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The Ga-Ni-Si (Gallium-Nickel-Silicon) System

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Very little work has been done for the Ga-Ni-Si system. Only one isothermal section has been established and is reported here.

Binary Systems

The Ga-Ni system [1991Nas] (Fig. 1) has eight intermediate phases, $GaNi_3$ (β_1), Ga_3Ni_5 (δ'), Ga_2Ni_3 (HT) (ε), Ga_2Ni_3 (LT) (γ'), GaNi (ν), Ga_4Ni_3 (θ), $Ga_3Ni_2(\beta_2')$, and Ga_4Ni (ρ), of which the ν phase melts congruently at 1220 °C. The β_1, β_2', ρ, and (Ga) phases form through peritectic reactions: $L + \gamma \leftrightarrow \beta_1$ at 1212 °C, $L + \nu \leftrightarrow \beta_2'$ at 895 °C, $L + \beta_2' \leftrightarrow \rho$ at 363 °C, and $L + \rho \leftrightarrow$ (Ga) at 30.2 °C. The γ phase is the terminal solid solution (Ni). The ε, δ', and θ phases form through peritectoid reactions: $\beta_1 + \nu \leftrightarrow \varepsilon$ at 949 °C, $\beta_1 + \varepsilon \leftrightarrow \delta'$ at 741 °C, and $\nu + \beta_2' \leftrightarrow \theta$ at 542 °C. The $\varepsilon \leftrightarrow \gamma'$ phase transformation occurs at ~680 °C. A eutectic reaction $L \leftrightarrow \beta_1 + \nu$ occurs at 1207 °C.

The Ga-Si system [Massalski2] (Fig. 2) is possibly a simple eutectic system with eutectic temperature close to Ga. There is practically no solid solubility of Ga in Si or Si in Ga.

The Ni-Si system [1991Nas] (Fig. 3) has eight intermediate phases, Ni_3Si (β_1), Ni_3Si (β_2 and β_3), $Ni_{31}Si_{12}(\gamma_1')$, Ni_2Si (δ), Ni_2Si (θ_1), Ni_3Si_2 (ε' and ε''), NiSi (η), and $NiSi_2$ (ζ and ζ'), of which several phases β_2 and β_3, ε', and ε'', and ζ and ζ' are polymorphic forms of Ni_3Si, Ni_3Si_2, and $NiSi_2$ phases, respectively. The β_1, β_3, δ, ε'', and ζ' phases form through peritectic or peritectoid reactions: $L + \gamma_1' \leftrightarrow \beta_3$ at 1178 °C, $L + \theta \leftrightarrow \delta$ at 1255 °C, $L + (Si) \leftrightarrow \zeta'$ at 993 °C, $\gamma + \beta_2 \leftrightarrow \beta_1$ at 1035 °C, and $\theta + \eta \leftrightarrow \varepsilon''$ at 845 °C. There are eight eutectic or eutectoid reactions in the Ni-Si system: $L \leftrightarrow \gamma + \beta_3$ at 1143 °C, $L \leftrightarrow \gamma_1' + \delta$ at 1215 °C, $L \leftrightarrow \theta_1 + \eta$ at 964 °C, $L \leftrightarrow \eta + \zeta$ at 966 °C, $\beta_2 \leftrightarrow \beta_1 + \gamma_1'$ at 990 °C, $\theta_1 \leftrightarrow \delta + \varepsilon''$ at 825 °C, $\varepsilon'' \leftrightarrow \delta + \varepsilon'$ at 820 °C, and $\varepsilon'' \leftrightarrow \varepsilon' + \eta$ at 800 °C. The γ_1', δ, η, and ζ phases are single-composition phases.

Binary and Ternary Phases

In the three binary systems Ga-Ni, Ga-Si, and Ni-Si, 16 intermediate phases form; several phases show polymorphic forms. In the Ga-Ni-Si system, five ternary intermediate phases have been reported. The binary and ternary phases and their structure data are given in Table 1.

