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Experimental Phase Diagram Investigations in the Ni-Rich Part of Al-Fe-Ni and Comparison with Calculated Phase Equilibria

Igor Chumak, Klaus W. Richter, Suzana G. Fries and Herbert Ipser

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The phase equilibria in the section Ni_3Fe-Ni_3Al and phase boundaries of $\gamma'(Ni_3Al)$ at 1000 °C were studied by a combination of powder X-ray diffraction (XRD), differential thermal analysis (DTA), and electron probe microanalysis (EPMA). The existence of a continuous solid solution at 450 °C was confirmed by a linear decrease of the lattice parameter from Ni_3Al to Ni_3Fe. The phase boundaries of γ' with γ and the B2-type phase were determined at 1000°C by EPMA. A vertical section of the phase diagram from Ni_3Al to Ni_3Fe above 450 °C, including the liquidus temperatures, is proposed based on the DTA investigations. The invariant four-phase equilibrium U: $L + \gamma' = \gamma +$ B2 is found to occur at 1366 ± 1 °C. The experimental data are compared with a calculated phase diagram obtained by extrapolation from the corresponding binary data sets.

Keywords aluminum alloys, differential thermal analysis (DTA), electron proble microanalysis (EPMA), experimental phase equilibria, X-ray diffraction (XRD)

1. Introduction

Considering the importance of the $\gamma(A1)/\gamma'(L1_2)$ transition, especially as starting point for the development of the Ni-base super alloys,[1] the section Ni_3Al-Ni_3Fe has been investigated by many authors. In spite of the large number of experimental investigations, the exact phase relationships within this section are still unclear. In a recent phase diagram assessment of the Fe-Ni-Al system, Eleno et al.[2] gave a good overview of the experimental work performed in the system. The considerable disparity in the equilibrium data within the section Ni_3Al-Ni_3Fe[3-7] is shown in Fig. 1, which was taken from Eleno et al.[2] Large differences in the experimental results are observed for the boundaries of the two-phase field [$\gamma' + \gamma$]. All previous investigations were carried out below a maximum temperature of 1350 °C, therefore the phase equilibria in the vicinity of Ni_3Al are essentially unknown in the ternary. Some information concerning this point, however, can be taken from the partial liquidus surface by Bradley,[5] which shows a ternary transition reaction at 1380 °C. This was later corrected to ~1365 °C by Eleno et al.[2] with consideration of the temperatures of the binary invariant reactions in Ni-Al.

In the current work we determined the phase boundaries of γ' at 1000 °C and investigated the phase equilibria in the section Ni_3Al-Ni_3Fe up to 1450 °C, including the determination of the liquidus temperatures within the section. The vertical section Ni_3Al-Ni_3Fe proposed here is based on our own investigations in combination with literature data.

2. Experimental

Samples with a total mass of 1000 mg were prepared from aluminum rod (99.999%, Alfa, Karlsruhe, Germany), iron foil (99.99%, Advent Res., Halesworth, UK) and nickel foil (99.99%, Advent Res., Halesworth, UK). Calculated amounts of the elements were weighed to an accuracy of 0.05 mg and arc melted on a water-cooled copper plate under an argon atmosphere. Zirconium was used as a getter material within the arc chamber. The samples were remelted one or two times and then weighed back in order to check for possible mass losses (which were generally found to be negligible). For equilibration the alloys were then annealed for 4 weeks at 450 °C and 1 week at 1000 °C in evacuated quartz glass ampoules and quenched in water.

Sample powders for X-ray diffraction were prepared with a diamond file with subsequent stress annealing for 20 min. Initial sample characterization was performed by X-ray powder diffraction, using the Guinier technique ($CuK\alpha_1$ radiation). The unit cell parameters were refined using the program TOPAS V2.1.[8] High-purity silicon was used as internal standard for the lattice parameter determination.

