\bar{3}m$</i>	MgCu ₂	<i>C15</i>	Congruent	1484	66.7-0-33.3	[2]
$L + \text{C15} \leftrightarrow \text{C36}$	Peritectic	1264	85.5-0-14.5	[2]
NbCo ₂ (C36)	<i>hP24</i>	<i>P6₃/mmc</i>	MgNi ₂	<i>C36</i>	Peritectic	1264	75.0-0-25.0	[2]
$L \leftrightarrow (\text{Co}) + \text{C36}$	Eutectic	1239	86.1-0-13.9	[2]
NbCo ₂ Al (Heusler)	<i>cF16</i>	<i>Fm$\bar{3}m$</i>	BiF ₃ or (MnCu ₂ Al)	<i>L2₁</i>	[4]

were drop cast into a cold copper mould of 12 or 22 mm diameter resulting in rods of about 100-120 mm length. Another seven ternary alloys were produced by arc melting. The resulting buttons were about 15 mm in diameter. For further examination the alloys were sectioned by electrical-discharge machining (EDM).

The microstructures of the as-cast alloys were studied in a scanning electron microscope (SEM; Hitachi S-530). Compositions of the primary phases, i.e., those which solidified first from the melt, were measured by energy-dispersive spectrometry (EDS; EDAX CDU LEAP system) attached to the SEM or wavelength-dispersive spectrometry (WDS) on an electron probe microanalyser (JEOL JXA-8100). While primary phases were analysed with a beam of 1 μm spot size the beam was widened to 3-10 μm for analysis of fine-scaled eutectics. The overall compositions of the alloys were determined by analysing large areas by SEM-EDS.

Phases were also partly identified by XRD of powders which were produced by crushing parts of a sample in a steel mortar and then sieving out the fraction < 90 μm . XRD spectra were recorded in the 2Θ range 20-125° using monochromatic $\text{CoK}\alpha_1$ radiation on a Huber and an Inel diffractometer and $\text{CuK}\alpha$ radiation on a PHILIPS PW-1827 diffractometer.

Liquidus temperatures and those of invariant reactions were determined by DTA (Setaram SETSYS-18 DTA) at a heating rate of 10 K/min. In some cases, additional measurements with lower heating rates of 2 and 5 K/min were carried out. The experiments were performed in alumina crucibles under argon atmosphere (purity 99.999 or 99.9999 vol.%; in

addition adsorbents for oxygen and moisture are employed). The DTA was frequently calibrated using pure elements by which the accuracy of the measurements is ± 2 K up to 1750 °C. For the temperatures of the invariant reactions the onsets during heating were taken. The liquidus temperatures were also determined during heating by taking the last maximum of the DTA curve before it finally returns back to the baseline and comparing these values to the onset during cooling. Only in those cases where the signals in the heating curves could not be resolved unambiguously further results obtained on cooling were consulted in addition.

The consistency of all experimental results was finally checked and a reaction scheme was established by calculating the liquidus surface by CALPHAD modelling with the aid of the Thermo-Calc software package (Thermo-Calc Software AB, version R. 2006; available from <http://www.thermocalc.se>). In the present modelling, the thermodynamic parameters for the Nb-Al system were taken from Ref [13], the description of the Co-Al system was provided by Dupin, based on her earlier work,^[14] but with an improved model for B2 as $(\text{Al,Co,Va})_{0.5}(\text{Al,Co,Va})_{0.5}\text{Va}_3$. The thermodynamic parameters for the Co-Nb system are from our own work.^[15]

3. Results and Discussion

Table 1 lists all crystallographic information, melting points and melting behavior of the phases that are stable at

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Table 2 Composition of the alloys, temperatures of invariant reactions, and compositions of primary phases and residual eutectics

Composition Al-Nb, at.%	Temperature, °C	Reaction	Composition Al-Nb, at.%	Phases/reaction
41.5-0	1630 ± 3	Liquidus	...	CoAl
45.2-0	1661 ± 3	Liquidus	...	CoAl
50.3-0	1675 ± 3	Liquidus	...	CoAl
60.0-0	1620 ± 3	Liquidus	...	CoAl
70.2-0	1395 ± 3	Liquidus	...	CoAl
0.9-37.3	1465 ± 3	Liquidus	0.7-34.9	C15
	1448	Peritectic	...	L + C15 ↔ C14
	1387	Eutectic	...	L ↔ C14 + Co ₇ Nb ₆
1.1-24.2	1440	Liquidus	0.8-27.1	C15
	1269	Peritectic	...	L + C15 ↔ C36
	1238	Eutectic	2.2-13.7	L ↔ C36 + (Co)
1.5-34.5(a)	1481 ± 5	Liquidus	...	C15
	1445	Peritectic	...	L + C15 ↔ C14
2.0-33.0(a)	1478	Liquidus	...	C15
	1455	Peritectic	...	L + C15 ↔ C14
	1390	Eutectic	...	L ↔ C14 + Co ₇ Nb ₆
2.0-40.0	1454 ± 3	Liquidus	3.0-35.8	C14
	1390	Eutectic	...	L ↔ C14 + Co ₇ Nb ₆
2.2-20.6	1408 ± 10	Liquidus	1.5-27.5	C15
	1270	Peritectic	...	L + C15 ↔ C36
	1238	Eutectic	3.4-13.6	L ↔ C36 + (Co)
2.3-27.3	1469 ± 4	Liquidus	...	C15
	1276	Peritectic	...	L + C15 ↔ C36
	1229	Eutectic	...	L ↔ C36 + (Co)
3.0-30.0(a)	1483 ± 6	Liquidus	...	C15
3.1-38.1	1461 ± 5	Liquidus	3.9-35.4	C14
	1394	Eutectic	...	L ↔ C14 + Co ₇ Nb ₆
4.0-33.0(a)	1475	Liquidus	...	Laves (C15?)
4.8-29.2	1476 ± 5	Liquidus	4.0-30.5	C15
	1323	Peritectic	...	L + C15 ↔ C36
	1270	Eutectic	...	L ↔ C36 + CoAl
6.0-33.0(a)	1475	Liquidus	...	Laves (C15 or C14)
8.0-33.0(a)	1477	Liquidus	...	Laves (C15 or C14)
9.4-28.2	1467 ± 3	Liquidus	8.7-30.8	C14
	1338(c)	Peritectic	...	L + C14 ↔ C36
	~1330	Peritectic	...	L + C36 ↔ NbCo ₂ Al
	1295(d)	U-Type	...	L + NbCo ₂ Al ↔ C36 + CoAl
9.7-42.8	1470 ± 2	Liquidus	14.4-36.8	C14
	1422	Eutectic	...	L ↔ C14 + Co ₆ Nb ₇
9.8-26.1	1451 ± 2	Liquidus	8.3-29.8	C14
	~1339	Peritectic	...	L + C14 ↔ C36
	1324	Peritectic	...	L + C36 ↔ NbCo ₂ Al
	~1295(d)	U-Type	...	L + NbCo ₂ Al ↔ C36 + CoAl
9.9-30.5	1480	Liquidus	10.0-30.7	C14
	1384(d)	Peritectic	...	L + C14 ↔ Co ₂ AlNb
10.0-10.5	1280	Liquidus	10.9-4.1	(Co)
	1226	Eutectic	9.4-12.8	L ↔ (Co) + C36
	1220	Tem. Eutectic	...	L ↔ (Co) + CoAl + C36
10.0-25.5	1446	Liquidus	8.5-29.0	C14
	1325	Peritectic	...	L + C14 ↔ C36
	1303	Eutectic	21.0-14.5	L ↔ CoAl + C36
	1295(d)	U-Type	...	L + NbCo ₂ Al ↔ C36 + CoAl

