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The Ge-In-Ni (Germanium-Indium-Nickel) System

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Introduction

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

Binary Systems

The Ge-In system [Massalski2] (Fig. 1) is a simple eutectic system with the eutectic point very close to In. The eutectic temperature is 156.29 °C. There is practically no solubility of In in Ge, nor of Ge in In.

The Ge-Ni system [1991Nas] (Fig. 2) has nine intermediate phases: βGeNi$_3$ (β), γ_1GeNi$_3$ (γ_1), δGe$_2$Ni$_5$ (δ), GeNi$_2$ (π), ε'Ge$_3$Ni$_5$ (ε'), εGe$_3$Ni$_5$ (ε), Ge$_{12}$Ni$_{19}$ (ζ), Ge$_2$Ni$_3$ (ξ), and GeNi (ι). The β and ε phases melt congruently at 1132 and 1185 °C, respectively and the $\varepsilon \rightarrow \varepsilon'$ transformation occurs congruently at ~398 °C. The γ_1, δ, ζ, ξ, and ι phases form through peritectic reactions: $L + \beta \leftrightarrow \gamma$ at 1118 °C, $L + \gamma_1 \leftrightarrow \delta$ at 1102 °C, $L + \varepsilon \leftrightarrow \zeta$ at 1050 °C, $L + \zeta \leftrightarrow \xi$ at 990 °C, and $L + \xi \leftrightarrow \iota$ at 850 °C. The π phase forms through a peritectoid reaction $\beta + \varepsilon \leftrightarrow \pi$ at 506 °C. Three eutectic reactions $L \leftrightarrow \gamma + \beta$, $L \leftrightarrow \delta + \varepsilon$, and $L \leftrightarrow \iota$ + (Ge) occur at 1124, 1099, and 762 °C, respectively. γ is the terminal face-centered cubic (fcc) solid solution (Ni). The γ_1 and δ phases exist only at high temperatures and undergo eutectoid transformation $\gamma_1 \leftrightarrow \beta + \delta$ and $\delta \leftrightarrow \beta + \varepsilon$ at 1082 and 1045 °C, respectively. The ζ, ξ, and ε phases undergo four eutectoid transformations: $\xi \leftrightarrow \zeta + \iota$, $\varepsilon \leftrightarrow \varepsilon' + \zeta$, $\zeta \leftrightarrow \varepsilon' + \iota$, and $\varepsilon \leftrightarrow \pi + \varepsilon'$ at 515, ~394, 382, and 290 °C, respectively.

The In-Ni system [1991Nas] (Fig. 3) has eight intermediate phase: InNi$_3$ (τ), InNi$_2$ (λ), In$_9$Ni$_{16}$ (ε), In$_9$Ni$_{13}$ (ρ), InNi (θ), InNi (δ_1), In$_3$Ni$_2$ (ν), and In$_{72}$Ni$_{28}$ (η), of which the ε and δ phases melt congruently at 990 and 950 °C, respectively. The ν and η phases form through peritectic reactions $L + \delta \leftrightarrow \nu$ at 870 °C and $L + \nu \leftrightarrow \eta$ at 409 °C. The τ, λ, ρ, and θ phases form through peritectoid reactions $\gamma + \varepsilon \leftrightarrow \tau$, $\tau + \varepsilon \leftrightarrow \lambda$, $\varepsilon + \delta_1 \leftrightarrow \rho$, and $\rho + \delta_1 \leftrightarrow \theta$ at 848, 665, 876, and 860 °C, respectively. The ε and δ phases undergo eutectoid transformation $\varepsilon \leftrightarrow \lambda + \rho$ at 482 °C and $\delta_1 \leftrightarrow \theta + \nu$ at 770 °C. Three eutectic reactions $L \leftrightarrow \gamma + \varepsilon$, $L \leftrightarrow \varepsilon + \delta$, and $L + \eta +$ (In) occur at 910, 918, and ~156 °C, respectively. The Ni$_2$In phase has an invariant composition.