Differential thermal analysis (DTA) measurements were carried out on a DTA 404S/3 (Netzsch, Selb, Germany) using open alumina crucibles and employing a slow permanent argon flow. A sample mass of approximately

Igor Chumak, Klaus W. Richter, and **Herbert Ipser,** Department of Inorganic Chemistry/Materials Chemistry, University of Vienna, Währingerstraße 42, 1090 Vienna, Austria; **Suzana G. Fries,** Laboratoire de Physicochimie de la Matière Condensée, LPMC, UMR-CNRS 5617, University of Montpellier 2, Pl. Bataillon, 34095 Montpellier, France; Contact e-mail: igor.chumak@univie.ac.at

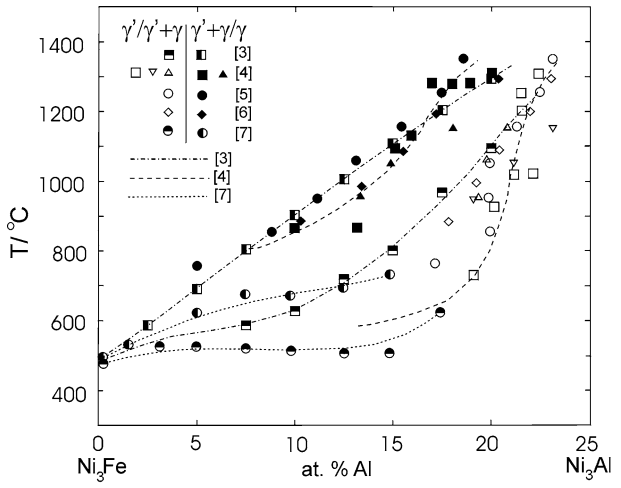

Fig. 1 Literature data in the vertical section of phase diagram from Ni_3Fe to Ni_3Al describing the [$\gamma + \gamma'$] two-phase field

250 mg was used for the experiments and the samples were checked routinely for possible mass changes during the DTA experiment. Two heating- and cooling-curves were recorded for each sample using a heating rate of 5 K min^{-1}. The Pt/Pt10%Rh thermocouples of the DTA instrument were calibrated at the melting points of high purity Ni, Au, and In.

The composition of the individual phases at 1000 °C was determined by EPMA on a Cameca SX electron probe 100 (Cameca, Courbevoie, France) using wavelength dispersive spectroscopy (WDS) for quantitative analyses and employing pure aluminum, iron, and nickel as standard materials. The measurements were carried out at 15 kV using a beam current of 20 nA. A conventional ZAF matrix correction was used to calculate the final composition from the measured X-ray intensities.

3. Results and Discussion

The phase equilibria of γ' with the neighboring phases γ and B2 at 1000 °C were investigated in three different samples by a combination of XRD and EPMA measurements. Phase compositions and lattice parameters of the identified phases are listed in Table 1 and the resulting partial isothermal section at 1000 °C is shown in Fig. 2. Phase compositions in the three-phase field [$\gamma' + \gamma +$ B2], which were determined by EPMA for the first time, agree reasonably well with the assessed phase diagram of Eleno et al.[2]

The results of the XRD-analyses within the section Ni_3Fe-Ni_3Al at 450 °C are presented in Table 2. The cubic lattice parameter decreases linearly with the Al content (Fig. 3; the lattice parameters of the binary Ni_3Fe and Ni_3Al from the Ref 9, 10 are included for comparison) following the equation

$$a/\text{Å} = 3.5554(4) + 5.9(3) \times 10^{-4}(X_{Al}),$$

where (X_{Al}) is the Al content in atomic percent. This dependence is in good agreement with data from

Table 1 Phase compositions (EPMA data) and lattice parameters of identified phases at 1000 °C

Nominal composition, at.%			Phase identified	Phase composition determined by EPMA, at.%			
Fe	Ni	Al		Fe	Ni	Al	*a*, Å
7	76	17	γ′	6.2	73.9	19.9	3.5684(1)
			γ	9.1	76.9	14.0	–[a]
7	67	26	γ′	6.7	68.7	24.6	3.5826(1)
			B2	7.6	60.9	31.5	2.8649(1)
15	62	23	γ′	15.9	64.1	20.0	3.5864(1)
			γ	23.5	61.3	15.2	–[a]
			B2	12.9	58.2	28.9	2.8658(1)

[a]Overlap with γ′

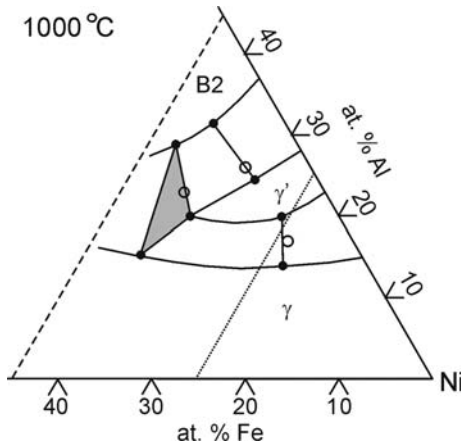

Fig. 2 Phase boundaries of γ' (Ni_3Al) at 1000 °C (○—nominal sample composition, ●—EPMA results; Ni_3Fe-Ni_3Al section is shown with dotted line)