Table 2 Continued

Composition Al-Nb, at.%	Temperature, °C	Reaction	Composition Al-Nb, at.%	Phases/reaction
10.1-20.1	1408	Liquidus	6.4-26.9	C15
	1320	Peritectic	...	L + C15 ↔ C36
	1234	Eutectic	19.9-12.8	L ↔ CoAl + C36
	1220	Tem. Eutectic	10.5-12.2	L ↔ (Co) + CoAl + C36
10.7-36.0	1487	Liquidus	12.4-34.3	C14
	1412	Eutectic	...	L ↔ C14 + Co₇Nb₆
13.0-32.0(a)	1488	Liquidus	...	C14
13.9-10.4	1260	Liquidus	23.7-5.4	CoAl
	1220	Tem. Eutectic	11.3-12.1	L ↔ (Co) + CoAl + C36
19.9-33.2	1535 ± 5	Liquidus	20.2-33.2	C14
	n.d.	Eutectic	...	L ↔ C14 + NbCo₂Al
20.4-48.3	1551	Liquidus	22.4-48.0	Co₇Nb₆
	1495 ± 5	?	...	Formation impurity phase X?
	1483	?	...	Reaction of X ?
21.0-59.4(b)	1611 ± 10	Liquidus	...	Nb₂Al
	1496	Peritectic	...	L + Nb₂Al ↔ Co₇Nb₆
	1476	U-type?	...	L + Nb₂Al ↔ (Nb) + Co₇Nb₆ ?
24.2-42.0	1580	Liquidus	30.6-36.6	C14
	~1510	Peritectic	...	L + C14 ↔ Co₇Nb₆
	1500	?	...	Formation impurity phase X?
24.9-48.9	1548 ± 15	Liquidus	27.5-46.2	Co₇Nb₆
	1488	Eutectic	...	L ↔ (Nb) + impurity phase X
25.0-60.0(a, b)	> 1670	Liquidus	28.7-64.8	Nb₂Al
	1565	Peritectic	...	L + Nb₂Al ↔ Co₇Nb₆
25.1-25.2	1495 ± 10	Liquidus	24.4-31.8	C14
	1471	Eutectic	...	L ↔ C14 + NbCo₂Al
	n.d.	U-type	...	L + C14 ↔ NbCo₂Al + C36
26.1-15.6	1464 ± 6	Liquidus	35.1-10.2	CoAl
	~1450	Peritectic	...	L + CoAl ↔ NbCo₂Al
	1304	Eutectic	...	L ↔ NbCo₂Al + C36
	1294	U-type	...	L + NbCo₂Al ↔ C36 + CoAl
	26.9-16.0	NbCo₂Al
	6.7-24.0	C36 (according to composition)
	25.8-6.6	CoAl
	~1215	Tem. Eutectic	10.4-11.0	L ↔ (Co) + CoAl + C36
28.7-35.4	1610	Liquidus	32.8-34.3	C14
	n.d.	Peritectic	...	L + C14 ↔ Co₇Nb₆
33.3-48.8	1610 ± 10	Liquidus	30.2-65.1	Nb₂Al
	1595 ± 10	Eutectic	36.8-47.0	L ↔ Nb₂Al + C14
	1578	Tem. Peritectic	...	L + Nb₂Al + C14 ↔ Co₇Nb₆
34.4-25.4	1568	Liquidus	31.8-47.2	Co₇Nb₆
	1494	Eutectic	34.2-33.2	C14
39.3-35.1	1670 ± 5	Liquidus	35.0-20.3	L ↔ CoAl + C14
	n.d.	Peritectic	41.2-34.0	C14
39.7-15.9	1545	Liquidus	...	L + C14 ↔ Co₇Nb₆
	1493	Eutectic	44.5-6.1	CoAl
46.2-20.7	~1580	Liquidus	35.6-21.5	L ↔ CoAl + C14
	1496	Eutectic	...	C14
	1319(d)	U-Type	48.2-14.3	L ↔ CoAl + C14
48.7-35.6	1680 ± 5	Liquidus	...	L + C14 ↔ NbAl₃ + CoAl
	1623	Eutectic	49.5-33.7	C14
			44.6-46.8	L ↔ Nb₂Al + C14

Table 2 Continued

Composition Al-Nb, at.%	Temperature, °C	Reaction	Composition Al-Nb, at.%	Phases/reaction
60.0-23.0(a)	> 1600	Liquidus	...	C14
	1492	?	...	?
	1322	U-Type	...	L + C14 ↔ NbAl ₃ + CoAl
60.0-25.0(a)	1633	Liquidus	52.7-32.4	C14
	1541	Eutectic	...	L ↔ C14 + NbAl ₃
	1495	?	...	?
	1322	U-Type	62.5-10.0	L + C14 ↔ NbAl ₃ + CoAl
66.1-32.8	1690	Liquidus	73.9-25.8	NbAl ₃
	1553	Tern. Eutectic	55.1-42.1	L ↔ NbAl ₃ + C14 + Nb ₂ Al
68.5-10.6	1420	Liquidus	73.4-24.9	NbAl ₃
	1322	U-Type	62.8-9.1	L + C14 ↔ NbAl ₃ + CoAl
	1174	U-Type	...	L + CoAl ↔ Co ₂ Al ₃ + NbAl ₃
	71.0-0.2	Co ₂ Al ₃

