The Homogeneity Ranges of the *L*1$_2$-Type Intermetallic Compounds Ni$_3$Ga and Ni$_3$Ge

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The homogeneity ranges of the *L*1$_2$-ordered compounds Ni$_3$Ga and Ni$_3$Ge and the boundaries of the neighboring phases have been examined by electron probe microanalysis using heterophase alloys in the temperature ranges 1073 to 1373 K (Ni-Ga) and 1073 to 1346 K (Ni-Ge). The composition ranges of the *L*1$_2$-ordered phases have been found to be narrower than those reported in the literature, on the Ga-rich side for Ni$_3$Ga and on the Ge-deficient side for Ni$_3$Ge.

1. Introduction

The existence of the *L*1$_2$-ordered Ni$_3$Ga (α') phase in the Ni-Ga system was first reported by [54Pea]. [57Pea] determined the phase boundaries around the α' phase by measuring the variation of the lattice parameter with Ga concentration. [79Fes] reexamined the phase boundary compositions by electron probe microanalysis (EPMA). These data are used in the latest phase diagram of the Ni-Ga system [91Lee].

In the Ni-Ge system, the range of existence of the *L*1$_2$-ordered Ni$_3$Ge (β) phase was first investigated by [40Rut] and reexamined by [80Day] by EPMA. According to the latter, the composition range of the β phase is from 22.5 to 25.0 at.% Ge over the temperature range 973 to 1273 K. These results are included in the assessed phase diagram of the Ni-Ge system [91Nas]. Recently, [95Kom] also reported the equilibrium compositions between α and β phases using a diffusion couple composed of pure Ni and Ni$_3$Ge.

In a series of interdiffusion experiments on Ni$_3$Ga and Ni$_3$Ge by the present authors [98Ike, 98Non], precipitates of second phase were found after long-time annealing in some of the alloys that were supposed to be of *L*1$_2$ single phase. The authors have thus reexamined the phase boundaries of Ni$_3$Ga and Ni$_3$Ge, as well as those of the neighboring intermetallic phases.

2. Experimental Procedure

Alloys of Ni-Ga and Ni-Ge were prepared by melting appropriate amounts of Ni of 99.97% purity, Ga of 99.9999% purity, and Ge of 99.9999% purity using an argon arc furnace. The compositions of the alloys are listed in Table 1. According to the phase diagram of the Ni-Ga system [91Lee], alloy 1a is in the heterophase region in equilibrium of α (Ni solid solution) + α' (Ni$_3$Ga) phases, while alloy 1b is in the α' + β (NiGa) region above 1222 K, in the α' + γ (Ni$_3$Ga$_2$) region between 1014 and 1222 K, and in the α' + δ (Ni$_5$Ga$_3$) region below 1014 K. Ni-Ge alloys 2a and 2c are in the α (Ni solid solution) + β phase (Ni$_3$Ge) region, while 2b is in the δ (Ni$_5$Ge$_2$) + ε (Ni$_5$Ge$_3$) region between 1318 and 1372 K, in the β + ε between 779 and 1318 K and in the β + Ni$_2$Ge region below 779 K, according to the phase diagram of the Ni-Ge system [91Nas]. Alloy 2d was prepared to have bulk composition of 25.0 at.% Ge, but turned out to contain precipitates of the δ phase in the matrix of the β phase in some parts. The β matrix in such parts must have more than 25.0% Ge as the local composition; such specimens were used to examine the equilibrium between the β and δ phases at high temperatures, while the exact composition is not known. The volume fraction of the precipitates of the δ phase was about 10%. Alloys 1a and 1b were unidirectionally solidified using an alumina crucible of 10 mm in diameter by the Bridgman method under a vacuum better than 3×10^{-3} Pa and were subjected to homogenization annealing at 1378 K for 24 h under a vacuum of 1×10^{-3} Pa. All alloys were cut into plates 2 mm thick. Each specimen thus prepared was wrapped with a Ta foil, sealed in a quartz capsule under a vacuum better

Table 1 Compositions of alloys of Ni-*X* (*X* = Ga or Ge)

Alloy	Composition (c_X), at.%
Ni-Ga	
1a	21.8
1b	31.5
Ni-Ge	
2a	18.0
2b	30.0
2c	23.2
2d	25.0(a)

(a) See text.