Table 2 Lattice parameter of γ′ from samples annealed at 450 °C

at.% Al	*a*, Å
0	3.5545(6)
2.5	3.5563(4)
5	3.5593(5)
7.5	3.5604(4)
10	3.5614(2)
12.5	3.5633(3)
15	3.5641(3)
17.5	3.5661(2)
20	3.5676(4)
22.5	3.5687(4)
25	3.5691(3)

Masahashi et al.,[4] who expressed the lattice parameter of the γ′-phase in the Ni_3Fe-Ni_3Al section by

$a/Å = 3.551 + 5.909 \times 10^{-4}$ (X_{Al}).

All alloys annealed at 450 °C are assumed to be single-phase γ′ in Table 2 although the superstructure reflections typical of $L1_2$ ordering are only found in samples containing 10 or more atomic percent Al. The fact that superstructure reflections are not found in the most Fe-rich compositions is consistent with the theoretical X-ray powder patterns calculated with POWDER CELL,[11] showing that the intensity of the 100 and 110 superstructure reflections are negligible (around 0.2% of the main 111 reflection) in binary Ni_3Fe and reaches about 2% of the main 111 reflection at a composition of 10 at.% Al. As $L1_2$ ordering in binary Ni_3Fe is well established by neutron diffraction experiments[7] and the respective thermal transitions were observed in our samples we are confident that all samples listed in Table 2 are single-phase γ′.

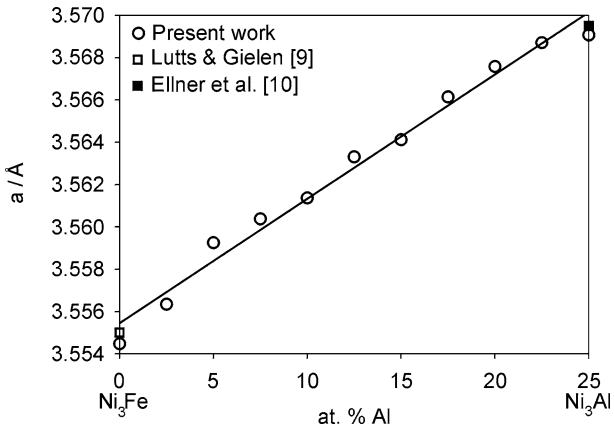

Fig. 3 Change of the lattice parameter of γ′ with the concentration of Al

Differential thermal analysis measurements were carried out on the annealed samples in the temperature range between 450 and 1450 °C. The results of the DTA measurements are listed in Table 3 together with the interpretation of the thermal effects. The vertical section of the phase diagram from Ni_3Fe to Ni_3Al is shown in Fig. 4. Due to the limitations of DTA to determine solid-solid phase reactions, the thermal effects for the γ′/[γ′ + γ] transition could only be detected in the two samples with 2.5 and 5 at.% Al. In contrast, the [γ′ + γ]/γ transition could be derived from the DTA data throughout the entire section. Both sets of phase boundaries confirm the data from Himuro et al.[3] which are given in Fig. 4 together with our own experimental datapoints. Additional information was derived from our EPMA results at 1000 °C given in Table 2. The respective phase boundary of γ at 1000 °C is in good agreement with our DTA results and the phase boundary of γ′ at 1000 °C deviates roughly 1.5 at.% from the value given by Himuro et al.[3] (compare Fig. 4).

Phase equilibria adjacent to the binary Al-Ni system are shown in detail in Fig. 4(b) with the binary equilibria drawn according to the currently accepted calculated binary Ni-Al phase diagram.[12] It should be pointed out, that Ni_3Fe-Ni_3Al is not a pseudobinary section; i.e., the tie lines connecting γ and γ′ are not situated within the section (compare Fig. 2). In the binary Ni-Al system the invariant reactions *e*: L = B2 + γ′ and *p*: $L + \gamma = \gamma'$ are known to