Compositions were established by EPMA and SEM-EDS and temperatures were measured by DTA. Phases given in bold have additionally been identified by XRD. The uncertainty in the determination is ± 1 °C if not stated otherwise. n.d. phases observed but reaction not detected by DTA

(a) Intended composition

(b) Inhomogeneous alloy

(c) Only observed on cooling

(d) Not observed on 1st heating

the liquidus in the Co-Al-Nb system in the composition range under consideration. For the Co-Al system the data of McAllister^[16] are accepted except that the current DTA data show that the melting point of CoAl is at 1675 °C. The Al-Nb system is adopted from Ref 17 except for the melting point of NbAl₃ and the temperature and the composition of the eutectic $L \leftrightarrow NbAl_3 + Nb_2Al$ which have been recently experimentally measured and assessed, respectively, by Witusiewicz et al.^[13] The Co-Nb system has been re-investigated within the scope of the present project^[2,15] except for the Nb-rich part which is adopted from the assessment by Hari Kumar et al.^[1] The compositions of the investigated alloys, of the primary phase, i.e., the phase that formed first from the melt, and of the eutectics measured by SEM-EDS and electron probe microanalysis (EPMA), as well as liquidus temperatures and temperatures of the invariant reactions determined by DTA are summarised in Table 2. Figure 1 shows a number of micrographs of samples which are decisive for establishing the liquidus projection. The liquidus projection itself is shown in Fig. 2. Isotherms shown in Fig. 2 have been constructed on the basis of experimental information.

The prominent feature of the liquidus surface is the large area of primary solidification of the C14-type Laves phase which “cuts off” those of the C15- and C36-types. By adding Al to Co-Nb the melting temperature of the C14 Laves phase increases from 1424 °C in the binary system to about 1700 °C. The exact composition of the maximum melting temperature has not been established, but the melting temperatures of alloys Co-39.3Al-35.1Nb (1670 °C) and Co-48.7Al-35.6Nb (1680 °C) indicate that this maximum may be located at about 45 at.% Al and

33.3 at.% Nb. In the binary Co-Nb system the C15 Laves phase is stable at the stoichiometric composition for the Laves phase of Co-33.3Nb (NbCo₂) while the C14-type Laves phase is only found at off-stoichiometric compositions. By alloying with Al, the primary phase changes from C15 to C14 at the stoichiometric composition when about 5 at.% Al are added. This value is in excellent agreement with that reported by von Keitz and Sauthoff.^[18] Due to the high melting temperatures of the C15 and C14 Laves phases and of NbAl₃ a ridge exists on the ternary liquidus surface between the Co-Nb and the Al-Nb system. Consequently the monovariant reactions which cross this ridge show a maximum. For the peritectic reaction $L + C15 \leftrightarrow C14$ this maximum is at about 1475 °C (M₄ in Fig. 2 and in the reaction scheme in Fig. 4), i.e., at a considerably lower temperature than that of about 1540 °C given in Ref 18. For the eutectic reaction $L \leftrightarrow C14 + NbAl_3$ the temperature of the maximum (M₂) is estimated from the form of the isotherms to be at about 1650 °C. Like the C14 Laves phase the μ phase Co₇Nb₆ can dissolve large amounts of Al whereby it is also stabilized to higher temperatures. From 1424 °C in the binary system the melting point increases up to about 1578 °C in the ternary system.

Figure 1(a) shows the as-cast microstructure of Co-10.1Al-20.1Nb. The composition of the alloy lies within the primary field of C15 (Fig. 2) which starts to solidify from the melt at 1408 °C (Table 2). On cooling the composition of the remaining melt becomes leaner in Nb and when it crosses the monovariant line p₄-P₃ (Fig. 2) at 1320 °C, C36 forms peritectically by the reaction $L + C15 \leftrightarrow C36$. Through formation of C36 on further cooling the melt becomes further depleted in Nb until it reaches the

