Monatshefte für Chemie 120, 283—289 (1989)

Monatshefte für Chemie
Chemical Monthly

Lattice Parameter and Melting Behavior of the Ternary B2-Phase in the Co—Ga—Ni System

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Summary. Lattice parameter and DTA-measurements were performed in the range of the ternary B2-phase in the Co—Ga—Ni system which exhibits a continuous range of homogeneity. Lattice parameter values are reported for three ternary sections with constant ratios of $x_{Co}/x_{Ni} = 0.33$, 1.00, and 3.00 as well as for the two limiting binaries. Solidus and liquidus temperatures are given for $0 \leqslant x_{Co}/x_{Ni} \leqslant 3.00$. The results of the DTA-measurements in the Ga—Ni binary system indicate a somewhat wider range of homogeneity on the gallium-rich side as compared with literature data.

Keywords. Cobalt—gallium—nickel; Phase diagram: Co—Ga—Ni; Lattice parameter: Co—Ga—Ni; B2-phase: Co—Ga—Ni; Phase diagram: Ga—Ni.

Gitterparameter und Schmelzverhalten der ternären B2-Phase im System Co—Ga—Ni

Zusammenfassung. Im Bereich der ternären B2-Phase im System Co—Ga—Ni, welche einen durchgehenden Homogenitätsbereich aufweist, wurden Gitterparameter bestimmt und Differenz-Thermo-Analysen durchgeführt. Werte für den Gitterparameter werden sowohl für drei ternäre Schnitte mit konstanten Verhältnissen $x_{Co}/x_{Ni} = 0.33$, 1.00 und 3.00 angegeben als auch für die zwei angrenzenden binären Systeme. Für $0 \leqslant x_{Co}/x_{Ni} \leqslant 3.00$ werden auch Solidus- und Liquidustemperaturen angegeben. Die Ergebnisse der DTA-Messungen im binären System Ga—Ni weisen auf der galliumreichen Seite — verglichen mit Literaturdaten — auf einen etwas breiteren Homogenitätsbereich hin.

Introduction

Both the Co—Ga and the Ga—Ni binary systems are characterized by the existence of a phase with the triple-defect B2-structure exhibiting a wide range of homogeneity [1]. Deviation from stoichiometry is accomplished by anti-structure atoms (on the transition metal-rich side) or by vacancies on the transition metal sublattice (on the gallium-rich side) [2]. Recently thermodynamic properties of the two binary phases and of ternary alloys in the composition range between 40 and 60 at% Ga were determined [3], and the applicability of a theoretical model which describes the composition dependence of thermodynamic properties in ternary triple-defect B2-phases [4] was tested. It was found—as expected—that the two binary phases form a continuous solid solution, however, a considerable narrowing of the ternary phase

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on the gallium-rich side was reported, with the phase boundary around 55 at% Ga at 1 173 K for all three investigated sections ($x_{Co}/x_{Ni} = 0.33$, 1.00, and 3.00) [3].

It was the purpose of the present study to investigate the extension of the ternary B2-phase by X-ray and DTA-measurements (differential thermal analysis) and to determine the composition dependence of the lattice parameter.

Experimental

Samples numbered 1 through 33 were those used for the emf-measurements [3]. Samples numbered A1 through D13 were prepared as described below. Starting materials were cobalt and nickel wire (both 0.5 mm ∅, 99.997%, Johnson-Matthey, Vienna, Austria) and gallium (99.99%, Koch-Light, UK). Co and Ni were cut into small pieces and cleaned by p.a. acetone, Ga was cleaned by melting in vacuum and filtering through quartz wool under a purified Ar-atmosphere. Calculated amounts of the pure elements (approx. 1 g total) were weighed on a semi-microbalance to within ± 0.05 mg. They were filled into quartz capsules which were then evacuated to 10^{-1} Pa, flushed several times with Ti-gettered Ar, and finally sealed under vacuum.

The samples were slowly (within two days) heated to 1 373 K and kept at this temperature for another two days. After furnace cooling the samples were melted in a high-frequency furnace. Then the quartz capsules were broken and one part of each sample (approx. 0.8 g) was sealed under vacuum in special quartz containers for DTA-measurements. The rest of each alloy was finely ground in an agate mortar, once again sealed in a quartz capsule, homogenized at 1 173 K for two weeks and quenched in ice water.

X-ray measurements were carried out with a Kristalloflex 2 (Siemens, Karlsruhe, FRG) in Debye-Scherrer cameras with a diameter of 57.3 mm using unfiltered Co-radiation. Lattice constant values were obtained by linear regression and extrapolation to zero using the function $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)/2$.