Table 3 DTA results for Ni_3Fe-Ni_3Al

	Thermal effects, °C						
Composition at. % Fe, Al	**γ′/[γ′ + γ]**	**[γ′ + γ]/γ**	**Others**	***U***	**γ/[*L* + γ]**	**Liquidus heating**	**Liquidus cooling[a]**
25, 0	510	510			1441	1451	1420
22.5, 2.5	530	582			1441	1453	1432
20, 5	535	584			1426	1441	1426
17.5, 7.5		780			1426	1440	1421
15, 10		893			1417	1432	1422
12.5, 12.5		1008			1408	1426	1411
10, 15		1116			1397	1414	1404
7.5, 17.5		1191			1382	1405	1393
6.25, 18.75[b]		1253			1379	1402	1389
5, 20		1297			1371	1395	1384
3.75, 21.25[b]			1356[c]	1366		1386	1368
2.5, 22.5			1341[d]	1366		1385	1370
1.25, 23.75[b]			1337	1367		1389	1377
0, 25			1370			1387	1368

[a]Strong supercooling observed in several samples
[b]Samples annealed at 1000 °C
[c][γ + B2]/[γ + B2 + *L*]
[d][γ + γ′]/[γ + γ′ + B2]

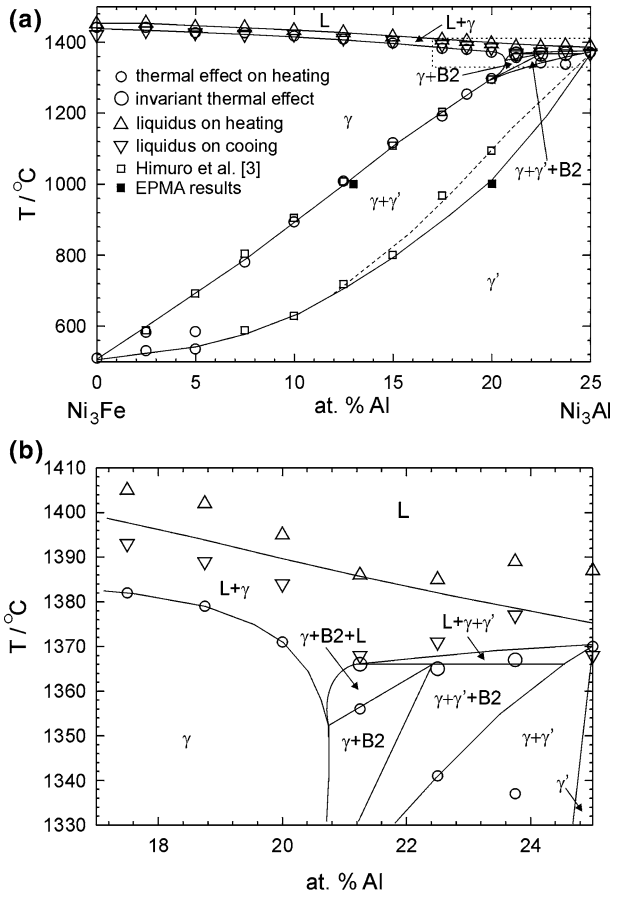

Fig. 4 The proposed vertical section of phase diagram from Ni_3Fe to Ni_3Al: (a) full section ($\gamma'/[\gamma + \gamma']$ phase boundary from Himuro et al. is shown with dotted line) and (b) detail around U: $L + \gamma' = \gamma + B2$

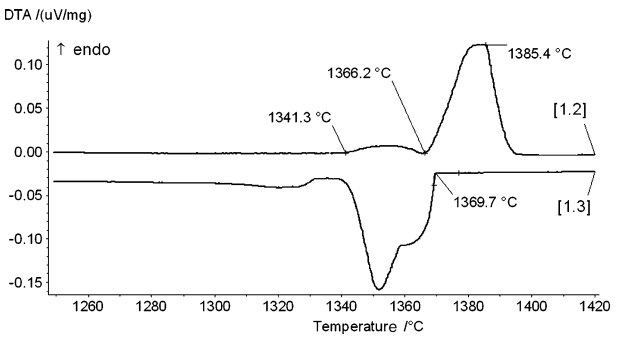

Fig. 5 The DTA curve of the sample with the composition $Ni_{75}Fe_{2.5}Al_{22.5}$ (1.2—heating curve, 1.3—cooling curve)

exist.[12] This suggests the existence of a ternary reaction adjacent to the binary system involving the four phases γ', γ, B2, and liquid. Our DTA data indicate the existence of a transition reaction U: $L + \gamma' = \gamma + B2$ at 1366 ± 1 °C which is in principal agreement with the previous results of