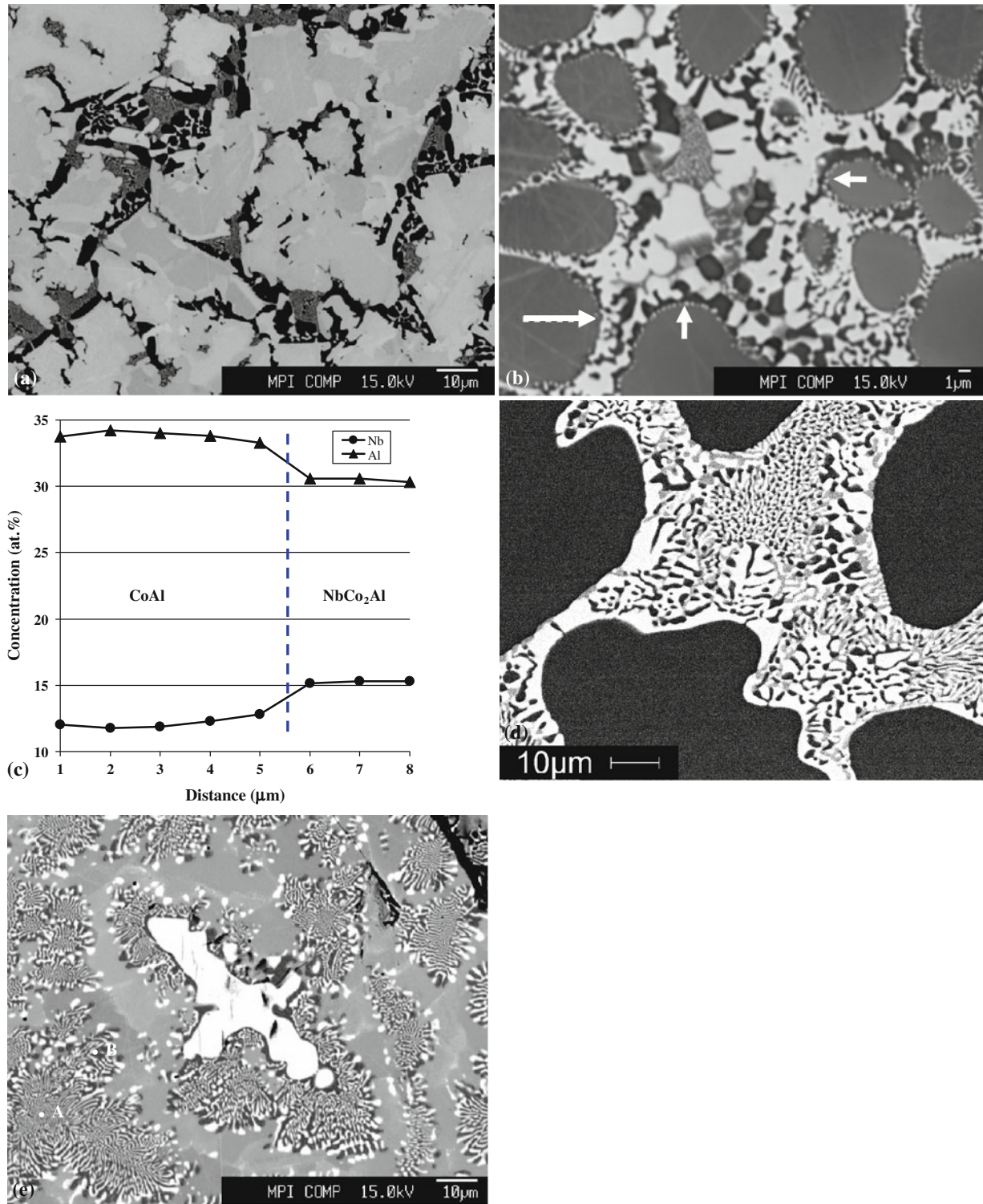


Fig. 1 Back-scattered electron micrographs of the microstructures of as-cast alloys. (a) Co-10.1Al-20.1Nb; primary phase: C15 (grey); peritectically formed phase: C36 (light grey); coarse eutectic: CoAl + C36; fine eutectic: CoAl + C36 + (Co) (E₂). (b) Co-26.1Al-15.6Nb; primary phase = core of the rounded grains: CoAl (grey), peritectic = outer part of the rounded grains: NbCo₂Al (grey); fine C36 (white; marked by solid arrows); coarse eutectic: CoAl (black) + C36 (white); fine-scaled eutectic: (Co) + CoAl + C36 (E₂). The dotted arrow denotes the position and direction of the EPMA profile shown in (c). (c) EPMA profile measured from the middle (left side) to the rim (right side) of the rounded grain in (b). Because the Co concentration stays about constant it is not shown. (d) Co-66.1Al-32.8Nb; primary phase: NbAl₃ (dark grey); eutectic E₁: C14 (light grey) + Nb₂Al (white) + NbAl₃ (dark grey). (e) Co-33.3Al-48.8Nb; white (primary phase): Nb₂Al; eutectic: Nb₂Al (white) + C14 (dark); grey: μ Co₇Nb₆

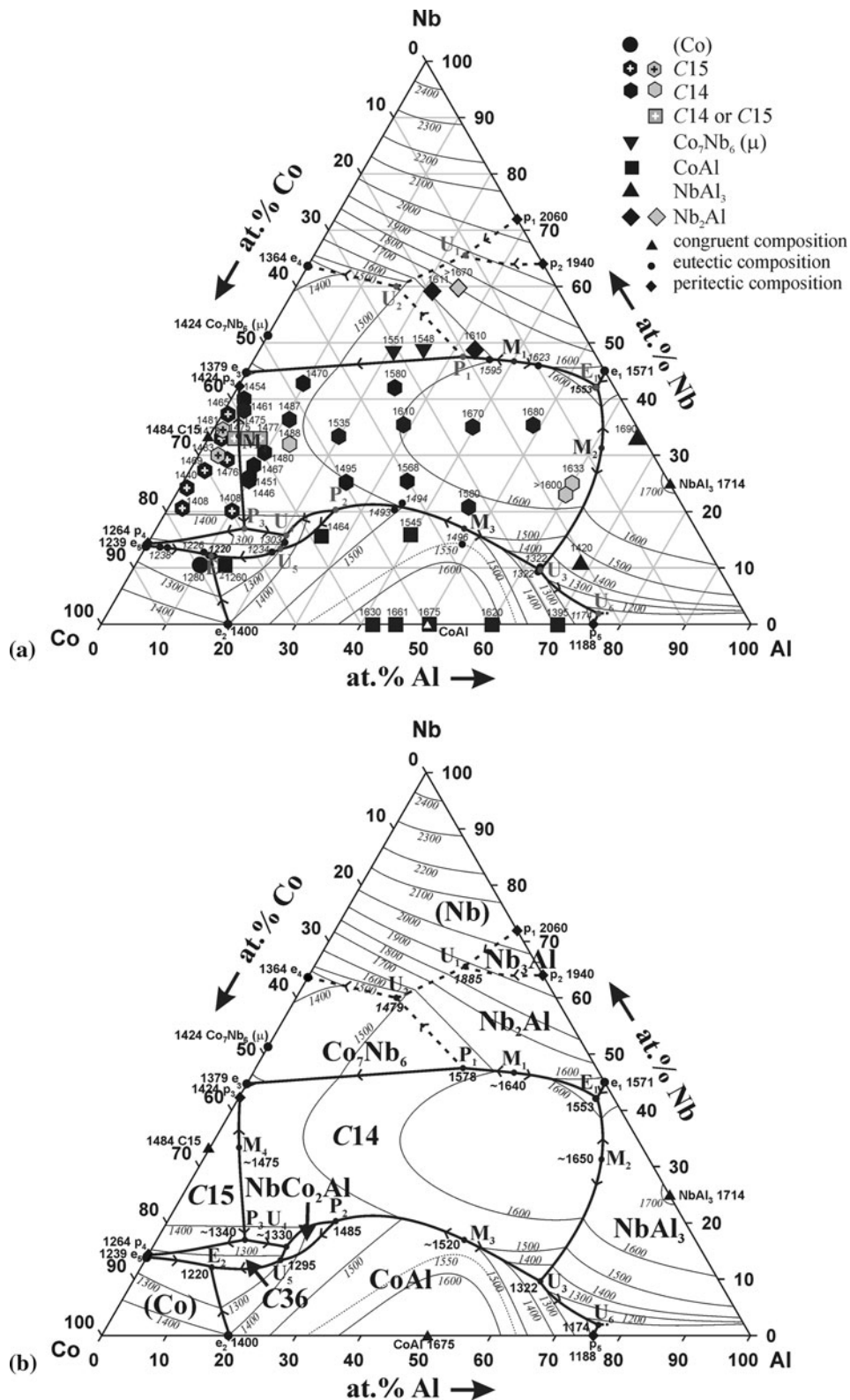


Fig. 2 Experimentally determined liquidus projection of the Co-Al-Nb system. (a) Compositions of the alloys, primary phases, and liquidus temperatures measured by DTA. Large black symbols indicate analysed compositions of the alloys while grey symbols indicate intended compositions. Isotherms have been constructed on the basis of experimental information. (b) Areas of primary crystallisation and established temperatures for the invariant reactions. The temperatures for the invariant reactions U_1 and U_2 given in italics are calculated values as they have not been observed experimentally