DTA-measurements were performed with a commercial thermal analyzer (DTA 404S/3, Netzsch, Selb, FRG). The Pt/Pt10% Rh-thermocouples were calibrated at the melting points of high purity Zn, Sb, and Au. The heating rate was usually 2 K min^{-1}, in some instances (for the Ga—Ni binary system) a heating rate of 10 K min^{-1} was employed.

Results and Discussion

The compositions of the investigated samples are listed in Table 1 together with the corresponding lattice parameter values; these are thought to be accurate within at least ± 2 pm. Fig. 1 shows the variation of the parameter a with changing Ga content for three different ratios x_{Co}/x_{Ni} and for the two limiting binary systems, as obtained in the present study.

One can see that as a general trend the lattice expands with increasing Ga content up to the stoichiometric composition, followed by a pronounced contraction on the gallium-rich side which is certainly due to the formation of vacancies in the transition metal sublattice. Whereas for $x_{Ga} > 0.5$ the slope of the composition dependence of the lattice parameter is more or less the same for all x_{Co}/x_{Ni} ratios, a systematic reduction of the slope with decreasing nickel content can be observed for $x_{Ga} < 0.5$, resulting in a practically constant parameter a on the cobalt-rich side of the Co—Ga binary system (cf. Fig. 1). This effect is somewhat surprising considering the very similar properties of the two elements Co and Ni. The absolute value of the lattice constant at the stoichiometric composition decreases continuously by about 0.5% going from the Ga—Ni to the Co—Ga binary system.

Table 1. Composition of samples, lattice parameter, and thermal effects

Sample no.	$\frac{x_{Co}}{x_{Ni}}$	at% Ga	a (pm)	Solidus (K)	Liquidus (K)	
					Heating	Cooling
1	0.00	30.1		1480[b]	1494	
2	0.00	35.0		1478	1498	1484
3	0.00	40.0		1477	1494	1483
4	0.00	41.0		1474	1496	1478
5	0.00	42.0	288.5[a]	1467	1489	1483
6	0.00	43.0	288.6	1466	1490	1483
7	0.00	43.1	288.6	1464	1485	1479
8	0.00	44.0	288.6	1460	1487	1471
9	0.00	45.0	288.7	1459	1483	1469
10	0.00	46.0	288.9	1453	1477	1465
11	0.00	47.0	289.0	1448	1473	1462
12	0.00	48.0	289.1	1443	1466	1463
13	0.00	50.1	289.3			
14	0.00	52.0	288.4	1415	1440	1437
15	0.00	54.0	287.6	1390	1431	1430
16	0.00	57.0	287.3[a]	1310	1410	1391
17	0.00	60.0	286.8[a]	1228[b]	1381	1378
C1	0.33	37.5	[a]			
18	0.33	40.0	287.4	1469	1490	1469
C2	0.33	42.5	288.1	1467	1482	1473
19	0.33	45.0	288.3	1458	1479	1462
C3	0.33	47.5	288.6	1453	1471	1464
C4	0.33	50.0	288.0			
20	0.33	50.0	287.9	1442	1461	1444
C5	0.33	52.5	287.7	1425	1450	1443
21	0.33	55.0	286.7[a]	1385	1439	1412
22	0.33	60.0	284.7[a]	1145	1402	1395
23	1.00	35.0	[a]	1479	1503	1478
B1	1.00	37.5	287.9			
24	1.00	40.0	287.4	1476	1493	1477
B2	1.00	42.5	287.9	1471	1489	1479
25	1.00	45.0	288.0	1467	1489	1473
B3	1.00	47.5	288.0	1459	1474	1468
B4	1.00	50.0	287.9			
26	1.00	50.0	287.7	1451	1478	1465
B5	1.00	52.5	287.6	1435	1460	1453
27	1.00	55.0	286.9[a]	1404	1453	1448
28	1.00	60.0	284.6[a]	1149	1416	1411
A1	3.00	37.5	287.5			
29	3.00	40.0	287.8	1470	1492	1474
A2	3.00	42.5	287.8	1474	1489	1481
30	3.00	45.0	287.5	1462	1474	1465

Table 1 (continued)

Sample no.	$\frac{x_{Co}}{x_{Ni}}$	at% Ga	a (pm)	Solidus (K)	Liquidus (K)	
					Heating	Cooling
A3	3.00	47.5	287.9	1 464	1 481	1 472
A4	3.00	50.0	287.4			
31	3.00	50.0	287.4	1 443	1 470	1 445
A5	3.00	52.5	287.2	1 443	1 466	1 457
32	3.00	55.0	286.3[a]	1 386	1 454	1 452
33	3.00	60.0	284.6[a]	1 162	1 426	1 414
D1	∞	39.0	287.5			
D7	∞	41.0	287.7			
D2	∞	43.0	287.6			
D3	∞	46.0	287.6			
D8	∞	48.0	287.3			
D9	∞	49.0	287.6			
D4	∞	50.0	287.3			
D10	∞	51.0	287.5			
D5	∞	53.0	286.9			
D11	∞	56.0	286.0			
D6	∞	57.4	285.4			
D12	∞	59.5	284.6			
D13	∞	63.5	284.2[a]			