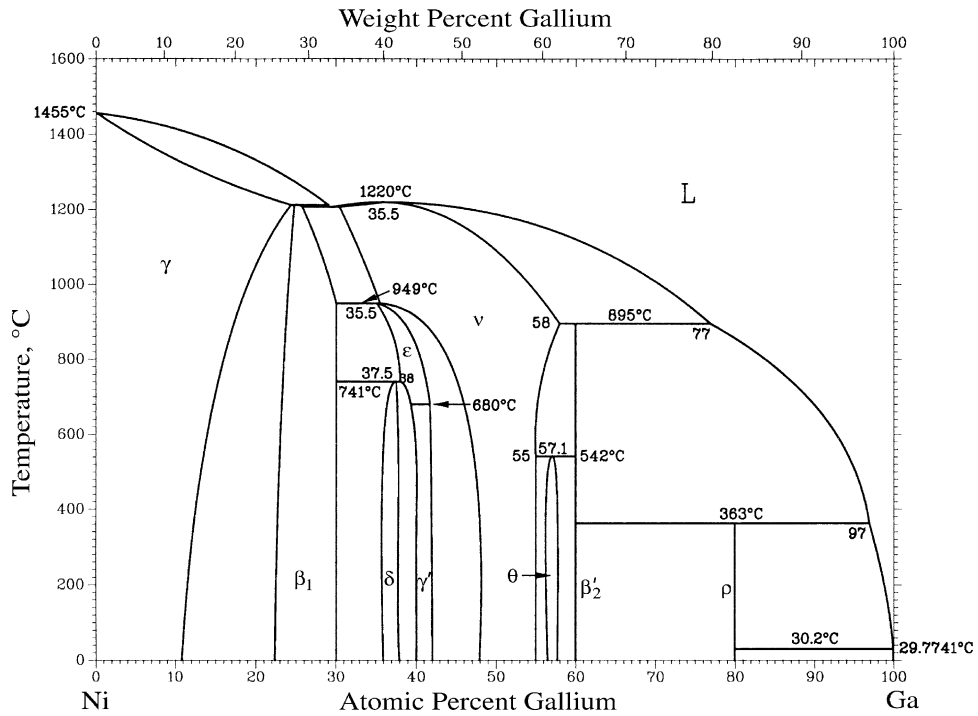

Fig. 1 Binary Ga-Ni system [Massalski2].

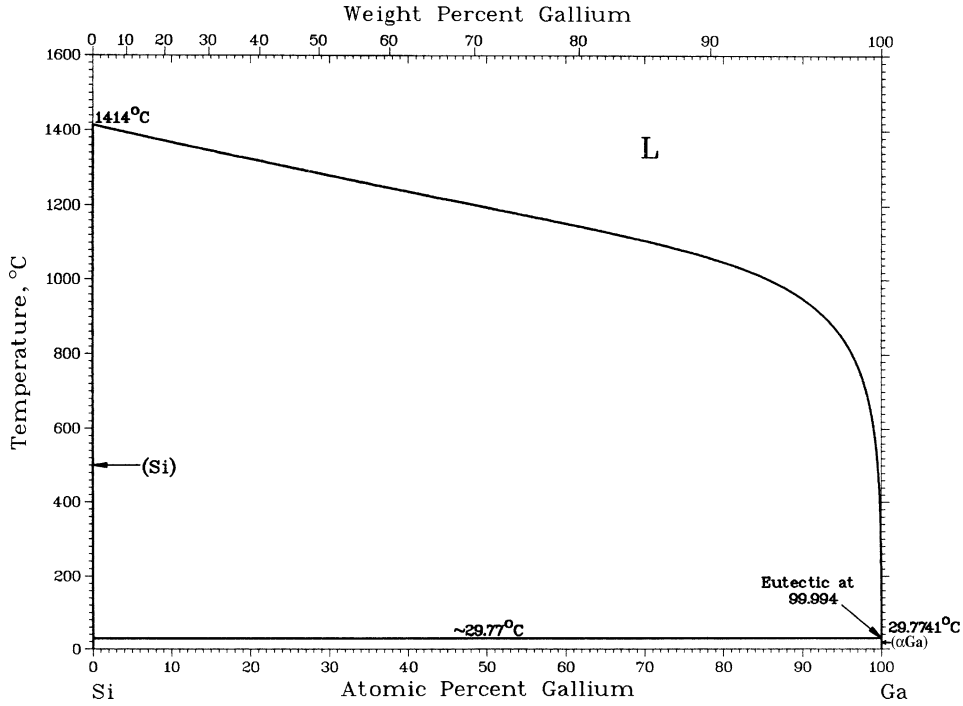

Fig. 2 Binary Ga-Si system [Massalski2].