monovariant line E_2-U_5 at 1234 °C. This line is the eutectic trough $L \leftrightarrow \text{CoAl} + C36$ and the corresponding two-phase structure surrounds the coarse $C15/C36$ grains (Fig. 1a). The composition of the melt follows the eutectic trough until at 1220 °C the ternary eutectic E_2 is reached where the residual melt solidifies according to $L \leftrightarrow (\text{Co}) + \text{CoAl} + C36$ which yields the fine-scaled eutectic in Fig. 1(a). The as-cast microstructure shown in Fig. 1(b) (Co-26.1Al-15.6Nb) was generated by the following solidification sequence: Solidification of primary CoAl (1464 °C) is followed by peritectic formation of NbCo_2Al after the melt has reached the monovariant line U_5-P_2 at about 1450 °C. The presence of NbCo_2Al is not visible in the micrograph (Fig. 1b) but only becomes discernible through EPMA (Fig. 1c). At 1304 °C the melt reaches the eutectic trough U_4-U_5 $L \leftrightarrow \text{NbCo}_2\text{Al} + C36$. This reaction is only discernible in Fig. 1(b) by the small rim of tiny $C36$ precipitates which surround the coarse CoAl/ NbCo_2Al grains. The coarse 2-phase CoAl + $C36$ forms at 1294 °C through the invariant reaction $L + \text{NbCo}_2\text{Al} \leftrightarrow C36 + \text{CoAl}$ (U_5) and the last melt again solidifies at E_2 . The ternary eutectic E_2 which is also observed in alloys Co-10.0Al-10.5Nb and Co-13.9Al-10.4Nb occurs at 1220 °C at the composition 77 Co, 11 Al, 12 Nb. Presumably this is the eutectic that has been reported by Haour et al.^[11] before (77.3 Co, 7.3 Al, 15.4 Nb at 1240 °C). There are three more invariant reactions in the Co corner, namely $P_3 \sim 1340$ °C: $L + C15 + C14 \leftrightarrow C36$, $U_4 \sim 1330$ °C: $L + C14 \leftrightarrow C36 + \text{NbCo}_2\text{Al}$; U_5 1295 °C: $L + \text{NbCo}_2\text{Al} \leftrightarrow \text{CoAl} + C36$. The composition and temperature of the ternary peritectic reaction P_3 are estimated from (a) the course of the monovariant line $L + C15 \leftrightarrow C14$ which according to the results of the numerous alloys investigated within this composition range is a more or less vertical line in Fig. 2(a); (b) the temperatures observed for the monovariant reaction $L + C15 \leftrightarrow C36$ in the alloys Co-1.1Al-24.2Nb (1269 °C), Co-2.2Al-20.6Nb (1270 °C), Co-2.3Al-27.3Nb (1276 °C), Co-4.8Al-29.2Nb (1323 °C) and Co-10.1Al-20.1Nb (1320 °C) which increases with increasing Al content, indicating that the temperature for P_3 must be above 1323 °C; and (c) the temperatures observed for the monovariant reaction $L + C14 \leftrightarrow C36$ for alloys Co-9.4Al-28.2Nb (1338 °C), Co-9.8Al-26.1Nb (~ 1339 °C) and Co-10.0Al-25.5Nb (1325 °C) which decreases with increasing Al content, indicating that the temperature for P_3 must be above ~ 1339 °C. Because the melting temperature of the $C36$ Laves phase increases when Al is added, the temperature of 1340 °C at the peritectic P_3 corresponds to the maximum melting point of $C36$ in the Co-Al-Nb system, which is about 80 °C higher than in the binary system. There is no direct evidence for the temperature and composition of U_4 . While the composition of this invariant reaction can only be estimated, the temperature must lie in between that of P_3 and U_5 , i.e., between ~ 1340 and 1295 °C. The temperature can be delimited a little bit more in that in alloy Co-9.8Al-26.1Nb the peritectic reaction $L + C36 \leftrightarrow \text{NbCo}_2\text{Al}$ was observed at 1324 °C by DTA (Table 2), i.e., the temperature of U_4 must lie between 1324 and ~ 1340 °C (P_3). The invariant reaction U_5 is observed in alloys Co-26.1Al-15.6Nb (Fig. 1b), Co-9.4Al-28.2Nb,

Co-9.8Al-26.1Nb and Co-10.0Al-25.5Nb but in the latter three only on second heating (Table 2). For the alloy Co-26.1Al-15.6Nb the compositions of the three solid phases that take part in reaction U_5 have been analysed by EPMA (Table 2).