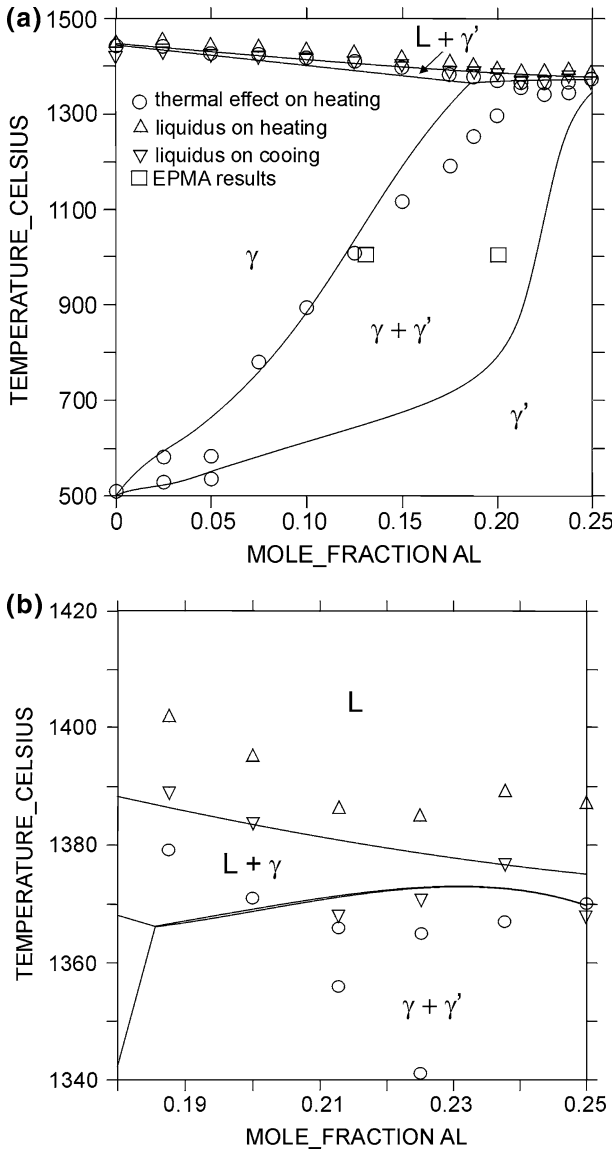

Fig. 6 Calculated vertical section of phase diagram from Ni_3Fe to Ni_3Al with experimental points: (a) full section and (b) detail around $[L + \gamma' + \gamma]$

Bradley[5] who suggested 1380 °C as reaction temperature. The DTA curve of the sample with the composition $Ni_{75}Fe_{2.5}Al_{22.5}$ is given as an example in Fig. 5. The small thermal effect at 1341 °C corresponds to the $[\gamma' + \gamma]/[\gamma' + \gamma + B2]$ phase transition and is followed by the massive invariant transition reaction at 1366 °C. The liquidus is situated between 1385 °C (heating value) and 1370 °C (cooling value).

According to our results, the equilibrium compositions (in at.%) of the phases involved in the transition reaction U at 1366 °C are estimated as follows:

L: 5% Fe, 73% Ni, 22% Al;
B2: 0.5% Fe, 71.5% Ni, 28% Al;

γ: 4% Fe, 76% Ni, 20% Al;
γ′: 0.5% Fe, 75% Ni, 24.5% Al.

The extensions of the different phase fields in Fig. 4 are drawn according to these estimated compositions.

The thermodynamic calculation of the phase equilibria in the section Ni_3Fe-Ni_3Al is based on an extrapolation from the descriptions of the binary subsystems. The corresponding binary data for Ni-Al were taken from Dupin et al.,[12] for Fe-Al from Seierstein[13] and for Fe-Ni from Dinsdale[14] and Ansara.[15] The calculations are in reasonable agreement with the experimental data as far as the liquidus temperatures are concerned (Fig. 6a.). However, the transition reaction U: $L + \gamma' = \gamma + B2$ at 1366 °C does not appear but is replaced by a very narrow three-phase field [$L + \gamma' + \gamma$] (Fig. 6b). This changes also the shape of the [$\gamma + \gamma'$] two-phase field and allows no explanation for a number of experimental data points, among them points at 1341 °C, 22.5 at.% Al (Fig. 5) and at 1356 °C, 21.25 at.%. Thus, it must be concluded that a reliable description of the ternary Al-Fe-Ni phase equilibria cannot be obtained without considering ternary interaction in the thermodynamic calculations.

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