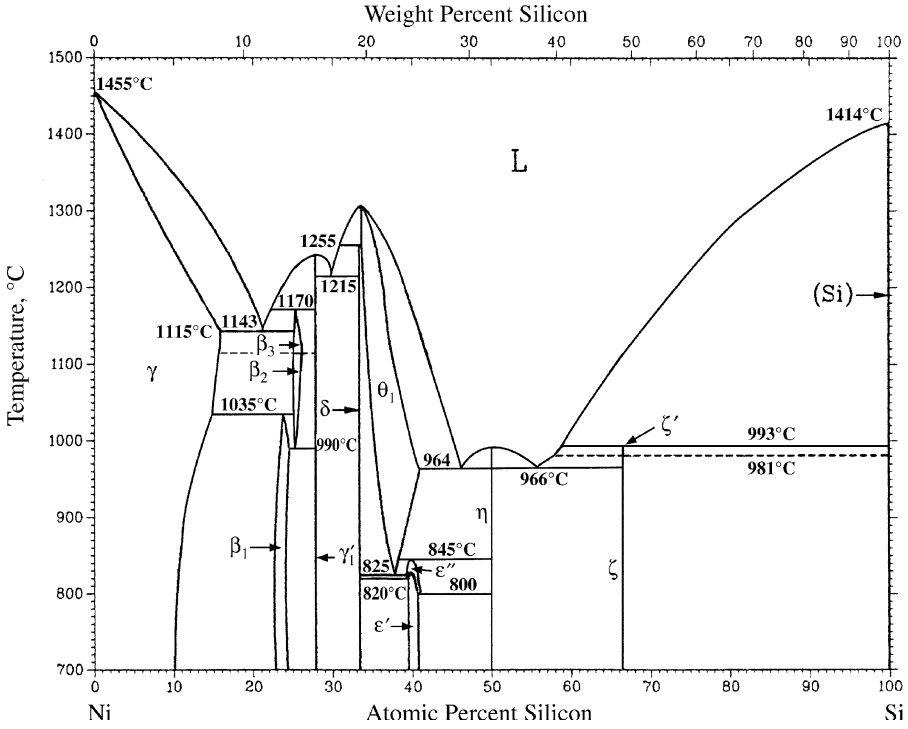

Fig. 3 Binary Ni-Si system [1991Nas].

Ternary System

The Ga-Ni-Si system has been studied by [1982Bor] at only one temperature. The alloys were melted in evacuated and sealed quartz tubes, using 99.9 mass% pure component elements, homogenized at 800 °C, and water quenched. The alloys were annealed further at 650 °C for 12 h and water quenched. For each alloy, powder for x-ray diffraction work

Table 1 Phases in the Ga-Ni-Si system and their structure data

Phase designation	Composition (a)	Pearson's symbol	Space group	Type	Lattice parameters, nm		
					a	*b*	*c*
γ	(Ni)	*cF*4	$Fm\bar{3}m$	Cu	···	···	···
Ga	(Ga)	*oC*8	*Cmca*	α Ga	···	···	···
Si	(Si)	*cF*8	$Fd\bar{3}m$	C (diamond)	···	···	···
β_1	$GaNi_3$	*cP*4	$Pm\bar{3}m$	$AuCu_3$	0.35850	···	···
δ'	Ga_3Ni_5	*oC*16	*Cmmm*	Ga_3Pt_5	0.376	···	0.339
ε	Ga_2Ni_3 (HT)(b)	*hP*4	$P6_3/mmc$	AsNi	0.3995	···	0.498
γ'	Ga_2Ni_3 (LT)(b)	···	···	···	1.3785	0.7883 β = 35.915°	0.8457
ν	GaNi	*cP*2	$Pm\bar{3}m$	CsCl	0.2873	···	···
θ	Ga_4Ni_3	*cI*112	*Ia*3*d*	Ga_4Ni_3	1.141	···	···
β_2'	Ga_3Ni_2	*hP*6	$Pm\bar{3}1$	Al_3Ni_2	0.405	···	0.489
ρ	Ga_4Ni	*cI*52	$I\bar{4}3m$	Cu_5Zn_8	0.8406	···	···
β_1	Ni_3Si (22.8-25.4)	*cP*4	$Pm\bar{3}m$	$AuCu_3$	0.350	···	···
β_2	Ni_3Si (24.5-25.5)	*mC*16	···	$GaPt_3$	0.697	0.625 β = 48.74°	0.507
β_3	Ni_3Si (24.5-25.5)	*mC*16	···	···	0.704	0.626 β = 48.84°	0.508
γ_1'	$Ni_{31}Si_{12}$	*hP*43	*P*321	$Ni_{31}Si_{12}$	0.667	···	1.228
δ	Ni_2Si (33.3)	*oP*12	*Pnma*	Co_2Si	0.706	0.499	0.372
θ_1	Ni_2Si (33.4-41.0)	*hP*6	$P6_3/m$	Ni_2Si	0.3805	···	0.489
ε'	Ni_3Si_2 (LT)	*oP*8	···	···	···	···	···
ε''	Ni_3Si_2 (HT)	···	···	···	···	···	···
η	NiSi	*oP*8	*Pnma*	MnP	0.562	0.518	0.334
ζ'	$NiSi_2$ (HT)	···	···	···	···	···	···
ζ	$NiSi_2$ (LT)	*cF*112	$Fm\bar{3}m$	CaF_2	0.5406	···	···
Γ	$Ga_{32}Ni_{63}Si_5$	*hP*4	$P6_3/mmc$	AsNi	0.3955	···	0.4960
Δ	$Ga_{30}Ni_{60}Si_{10}$	*m*	···	···	···	···	···
Ψ	$Ga_{15}Ni_{54}Si_{31}$	···	···	···	···	···	···
T	$Ga_3Ni_5Si_2$	*cP*8	$P2_13$	FeSi	0.4575	···	···
Σ	$Ga_8Ni_{50}Si_{42}$	*o*	···	···	0.5706	0.5281	0.3211