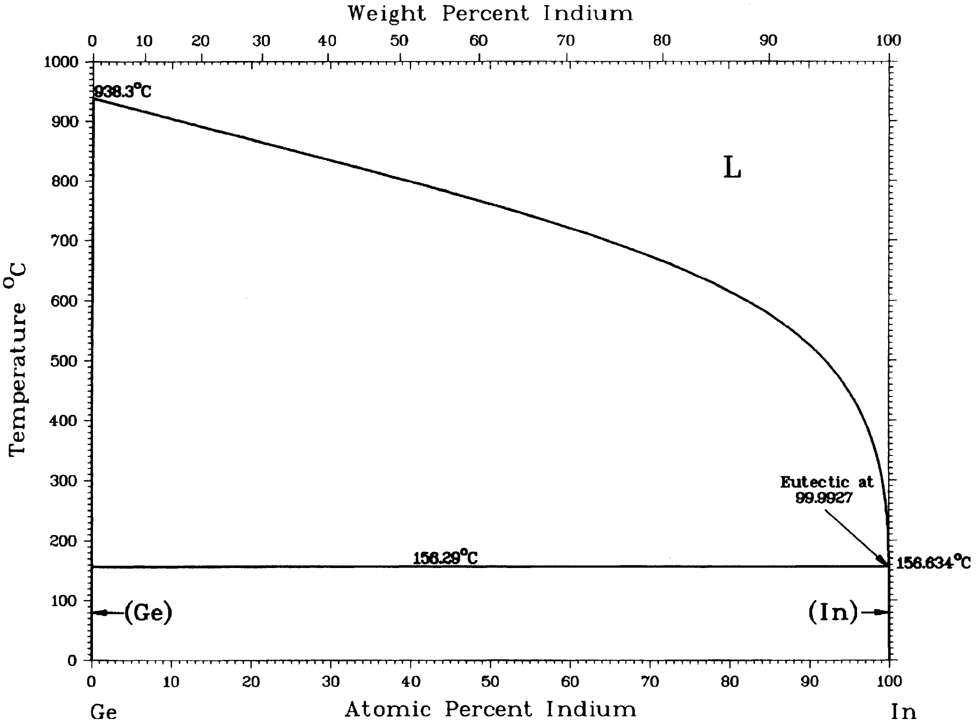

Fig. 1 Binary Ge-In phase diagram [Massalski2]

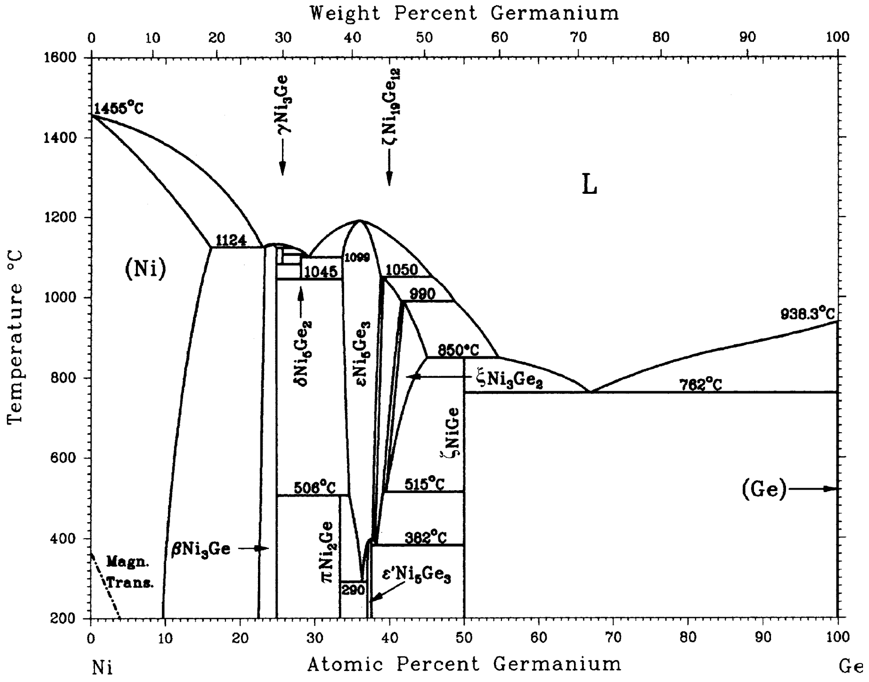

Fig. 2 Binary Ge-Ni phase diagram [1991Nas]

