JPEDAV (2008) 29:374–377
DOI: 10.1007/s11669-008-9346-4
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The Ga-Ni-Sn (Gallium-Nickel-Tin) System

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Introduction

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

Binary Systems

Data available prior to 1991 for the Ga-Ni and Ni-Sn systems were critically assessed by Nash [1991Nas] to develop the phase diagrams (Ga-Ni, Fig. 1; Ni-Sn, Fig. 2) for the two binary systems. These diagrams were included in the compilation of Massalski and Okamoto [Massalski2]. Similarly, data for the Ga-Sn system were assessed by T.J. Anderson and I. Ansara, but their Ga-Sn phase diagram was not published elsewhere before inclusion in the Massalski compilation. The Ga-Ni diagram [1991Nas] shows 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 (ϕ), Ga_3Ni_2 (β'), and Ga_4Ni (ρ), of which ν melts congruently at 1220 °C. The β_1, β', ρ, and (Ga) phases form through peritectoid reactions: $L + \gamma \leftrightarrow \beta_1$ at 1212 °C, $L + \nu \leftrightarrow \beta'$ at 895 °C, $L + \beta' \leftrightarrow \rho$ at 363 °C and $L + \rho \leftrightarrow$ (Ga) at 30.2 °C; here γ is the fcc terminal solid solution (Ni). The ε, δ', and ϕ phases form through peritectoid reactions: $\beta_1 + \nu \leftrightarrow \varepsilon$ at 949 °C, $\beta_1 + \varepsilon \leftrightarrow$ at 741 °C, $\nu + \beta' \leftrightarrow \theta$ at 542 °C. The $\varepsilon \leftrightarrow \gamma'$ phase transformation occurs near 680 °C. A eutectic reaction $L \leftrightarrow \beta_1 + \nu$ occurs at 1207 °C.

The Ni-Sn system [Massalski2] (Fig. 2) has four intermediate phases, Ni_3Sn (HT) (π'), Ni_3Sn (LT) (π), Ni_3Sn_2 (ε_1), and Ni_3Sn_4 (ρ_1) of which π and ε_1 melt congruently at 1174 and 1264 °C, respectively. A polymorphic phase transition $\pi' \leftrightarrow \pi$ occurs at 977 °C. There is also evidence for a transition in the ε_1 phase, but the transition temperature and the nature of the transition are not well defined. The ρ_1 phase forms by a peritectic reaction at 794.5 °C: $L + \varepsilon_1 \leftrightarrow \rho_1$. Three eutectic reactions occur: $L \leftrightarrow \gamma + \pi'$ at 1130 °C, $L \leftrightarrow \pi + \varepsilon_1$ at 1160 °C, and $L \leftrightarrow \rho_1 +$ (βSn) at 231.5 °C. Two eutectoid reactions also occur: $\pi' \leftrightarrow \gamma \leftrightarrow \gamma + \leftrightarrow \pi$ at 920.5 °C and $\pi + \pi + \varepsilon_1$ at 850 °C.

The Ga-Sn system [Massalski2] system in Fig. 3 is a simple eutectic system with the eutectic composition at 8.4 at.% Ga and the eutectic temperature being 20.5 °C only slightly above the Sn transition temperature at 13 °C.