(a) Compositions within parentheses are in at.% Si.

(b) (HT) and (LT) are, respectively, high-temperature and low-temperature modifications of a given phase.

was prepared, annealed in sealed quartz tubes, and water quenched. Only x-ray diffraction was used for phase identification and phase boundary determination. The isothermal section at 650 °C was established and is given in Fig. 4 after incorporating some changes so that the isothermal section at 650 °C conforms to the accepted binary data. The probable phase boundaries are shown in Fig. 4 by dashed lines.

[1982Bor] in their published 650 °C isothermal section showed all the binary phases, except the ν phase, to have ~2 at.% solid solubility. The accepted binary diagrams, however, show that the β_1' phase in Ga-Ni system and the γ_1', δ, and η phases in the Ni-Si system are single-composition phases, whereas the $GaNi_3$ phase has a wider solid solubility than ~2 at.%. Moreover, there is practically no solubility of Ga or Ni in Si, and solid Ga phase does not exist at 650 °C. These changes have been incorporated in Fig. 4, and at the Ga corner the existence of a liquid region and phase equilibrium involving a liquid is shown. All these changes in phase boundaries are shown in dashed lines and should be established through proper experimentation.

The extension of the binary phase regions into the ternary are found, by and large, to be approximately along fixed Ni content lines. The $GaNi_3$ and the Ni_3Si isostructural phases form a continuous solid solution region. Reasonably large extensions of several binary phases, γ_1' (up to ~8 at.% Ga), δ (up to ~12 at.% Ga), ζ (up to ~20 at.% Ga), γ' (up to ~8 at.% Si), and β_1' (up to ~26 at.% Si), were found. The ν, ε, and η phases extended into the ternary system up to ≤4 at.% Si or Ga. The δ' phase was not detected in the ternary alloys investigated, indicating that it has possibly only limited solubility of Si. Lattice parameters of the δ phase were measured along its line of extension and are given in Fig. 5.

In the Ga-Ni-Si system the existence of five ternary intermediate phases, Σ, Ψ, T, Δ, and Γ have been reported by [1982Bor]. All the ternary intermediate phases are found to extend along approximately fixed Ni content lines, and