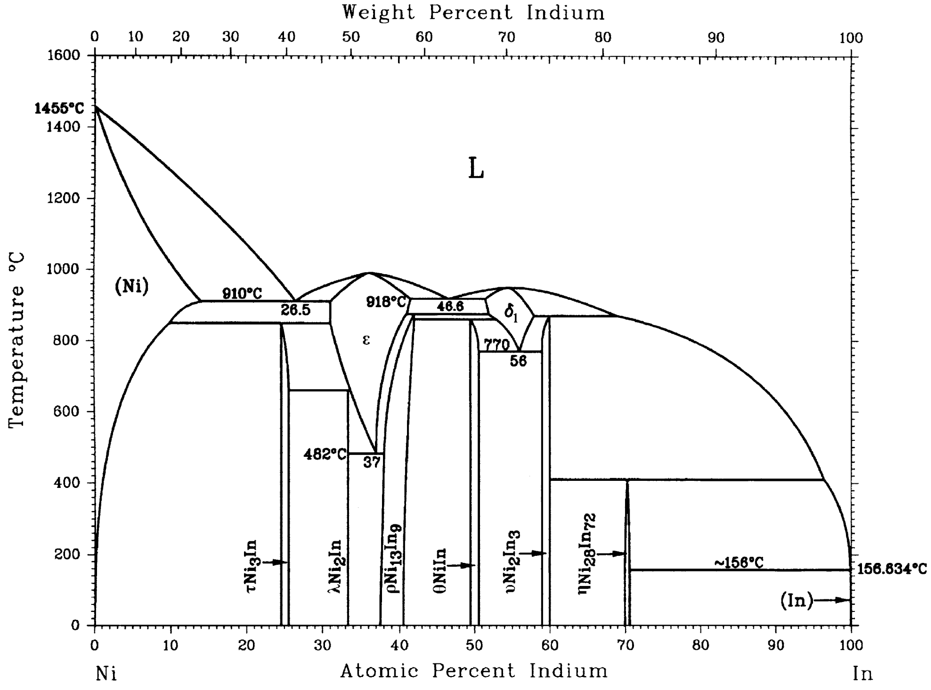

Fig. 3 Binary In-Ni phase diagram [1991Nas]

Binary and Ternary Phases

In the three binary systems Ge-In, Ge-Ni, and In-Ni, 17 intermediate phases form. No ternary intermediate phase has been reported in the Ge-In-Ni system. The binary phases and their structure data are given in Table 1.

Ternary System

The Ge-In-Ni system has been investigated by [1982Bor]. The alloys were melted, using pure metals of 99.9 mass% purity, in evacuated and sealed quartz tubes, homogenized at 800 °C, then annealed at 650 °C for 12 h and water

Table 1 Phases in the Ge-In, Ge-Ni, and In-Ni binary systems and their structure data

Phase designation	Composition (a)	Pearson's symbol	Space group	Type	Lattice parameter, nm		
					a	***b***	***c***
γ	(Ni)	*cF*4	$Fm\bar{3}m$	Cu	···	···	···
In	(In)	*tI*2	$I4/mmm$	In	···	···	···
Ge	(Ge)	*cF*8	$Fd\bar{3}m$	C (diamond)	···	···	···
β	$\beta GeNi_3$	*cP*4	$Pm\bar{3}m$	$AuCu_3$	0.357	···	···
γ_1	$\gamma_1 GeNi_3$	···	···	···	···	···	···
δ	δGe_2Ni_5	*hP*84	$P6_3/mmc$	Pd_5Sb_2	0.6827	···	1.2395
π	$GeNi_2$	*oP*12	$Pnma$	Co_2Si	0.7264	0.511	0.383
ε'	$\varepsilon' Ge_3Ni_5$	*mC*32	$C2$	Ge_3Ni_5	1.1682 β = 52.1°	0.6737	0.6364
ε	εGe_3Ni_5	*hP*4	$P6_3/mmc$	AsNi	0.3955	···	0.5047
ζ	$Ge_{12}Ni_{19}$	*mC*62	$C2$	$Ge_{12}Ni_{19}$	1.1631	0.6715 β = 90°	1.0048
ξ	Ge_2Ni_3	*hP*4	$P6_3/mmc$	AsNi	0.386	···	0.500
ι	GeNi	*oP*8	$Pnma$	MnP	0.581	0.538	0.343
τ	$InNi_3$	*hP*8	$P6_3/mmc$	Ni_3Sn	0.5320	···	0.4242
λ	$InNi_2$	*hP*6	$P6_3/mmc$	$InNi_2$	0.4179	···	0.5131
ε	In_9Ni_{16} (31.0-41.5)	*hP*4	$P6_3/mmc$	AsNi	0.41889	···	0.51230
ρ	In_9Ni_{13} (38.5-42.2)	···	···	···	···	···	···
θ	InNi	*hP*6	$P6/mmm$	CoSn	0.4537	···	0.4345
δ_1	InNi	*cP*2	$Pm\bar{3}m$	CsCl	0.3093	···	···
ν	In_3Ni_2	*hP*5	$Pm31$	Al_3Ni_2	0.918	···	···
η	$In_{72}Ni_{28}$	···	···	γ brass	···	···	···