[a] Additional diffraction lines
[b] Invariant thermal arrest

Our lattice parameter values in Fig. 1 (which refer to samples quenched from 1 173 K) are compared with different sets of literature data. For the Ga—Ni binary system the data by Wasilewski et al. [5] (quenched from 1 123 K) and by Donaldson and Rawlings [6] (1 073 K) are shown. The agreement is quite good considering the different quenching temperatures. For the Co—Ga binary system the results of Schubert et al. [7] (where no quenching temperature is reported) and of Berner et al. [8] (1 173 K) are included in Fig. 1. In this case the agreement with our data is excellent.

Lattice parameter values for a number of ternary samples were determined by Chen and Dodd [9]; they are also given in Fig. 1. The agreement with our data is reasonable although unfortunately the annealing temperature is not specified in Ref. [9]. Chen and Dodd reported that their sample $Co_{0.3}Ga_{0.4}Ni_{0.3}$ was single-phase B2 up to 1 073 K with an fcc phase appearing at higher temperatures. This contradicts our findings: for $x_{Co}/x_{Ni} = 1.00$ no additional diffraction lines besides those of the B2-phase were found down to 37.5 at% Ga (for samples quenched from 1 173 K), whereas at 35 at% Ga the B2-phase has practically completely disappeared.

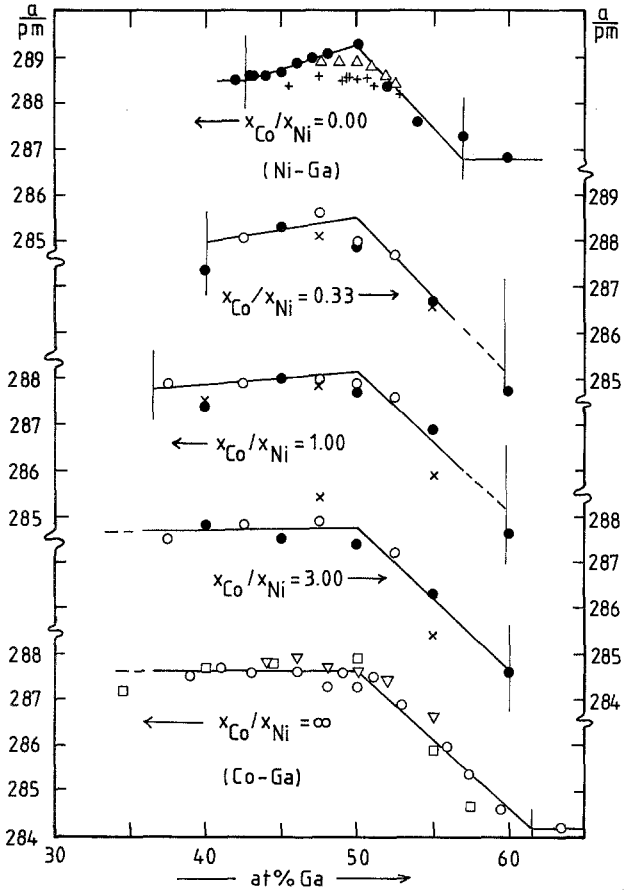

Fig. 1. Variation of the lattice parameter at 1 173 K for different x_{Co}/x_{Ni}-ratios; ● = samples from emf-measurements; ○ = new samples; △ = Wasilewski et al. [5]; + = Donaldson and Rawlings [6]; □ = Schubert et al. [7]; ▽ = Berner et al. [8]; × = Chen and Dodd [9]

On the other hand, ternary samples with 55 at% Ga were reported to be single-phase B2 for temperatures above 873 K (with the diffraction lines of a cubic gamma-brass type phase appearing below that temperature) [9]. In contrast to that, additional reflections were observed in our samples with the same composition after quenching from 1 173 K, and this was originally assumed in Ref. [3] to be an indication that the phase boundary is below 55 at% Ga. However, after delineation of the solidus and liquidus curves from the data points given in Table 1 for each of the three ternary isopleths it was found that the phase boundary at 1 173 K must be at considerably higher Ga contents, i.e. between 59 and 60 at% Ga; these boundaries, as obtained from the thermal analyses, are shown in Figs. 1 and 3. It is thought that the additional diffraction lines for our samples with 55 at% Ga were caused by decomposition of the B2-phase due to an insufficient quenching rate (which again would indicate a considerable narrowing of the B2-phase at lower temperatures).