Table 2 Annealing conditions for Ni-Ga alloys

Specimen	Temperature, K	Time, h
1a-1	1373	168
1b-1	1373	228
1a-2	1273	597
1b-2	1273	597
1a-3	1183	615
1b-3	1183	615
1a-4	1073	1612
1b-4	1073	1612

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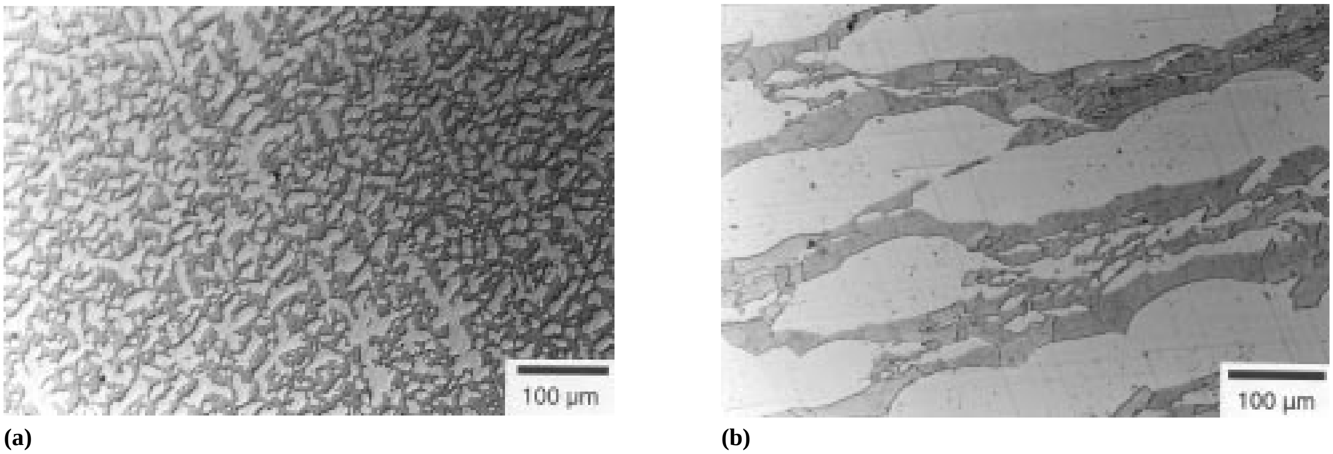
than 1 × 10^{-3} Pa and annealed under the conditions shown in Table 2 for Ni-Ga alloys and in Table 3 for Ni-Ge alloys. The temperature was measured with a Pt/Pt-13% Rh thermocouple and was held constant within ±1 K. After annealing, the specimen was quenched by dropping the capsule into water.

Metallographic examinations were made by optical microscopy after annealing. The surface was polished mechanically and etched using a solution of 20 g Cu_2SO_4 + 100 cm^3 HCl + 100 cm^3 H_2O.

The compositions of the constituent phases were determined by EPMA. The compositions of more than three points in each phase were measured using Shimadzu EPMA C1 model 40 with a wavelength-dispersive detector, which is equipped with a LiF crystal at a takeout angle of 52.5°. The accelerating voltage was 20 kV, and the nominal probe size was 1 μm. The intensities of Ni $K\alpha$ and Ga $K\alpha$ or Ge $K\alpha$ were measured from constituent phases and were converted to compositions by the ZAF method [94Fle]. (ZAF is an x-ray program that corrects for atomic number, *Z*, absorption, *A*, and fluorescence, *F*, effects in a matrix.) For Ni-Ga alloys, the standard intensities used for the conversion were obtained from a specimen of α' single phase, $Ni_{74.78}Ga_{25.22}$, whose composition was