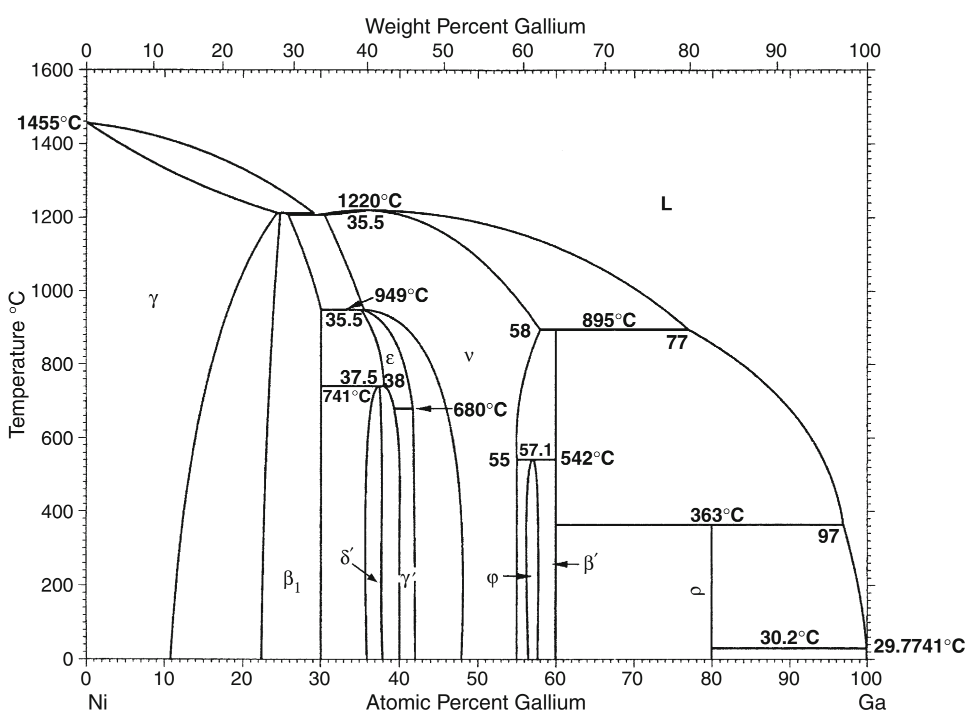

Fig. 1 Binary Ga-Ni phase diagram [1991Nas]

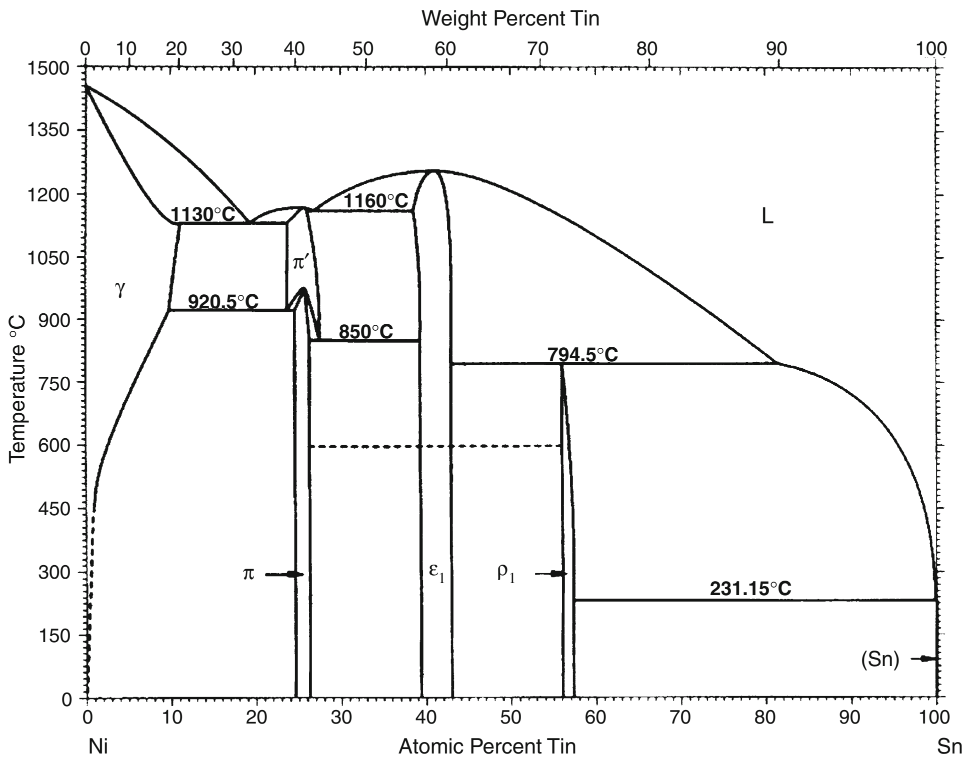

Fig. 2 Binary Ni-Sn phase diagram [1991Nas]