The Heusler phase NbCo_2Al ^[4] is the only ternary compound that exists in the Co-Al-Nb system. It forms by the peritectic reaction P_2 : $L + C14 + \text{CoAl} \leftrightarrow \text{NbCo}_2\text{Al}$ at about 1485 °C. The composition of P_2 can only be estimated from the compositions determined for the eutectic $L \leftrightarrow C14 + \text{CoAl}$ in the as-cast alloys Co-34.4Al-25.4Nb and Co-39.7Al-15.9Nb and the temperature of P_2 has to be slightly lower than the eutectic temperatures measured in those two alloys which are 1494 and 1493 °C, respectively (Table 2). The monovariant reaction $L \leftrightarrow C14 + \text{CoAl}$ has a maximum (M_3) at about 1520 °C. The temperature is again estimated from the temperatures determined for $L \leftrightarrow C14 + \text{CoAl}$ in alloys Co-34.4Al-25.4Nb and Co-39.7Al-15.9Nb and the presumable course of the isotherms. According to Alkemade's theorem the position of the maximum should be at the intersection of the monovariant line with the line that connects the congruent melting points of $C14$ and CoAl (Alkemade line). Because the congruent composition of $C14$ is not exactly known, the composition of the maximum M_3 —as well as those of M_1 and M_2 —can not be exactly determined. The latter two maxima are also observed for the monovariant reactions involving the $C14$ Laves phase, namely at about 1650 °C on $L + C14 + \text{NbAl}_3$ (M_2) and at about 1640 °C on $L + C14 + \text{Nb}_2\text{Al}$ (M_1). In between these maxima is the ternary eutectic E_1 : $L \leftrightarrow C14 + \text{Nb}_2\text{Al} + \text{NbAl}_3$ at 1553 °C which has been observed in alloy Co-66.1Al-32.8Nb (Fig. 1d). In this alloy NbAl_3 solidified first followed by a small amount of two-phase $\text{NbAl}_3 + C14$ before finally the ternary eutectic $C14 + \text{Nb}_2\text{Al} + \text{NbAl}_3$ with a composition of 2.8 Co, 55.1 Al, 42.1 Nb solidified (Fig. 1d, 2). It is noted that a comparable eutectic $C14 + \text{Nb}_2\text{Al} + \text{NbAl}_3$ exists at about the same composition (2.4 Ni, 57.2 Al, 40.4 Nb) and temperature (1553.6 °C) in the Ni-Al-Nb system.^[19]

In the Al-rich part two more U-type reactions were observed. At 1322 °C the invariant reaction U_3 : $L + C14 \leftrightarrow \text{NbAl}_3 + \text{CoAl}$ takes place (alloys Co-60.0Al-25.0Nb, Co-60.0Al-23.0Nb, Co-68.5Al-10.6Nb). In alloy Co-68.5Al-10.6Nb an additional signal is observed at 1174 °C which is associated with the invariant reaction U_6 : $L + \text{CoAl} \leftrightarrow \text{NbAl}_3 + \text{Co}_2\text{Al}_5$. This temperature is exactly the same that has been determined by Subramanian and Simmons^[12] for U_6 . It is noted that the two alloys which contain the $C14$ Laves phase with the highest Al content (alloys Co-60.0Al-25.0Nb and Co-60.0Al-23.0Nb) show a small but distinct additional first order signal at about 1495 °C which can not be allocated to any reaction (marked “?” in Table 2).

According to the reaction scheme in Fig. 4, three more invariant reactions (U_1 , U_2 , and P_1) take place in the Nb-rich part of the system whose temperatures can only be given tentatively because they are difficult to determine experimentally. These difficulties are twofold. First of all it is difficult to produce homogeneous alloys because of the very high melting point of Nb and actually the alloys

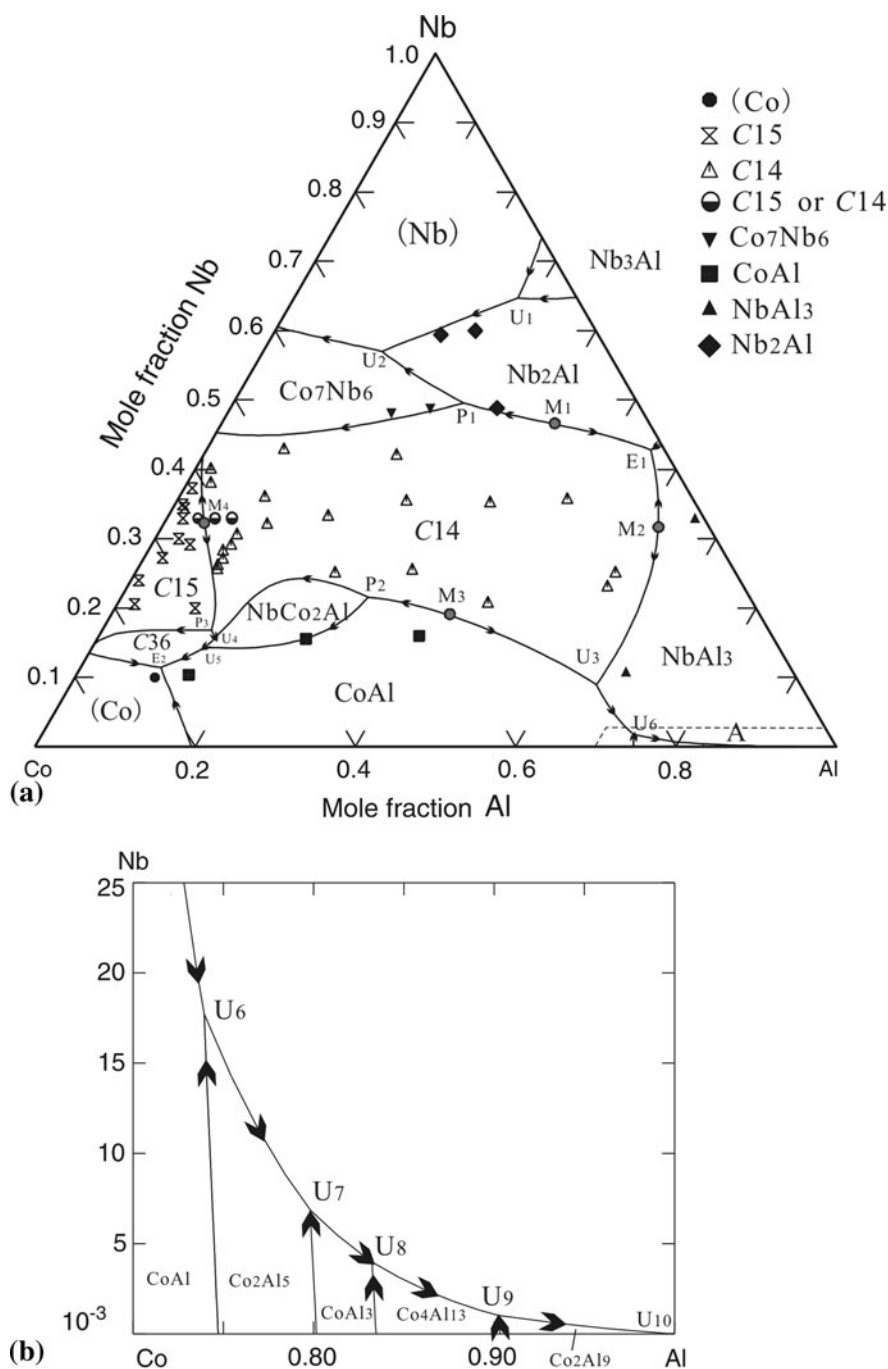


Fig. 3 (a) Calculated liquidus projection of the Co-Al-Nb system. (b) Enlarged area “A” of a showing the invariant points U₆-U₁₀ in the Al-rich corner of the Co-Al-Nb system