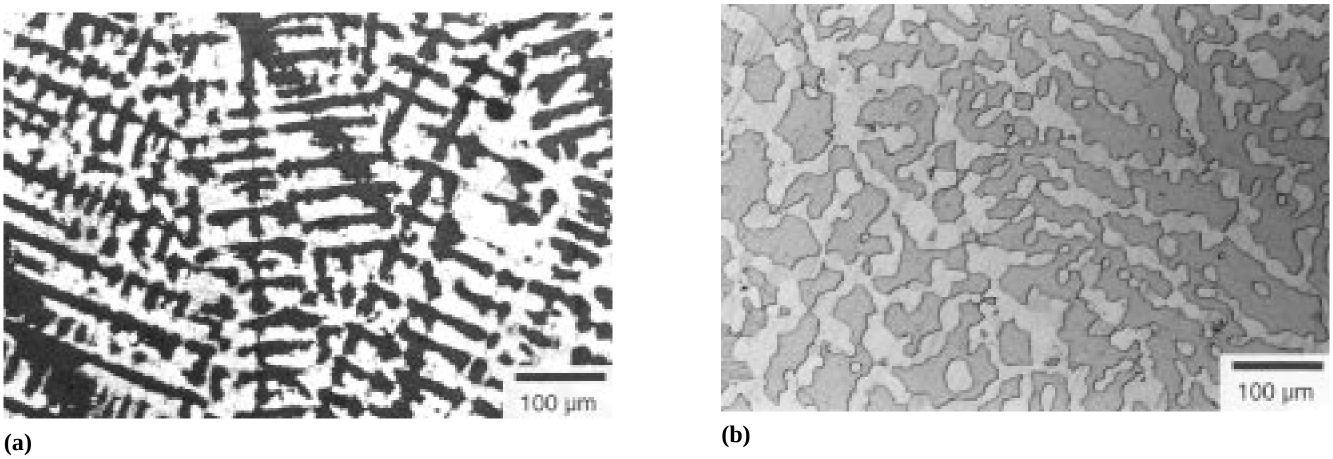
Table 3 Annealing conditions for Ni-Ge alloys

Specimen	Temperature, K	Time, h
2a-1	1346	116
2b-1	1351	31
2d	1341	90
2a-2	1303	138
2b-2	1303	138
2a-3	1203	1054
2b-3	1203	1054
2a-4	1123	888
2c	1123	335
2b-4	1123	888
2a-5	1073	1224
2b-5	1073	1224



(a) (b)

Fig. 1 Optical micrographs of Ni-Ga alloys. (a) Specimen 1a-1 (21.8 at.% Ga) after annealing at 1373 K; bright parts: α' (Ni_3Ga) phase, dark parts: α phase. (b) Specimen 1b-4 (31.5 at.% Ga) after annealing at 1073 K; bright parts: α' phase, dark parts: γ phase



(a) (b)

Fig. 2 Optical micrographs of Ni-Ge alloys. (a) Specimen 2a-1 (18.0 at.% Ge) after annealing at 1346 K; bright parts: β (Ni_3Ge) phase, dark parts: α phase. (b) Specimen 2b-4 (30.0 at.% Ge) after annealing at 1123 K; bright parts: β phase, dark parts: ε phase