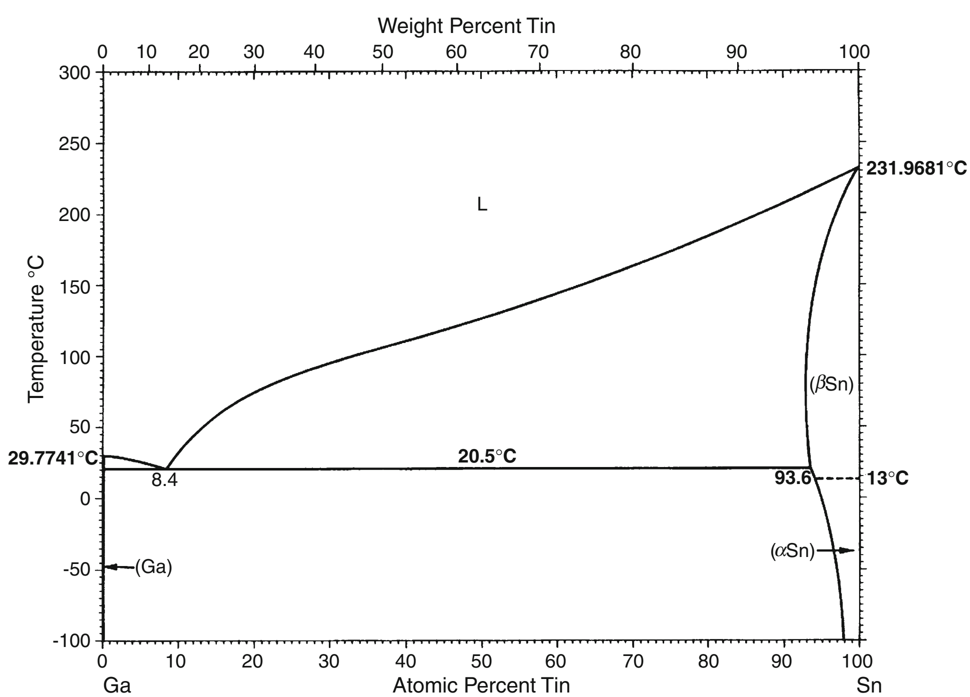

Fig. 3 Binary Ga-Sn phase diagram [Massalski2]

Binary and Ternary Phases

The three binary systems Ga-Ni, Ga-Sn, and Ni-Sn have 10 binary intermediate phases. Four ternary intermediate phases have been reported to exist in the Ga-Ni-Sn ternary systems. The binary and ternary phases and their structure data are given in Table 1.

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

Phase designation	Composition(a)	Pearson symbol	Space group	Type	Lattice parameter, nm		
					a	*b*	*c*
γ	(Ni)	*cF*4	$Fm\bar{3}m$	Cu	...	...	...
Ga	(Ga)	*oC*8	*Cmca*	αGa	...	...	...
Sn	βSn > 13 °C	*tI*4	$I4_1/amd$	βSn	...	...	...
	αSn > 13 °C	*cP*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)	*hP*4	$P6_3/mmc$	AsNi	0.3995	...	0.498
γ'	Ga_2Ni_3 (LT)	...	...	...	1.3785	0.7883 β = 35.915°	0.8457
ν	GaNi	*cP*2	$Pm\bar{3}m$	CsCl	0.2873	...	...
ϕ	Ga_4Ni_3	*cI*112	*Ia*3*d*	Ga_4Ni_3	1.141	...	...
β'	Ga_3Ni_2	*hP*6	$Pm\bar{3}1$	Al_3Ni_2	0.405	...	0.489
ρ	Ga_4Ni	*oI*52	$I\bar{4}3m$	Cu_5Zn_8	0.8406	...	...
π_1	Ni_3Sn (HT)	*cF*16	$Fm\bar{3}m$	B_1F_3	0.598	...	...
π	Ni_3Sn (LT)	*hP*8	$P6_3/mmc$	$CdMg_3$	0.5286	...	0.4243
ε_1'	Ni_3Sn_2 (LT)	*hP*4	$P6_3/mmc$	AsNi	0.4125	...	0.5198
ε_1	Ni_3Sn_2 (HT)	*oP*20	*Pnma*	Ni_3Sn_2	0.711	0.521	0.823
ρ_1	Ni_3Sn_4	*mC*14	*C*2*m*	CoSn	1.2223	0.4061	0.5187
Δ	$Ga_3Ni_5Sn_2$	*c*	*Cmcm*	...	0.4076	1.2331	1.1349
Γ	$Ga_{35}Ni_{60}Sn_9$	...	...	(b)	...	...	...
θ	$Ga_{35}Ni_{60}Sn_5$	...	...	(c)	...	...	...
Ω	$Ga_{10}Ni_{40}Sn_{50}$	...	...	(d)	...	...	...