Co-21.0Al-59.4Nb and Co-25.0Al-60.0Nb were not homogeneous but showed a significant enrichment in Nb in some parts which resulted from incomplete dissolution of Nb during melting. Secondly, in some of the Nb-rich alloys an additional phase was observed which has about the same Nb content as the μ phase, i.e., 48 at.%, but much lower Al contents. Though it was not possible to establish its structure by XRD because the volume fraction of this phase

was always small, it is inferred that the phase might have the Ti₂Ni structure. A phase of this structure type is frequently observed in—particularly slow cooled—Fe-Nb alloys and it has been demonstrated that this phase is stabilised by minor amounts of impurities, especially of phosphorous and sulphur.^[20] Whether this is the same phase that had been identified earlier as μ' is open to speculation. The presence of this phase is presumably responsible for additional DTA

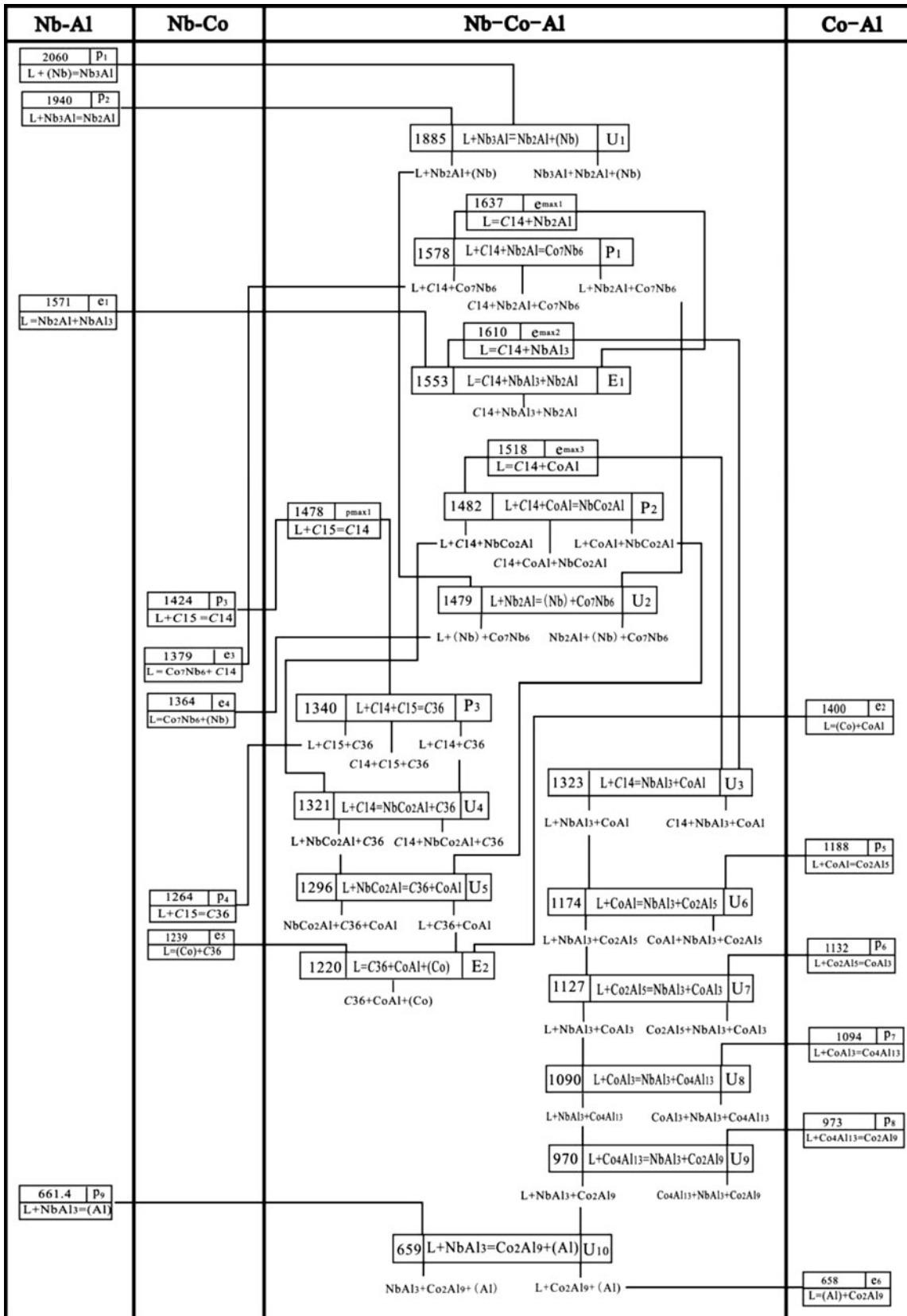


Fig. 4 Calculated reaction scheme for the liquidus of the Co-Al-Nb system. Monotectic equilibria not any longer containing the liquid are underlined

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signals in the Nb-rich alloys Co-20.4Al-48.3Nb, Co-24.2Al-42.0Nb, and Co-24.9Al-48.9Nb.

The ternary peritectic reaction $P_1: L + Nb_2Al + C14 \leftrightarrow Co_7Nb_6$ by which the μ phase forms may take place at 1578 °C. The alloy Co-33.3Al-48.8Nb shows two reactions below the melting, one at 1595 °C which is presumably associated with the eutectic reaction $L \leftrightarrow C14 + Nb_2Al$ and a second one at 1578 °C, which presumably is associated with P_1 . However, because the composition of the alloy is apparently close to that of P_1 the microstructure is difficult to interpret. The microstructure of alloy Co-33.3Al-48.8Nb (Fig. 1e) is composed of a small volume fraction of primary Nb_2Al , the eutectic $Nb_2Al + C14$ and Co_7Nb_6 . Along the monovariant line e_3-P_1 the type of the reaction for $L + C14 + Co_7Nb_6$ changes from eutectic in the binary to peritectic.