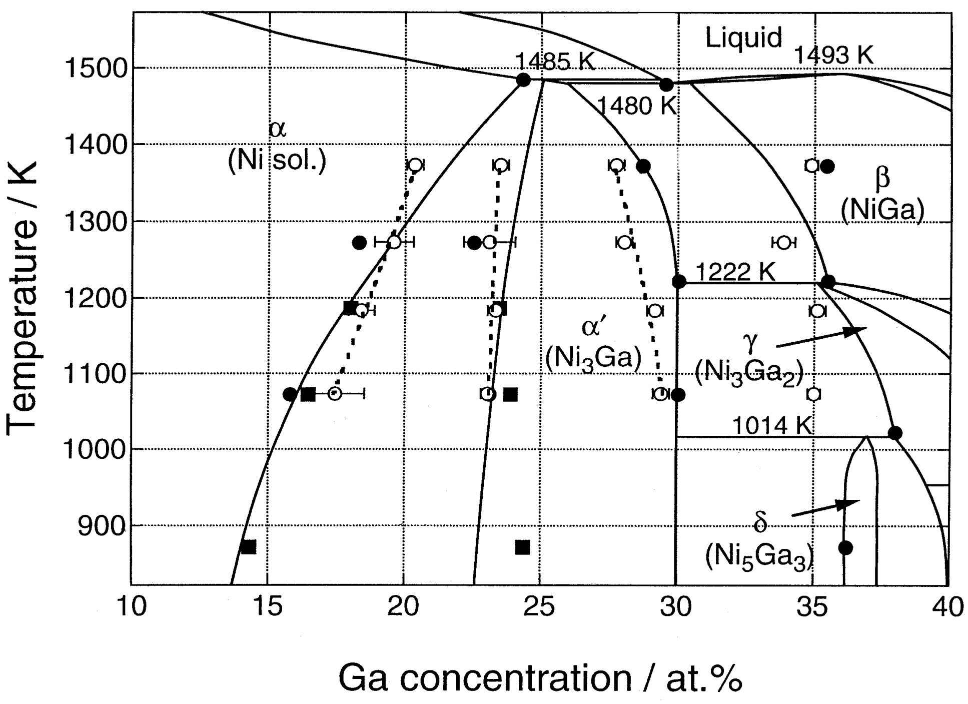


Fig. 3 Partial phase diagram of the Ni-Ga system. Open circle, this study; closed square, [57Pea]; closed circle, [79Fes]. Dashed lines: determined by this study. Solid lines: assessed by [91Lee]

Table 4 Phase-boundary compositions of the phase equillibrium between α (Ni solid solution) and α′ (Ni_3Ga) phases and between α′ and β (NiGa) or γ (Ni_3Ga_2) phases in the Ni-Ga system

Temperature	Composition (c_{Ga}), at.%					
(*T*), K	Specimen	α in (α + α′)	α′ in (α + α′)	Specimen	α′ in (α′ + β or γ)	β or γ in (α′ + β or γ)
1373	1a-1	20.36 ± 0.27	23.52 ± 0.27	1b-1	27.74 ± 0.28	34.87 ± 0.25 (β)
1273	1a-2	19.57 ± 0.73	23.12 ± 0.97	1b-2	28.11 ± 0.25	33.85 ± 0.42 (β)
1183	1a-3	18.39 ± 0.45	23.36 ± 0.27	1b-3	29.19 ± 0.28	35.12 ± 0.27 (γ)
1073	1a-4	17.42 ± 1.08	23.06 ± 0.25	1b-4	29.38 ± 0.27	35.01 ± 0.26 (γ)

determined by inductively coupled plasma spectrometry with an estimated error of ±0.24 at.%. The standard intensities for Ni-Ge alloys were obtained from the β phase (Ni_3Ge) formed in specimen 2b-2; its composition was found to be 25.0 at.% Ge by an analysis based on the standard intensities from the NiGe phase, which is a line compound at 50 at.% Ge [91Nas].

3. Results and Discussion

Figures 1 and 2 show optical micrographs of the Ni-Ga and Ni-Ge alloys, respectively. The dimensions of the microstructure, 5 to 50 μm, are sufficiently large for EPMA with a probe size 1 μm. The composition of each phase was determined by averaging 3 to 11 measurements. The results are summarized in Table 4 for Ni-Ga alloys and in Table 5 for Ni-Ge alloys. The concentrations in the tables are the average values of measured points. These results are shown as partial phase diagrams in Fig. 3 and 4. The composition of the β phase in the Ni-Ge system coexisting with the α phase at 1123 K was not obtained since the microstructure of the β phase in specimen 2a-4 after annealing was not sufficiently large. The composition of the β phase was obtained from 2c.

Figure 3 shows the Ni-rich part of the phase diagram of the Ni-Ga system. The solubility of Ga in Ni and the boundary composition of the α′ phase on the Ga deficient side are in agreement with the previous reports. On the other hand, the boundary composition of the α′ phase on the Ga-rich side obtained by the present work is off from the line assessed by [91Lee] toward lower Ga concentrations by 1 or 2 at.%. The boundary composition of the γ phase coexisting with the α′ phase also deviates by 2 to 3 at.%. The assessment by [91Lee] is mostly based on the EPMA of two-phase alloys by [79Fes]. The discrepancies are probably due to much shorter annealing times (two orders of magnitude) employed by [79Fes]; their specimens might not be in complete equilibrium. The position of the α′ + β/β boundary obtained in the present work also deviates from that based on the work by [79Fes].