(a) (HT) and (LT) refer to high temperature and low temperature, respectively. (b) deformed superstructure of AsNi structure. (c) Contains more diffraction lines than the Ga_2Ni_3 phase. (d) Structure similar to the Ni_3Sn_4 type structure

Ternary System

The Ga-Ni-Sn system has been studied by [1982Bor]. The alloys were prepared by melting 99.9 mass% pure component elements in evacuated and sealed quartz tubes, homogenized at 800 °C, finally annealed at 650 °C for 12 h and quenched in water. X-ray diffraction was used for phase identification, phase analysis, and phase boundary delineation. The isothermal section of the Ga-Ni-Sn system at 650 °C is given in Fig. 4 with some modifications as stated below.

[1982Bor] used the binary phase equilibria data of Ga-Ni, Ga-Sn, and Ni-Sn systems available at that time and accordingly showed, in their 650 °C isothermal section, all the binary phase regions, except the ν phase, with ~2 at.% solubility regions. They have also shown in the 650 °C isothermal section the presence of a solid Sn solid-solution region, and phase equilibria at the high-Sn side has been shown with one of the phases being solid Sn. Since Sn exists in the liquid state at 650 °C, the phase equilibria given by [1982Bor] at 650 °C is not correct. Hence, in Fig. 4 the probable liquid region L at the Ga-Sn side of the diagram is shown schematically and phase equilibria at the high-Sn side of Ga-Ni-Sn system has been shown with L as one of the phases instead of Sn. The Ni solid-solution region γ and the binary phase regions are shown in Fig. 1 so that they conform to the accepted binary data. The probable phase boundaries are given in these cases by dashed lines.

Figure 4 shows extension of the $GaNi_3$ (β_1) and Ni_3Sn (π) phases toward each other; the former phase extends up to ~10 at.% Sn, whereas the latter phase extends up to ~5 at.% Ga. At 650 °C, the binary phase region at 40 at.% Ga has been mentioned by [1982Bor] as the Ga_9Ni_{13} phase. The accepted Ga-Ni binary does not have the Ga_9Ni_{13} phase, but at 40 at.% Ga the Ga_2Ni_3 (LT) phase (γ') exists at 650 °C. The δ' and γ' phases extend only up to ~2 at.% Sn. The ε_1 phase of the Ni-Sn system extends toward the γ' phase up to ~27 at.% Ga. Between the ε' and γ' phase regions the existence of two intermediate phases have been reported. At 40 at.% Ni and ~5 at.% Sn the θ phase exists. The x-ray diffraction pattern of the Φ phase shows several additional diffraction lines compared to that of the γ' phase. At 40 at.% Ni and between 7 and 10 at.% Sn various deformed structures of AsNi type were detected. Whether they are different phases or not is not known and has been represented in Fig. 4 by a phase region Γ. The ternary intermediate phase Δ exists at around the composition of $Ga_3Ni_5Sn_2$, is a narrow phase region, ~2 at.% wide, and extends from about 20 to 30 at.% Sn. The Δ phase has been identified as the $Ga_3Ni_5Ge_2$ type phase with lattice parameters a = 0.4076 nm, b = 1.2331 nm, and c = 1.1349 nm. The crystal structure of the ternary intermediate phase at