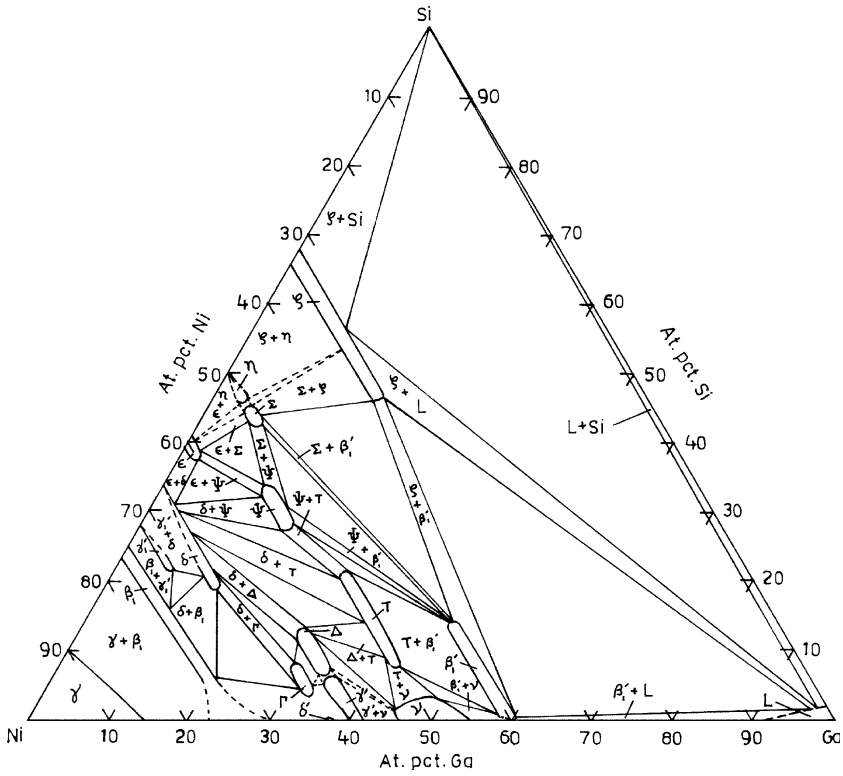

Fig. 4 The 650 °C isothermal section of the Ga-Ni-Si system.

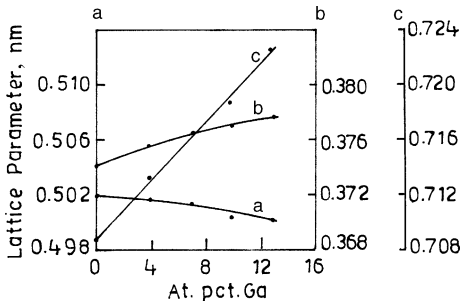

Fig. 5 Lattice parameter of the δ phase ($Ga_MNi_{67}Si_{33-M}$) as a function of Ga content.

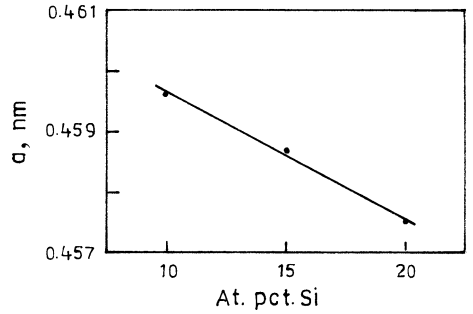

Fig. 6 Lattice parameter of the T phase ($Ga_{50-N}Ni_{50}Si_N$) as a function of Si content

the phase regions are approximately ∼2 at.% wide. The Σ phase exists close to the binary η phase region and extends along ∼50 at.% Ni from 41 to 45 at.% Si. The crystal structure of the Σ phase was not determined, but is reported to be closely related to the η phase. The Σ phase alloys with low Ga content show a martensitic structure. The Ψ phase was found along ∼52 at.% Ni, and it extends from ∼25 to 32 at.% Si. The Ψ phase crystal structure is not known. The diffraction pattern of the Ψ phase has been reported to have many diffraction lines. The T phase exists along the ∼50 at.% Ni line and extends from ∼7 to 22 at.% Si. It is of FeSi type structure. Lattice parameters of the T phase are measured as a function of Si content and are given in Fig. 6. The Δ phase exists close to the γ′ phase, extends along the 60 at.% Ni line, and extends from about 5 to 13 at.% Si. The crystal structure of the Δ phase is not known. The Γ phase exists along ∼62 at.% Ni and extends from ∼3 to 8 at.% Si. The Γ phase was found to have an AsNi structure with lattice parameter a = 0.3855 nm and c = 0.4960 nm. In the Ga-Ni system the Ga_2Ni_3 (HT) phase (ε) also has an AsNi structure, and it exists above 680 °C. The Ga_3Ni_5 phase δ′ was not found to extend into the ternary. The existence of the Γ phase in the ternary with the same crystal structure as the binary ε phase suggests possible stabilization of the ε phase to lower temperatures due to addition of Si. If this is true then the Γ phase will not be a true ternary intermediate phase. This should be verified through experimental study of the Ga-Ni-Si system at various higher temperatures between 650 and ∼680 °C.

References

1982Bor: P. Nash, *Phase Diagrams of Binary Ni Alloys*, ASM International, Cleveland, Ohio, 1991 (Review)

1991Nas: M. El-Boragy, T. Rajasekharan, K. Schubert, On the Mixtures $NiGa_MSi_N$, $NiIn_MSi_N$, $NiIn_MGe_N$ and $Ni-Ga_MSn_N$, *Z. Metallkde*, **73**, 1982, p 193-197 (Phase Equilibria, #)

# Indicates presence of phase diagram.

Ga-Ni-Si evaluation contributed by **K.P. Gupta**, The Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector V, Calcutta, India. Literature searched through 1996. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary nickel alloys.