Figure 4 shows the Ni-rich part of the phase diagram of the Ni-Ge system assessed by [91Nas], together with the phase-

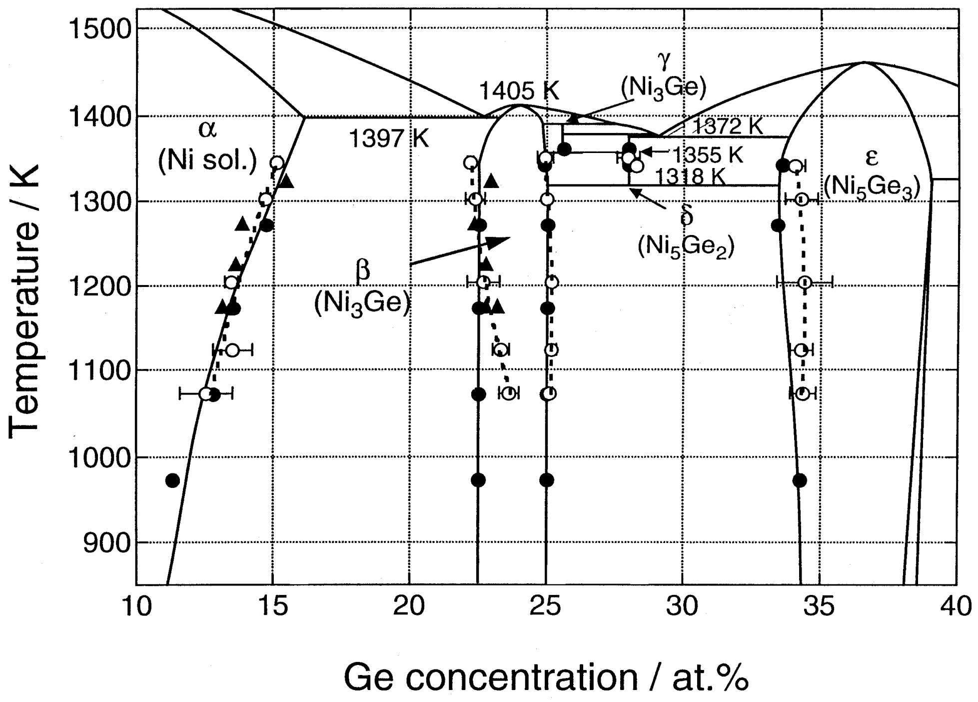


Fig. 4 Partial phase diagram of the Ni-Ge system. Open circle, this study; closed circle, [80Day]; closed triangle, [95Kom]. Dashed lines: determined by this study. Solid lines: assessed by [91Nas]

Table 5 Phase-boundary compositions of the phase equillibrium between α (Ni solid solution) and β (Ni_3Ge) phases and between β and δ (Ni_5Ge_2) or ε (Ni_5Ge_3) phases in the Ni-Ge system

Temperature (*T*), K	Composition (c_{Ge}), at.%					
	Specimen	α in (α + β)	β in (α + β)	Specimen	β in (β + δ or ε)	δ or ε in (β + δ or ε)
1351	…	…	…	2b-1	24.91 ± 0.29	27.95 ± 0.40 (δ)
1346	2a-1	15.13 ± 0.15	22.23 ± 0.14	…	…	…
1341	…	…	…	2d	…	28.29 ± 0.14 (δ) 34.03 ± 0.34 (ε)
1303	2a-2	14.68 ± 0.17	22.37 ± 0.36	2b-2	Standard for the ZAF conversion	34.27 ± 0.61 (ε)
1203	2a-3	13.46 ± 0.25	22.69 ± 0.62	2b-3	25.19 ± 0.11	34.40 ± 0.99 (ε)
1123	2a-4(a)	13.49 ± 0.71	…	2b-4	25.20 ± 0.16	34.30 ± 0.39 (ε)
	2c	…	23.36 ± 0.28	…	…	…
1073	2a-5	12.57 ± 0.95	23.65 ± 0.33	2b-5	25.15 ± 0.14	34.36 ± 0.47 (ε)

(a) See text.

boundary compositions determined in the present experiment. One important difference is the composition limit of the Ge-deficient side of the β phase. The present result shows reduction of the homogeneous range with decreasing temperature, while in the previous diagram based on the report by [80Day] is virtually temperature-independent. The experiment on Ni/Ni_3Ge couples by [95Kom] supports the trend observed in the present work.

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