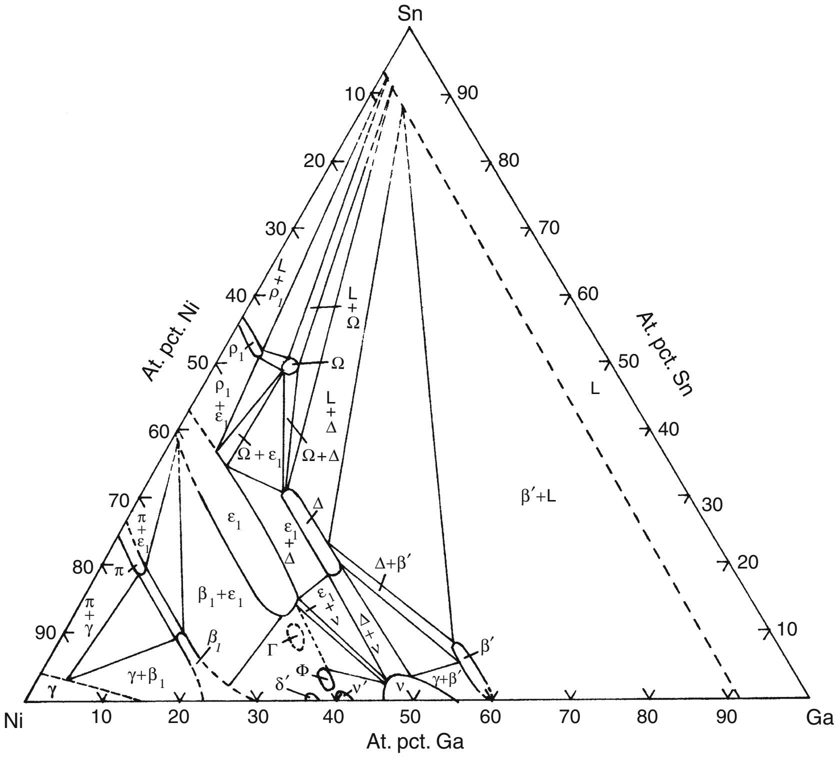

Fig. 4 An isothermal section of Ga-Ni-Sn system at 650 °C [1982Bor]

$Ga_{10}Ni_{40}Sn_{50}$ has been reported to have some similarity with that of the Ni_3Sn_4 (ρ_1) phase. The crystal structures of the ternary intermediate phases have to be determined using single crystal x-ray diffraction techniques.

The phase equilibria established in the Ga-Ni-Sn system at 650 °C (Fig. 4) shows the existence of several three-phase equilibrium regions: $\gamma + \pi + \beta_1$, $\pi + \varepsilon_1 + \beta_1$, $\varepsilon_1 + \Delta + \nu$, $\Delta + \beta' + \nu$, $\varepsilon_1 + \Delta + \Omega$, $\varepsilon_1 + \Omega + \rho_1$, $L + \Delta + \beta'$, $L + \rho_1 + \Omega$, and $L + \Delta + \Omega$. A probable three-phase region between $\varepsilon_1 + \nu + \Phi$ is shown in Fig. 4 on the basis of the two-phase equilibrium shown between Φ and ν and ν and ε_1. The phase equilibria around the 40 at.% Ni line, between the ε_1 and γ' phases, has not been established. Only the phase boundary for the $\varepsilon_1 + \beta_1$ region is indicated because the phase equilibria between the β_1, Γ, Φ, and δ' phases was not established. The three-phase boundaries in most cases are shown on the basis of one or two three-phase alloys, and hence the three-phase region boundaries are to be treated as tentative.

References

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# indicates presence of phase diagram.

Ga-Ni-Sn 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.