Compositions and temperatures of the invariant reactions $U_1: L + Nb_3Al \leftrightarrow Nb_2Al + (Nb)$ and $U_2: L + Nb_2Al \leftrightarrow (Nb) + Co_7Nb_6$ were not established by the experiments. The existence of these reactions has been established by the Thermo-Calc calculations (see following paragraph). However, it may be possible that the DTA signal observed at 1476 °C in the alloy Co-21.0Al-59.4Nb may be associated with reaction U_2 (calculated temperature: 1479 °C).

All experimental results were finally used to optimize the thermodynamic parameters of each phase in the Co-Al-Nb system by CALPHAD modelling with the aid of the Thermo-Calc software package (Table 3). Based on the present thermodynamic description, the liquidus projection was calculated and a reaction scheme has been established (Fig. 3 and 4). Comparison of the experimentally determined (Fig. 2b) and calculated liquidus projection (Fig. 3)

Table 3 Models used for the CALPHAD modeling for the phases in the Co-Al-Nb system

Phase	Model in binary system	Model in Co-Al-Nb system
Liquid	(Co,Nb)	(Al,Co,Nb)
(Nb)	(Co,Nb,Va)1Va3	(Al,Co,Nb,Va)1Va3
CoAl	(Al,Co,Va)0.5(Al,Co,Va)0.5Va3	(Al,Co,Nb,Va)0.5(Al,Co,Nb,Va)0.5Va3
(Co)	(Al,Co,Nb)Va	(Al,Co,Nb)Va
Laves C15	(Co,Nb)2(Co,Nb)	(Al,Co,Nb)2(Al,Co,Nb)
Laves C14	(Co,Nb)2(Co,Nb)	(Al,Co,Nb)2(Al,Co,Nb)
Laves C36	(Co,Nb)2(Co,Nb)	(Al,Co,Nb)2(Al,Co,Nb)
Co_7Nb_6 (μ)	Co(Co,Nb)2Nb4(Co,Nb)6	Co(Co,Nb)2Nb4(Al,Co,Nb)6
Nb_3Al	(Nb)3(Al,Nb)	(Co,Nb)3(Al,Co,Nb)
Nb_2Al	(Al,Nb)5Nb2(Al,Nb)8	(Al,Co,Nb)5Nb2(Al,Co,Nb)8
$NbCo_2Al$...	(Al,Nb)Co2(Al,Co,Nb)

Elements listed in bold denote the major species on the sub-lattices

Table 4 Comparison between the calculated ($T_{Calc.}$) and measured (T_{DTA}) temperatures for the various invariant reactions in the Co-Al-Nb system

Invariant reaction	Type	Label	$T_{Calc.}$, °C	T_{DTA} , °C
$L + Nb_3Al \leftrightarrow Nb_2Al + (Nb)$	Transition	U_1	1885	n.d.
$L \leftrightarrow C14 + Nb_2Al$	Maximum	M_1	1637	~1640
$L \leftrightarrow C14 + NbAl_3$	Maximum	M_2	1610	~1650
$L + Nb_2Al + C14 \leftrightarrow Co_7Nb_6$	Peritectic	P_1	1578	1578
$L \leftrightarrow C14 + Nb_2Al + NbAl_3$	Eutectic	E_1	1553	1553
$L \leftrightarrow C14 + CoAl$	Maximum	M_3	1518	~1520
$L + C14 + CoAl \leftrightarrow NbCo_2Al$	Peritectic	P_2	1482	1485
$L + Nb_2Al \leftrightarrow (Nb) + Co_7Nb_6$	Transition	U_2	1479	1476 (?)
$L + C15 \leftrightarrow C14$	Maximum	M_4	1478	~1475
$L + C15 + C14 \leftrightarrow C36$	Peritectic	P_3	1340	~1340
$L + C14 \leftrightarrow NbAl_3 + CoAl$	Transition	U_3	1323	1322
$L + C14 \leftrightarrow C36 + NbCo_2Al$	Transition	U_4	1321	~1330
$L + NbCo_2Al \leftrightarrow CoAl + C36$	Transition	U_5	1296	1295
$L \leftrightarrow (Co) + CoAl + C36$	Eutectic	E_2	1220	1220
$L + CoAl \leftrightarrow NbAl_3 + Co_2Al_5$	Transition	U_6	1174	1174

Temperatures in italics have not been directly measured by DTA but have been derived from the course of the isotherms or as detailed in the text; n.d. not determined

shows that the experimentally determined liquidus projection is well described by the calculated one. The four maxima M_1 - M_4 , whose existence was deduced from the experiments, are confirmed by the calculation. Also the temperatures for the maxima fit quite nicely. Only for M_2 a larger difference is observed (1610 °C vs. ~1650 °C; Table 4) presumably due to the few experimental data. While most of the primary phases are well accounted for by the modelling, there is some difference in the extension of the primary NbCo₂Al phase region. Again this difference is caused by the lack of experimental data in this composition range.

In Table 4 the calculated temperatures for the invariant reactions are compared with the experimentally determined ones and they are in good agreement as the difference is only 5 °C or less for all the invariant reaction temperatures that have been determined by DTA. The calculated temperatures of the invariant reactions U_1 and U_2 , which both have not been determined experimentally, are 1885 and 1479 °C, respectively. However, the actual temperatures of these two invariant reactions could differ substantially from the calculated ones because in this Nb-rich part of the system the calculation is not supported by any experimental data.

4. Summary

A partial liquidus projection for the Co-Al-Nb system has been experimentally determined for the first time. The experimental data were then used to optimise the thermodynamic description of all phases based on which a liquidus projection and a reaction scheme have been calculated by the CALPHAD method using the Thermo-Calc program. In the investigated range of compositions, which excludes the Al corner of the system at Al contents > 80 at.% Al, eleven invariant reactions were identified. The prominent features of the liquidus projection are the extended fields of primary crystallisation of the Co-Nb phases. By the addition of Al the melting temperature of C14 increases from 1424 °C in the binary Co-Nb system to about 1700 °C, that of Co₇Nb₆ from 1424 °C to 1578 °C and that of C36 from 1264 °C to 1340 °C. The only exception is C15, whose melting temperature decreases slightly from 1485 °C to 1475 °C by alloying with Al. The only ternary compound, the Heusler phase NbCo₂Al, melts incongruently with a maximum temperature of 1485 °C.

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