The transition metal-rich boundary of the B2-phase could not be obtained from the DTA-measurements due to its steepness, and the values shown in Fig. 1 for $0 \leqslant x_{Co}/x_{Ni} \leqslant 1.00$ were estimated from the lattice parameter measurements (i.e. from the appearance of additional reflections).

DTA-measurements were also performed on all samples in the Ga—Ni binary system, and the results are included in Table 1. The resulting partial phase diagram is

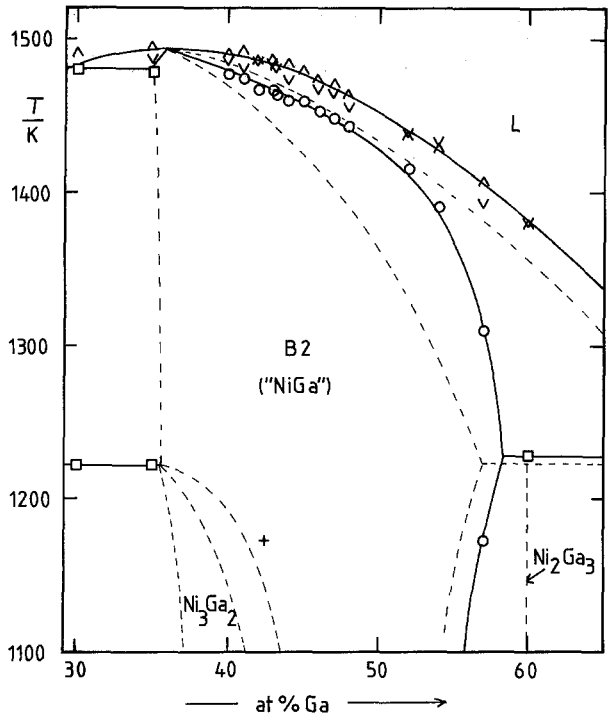

Fig. 2. Partial Ga—Ni phase diagram with experimental data points; ∧, ∨ = liquidus on heating or cooling, resp.; ○ = solidus (or solvus); □ = invariant thermal arrest; + = phase boundary according to X-ray measurements. Diagram by Feschotte and Eggimann [1] is shown by broken lines

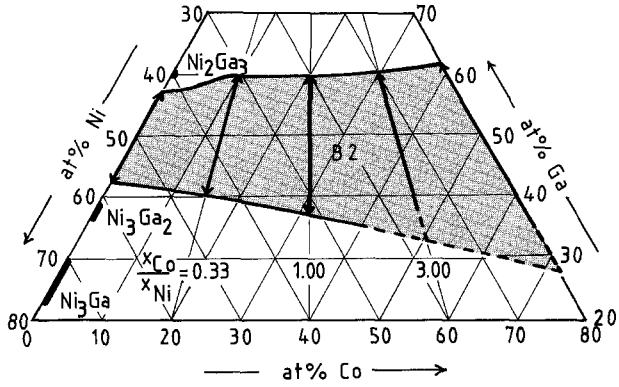

Fig. 3. Extension of the B2-phase in the ternary Co—Ga—Ni system at 1 173 K

shown in Fig. 2 in comparison with the diagram given by Feschotte and Eggimann [1]. Our results indicate a somewhat larger extension of the B2-phase on the gallium-rich side. On the nickel-rich side the number of data points is obviously too small to allow a reconstruction of the phase diagram. The phase boundary, estimated from the lattice parameter measurements (about 42.5 at% Ga) is in reasonable agreement with the value deduced from the diagram in Ref. [1] (about 41.5 at% Ga).

No DTA-measurements were carried out in the Co—Ga binary system; the gallium-rich boundary of the B2-phase was estimated to be at about 61.5 at% Ga (cf. Fig. 1), in fair agreement with the value deduced from Ref. [1] (about 63.5 at% Ga).

Fig. 3 finally shows the extension of the ternary B2-phase at 1 173 K according to our experimental results. The phase widths for the two binaries and the three ternary

sections are indicated by the arrows, the cobalt-rich limit in the Co—Ga binary was taken from the literature [1]. The solubility of Co in the other binary phases of the Ga—Ni system was not investigated. On the gallium-rich side the results of the thermal analyses show that for $0.33 \leqslant x_{Co}/x_{Ni} \leqslant \infty$ the B2-phase is in equilibrium with the liquid phase at 1 173 K, whereas for higher Ni contents a two-phase field with Ni_2Ga_3 is to be expected at this temperature.

No attempt was made to construct the liquidus surface of the ternary system from the DTA-results listed in Table 1 because of its flatness and the lack of any pronounced topological features in the investigated composition range.

Acknowledgement

The authors want to thank Prof. Dr. K. L. Komarek for his interest in this study.

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Received September 15, 1988. Accepted November 4, 1988