(a) Numbers in parentheses are in at.% In

quenched. Only x-ray diffraction (XRD) was used for phase identification and phase boundary determination. For XRD work the alloys were powdered, sealed in evacuated quartz tubes, recrystallized at 650 °C, and then quenched in water. The 650 °C isothermal section established by [1982Bor] is given in Fig. 4 after making some adjustments of phase boundaries to agree with the accepted binary data.

To determine the 650 °C isothermal section [1982Bor] used only a few alloys containing from about 25 at.% Ge and In to about 65 at.% Ge and In, and hence only a partial isothermal section was established. The fcc γ phase boundary at the Ni corner was not experimentally determined, and the γ phase boundary does not agree with the binary In-Ni and Ge-Ni systems. The probable γ phase boundary is shown schematically in Fig. 4. The binary phases τ, β, λ, ρ, ν, and ι phases were found to extend into the ternary only marginally, <2 at.% In or Ge. The τ and β phases were found in equilibrium with each other and are found in equilibrium with the ε phase. A three-phase region $\gamma + \tau + \beta$ should exist and is shown schematically in Fig. 4. The isostructural Ge_3Ni_5 and In_9Ni_{16} phases form a continuous solid solution region ε extending from the Ge-Ni binary to the In-Ni binary. [1982Bor], however, had shown the ε phase region to extend up to ~41 at.% Ge at the Ge-Ni binary, which does not agree with the accepted binary data. The Ge-Ni binary indicates at 650 °C the solubility of Ge in the ε phase to be about 38 at.% Ge, and between 38 and 41 at.% Ge two more intermediate phases ζ and ξ exist in the Ge-Ni binary. [1982Bor] did not show these two phases. [1982Bor] also found a phase Ni_3In_7 extending from the In-Ni binary up to ~15 at.% Ge. The accepted In-Ni binary does not have an In_7Ni_3 phase, but has an $In_{72}Ni_{28}$ phase that exists at temperature <409 °C. The In_7Ni_3 phase is possibly the $In_{72}Ni_{28}$ phase (η). This probably means that the low-temperature phase $In_{72}Ni_{28}$ phase is stabilized to higher temperature by the addition of Ge. The η phase in the ternary thus cannot extend to the In-Ni binary at 650 °C. Accordingly, the η phase boundary has been terminated close to the In-Ni binary and an expected three-phase equilibrium triangle $L + \eta + \nu$ has been shown schematically in Fig. 4. At 650 °C a liquid region (L) should exist at the In corner of the Ge-In-Ni system and phase equilibrium involving the L and η and Ge should exist. This was not shown by [1982Bor], and in Fig. 4 a three-phase equilibrium triangle $L + \eta + Ge$ is shown schematically by dashed lines. The ε, ν, and θ phases were found in equilibrium. Phase equilibrium involving the λ and ρ phases was not determined by [1982Bor]. The probable three-phase equilibrium $\varepsilon + \tau + \lambda$ and $\varepsilon + \rho + \theta$ are shown schematically in Fig. 4. At the high Ge side of the Ge-In-Ni system the η phase was found in equilibrium with the ι phase and Ge. [1982Bor] reported that the η phase is in equilibrium with the ι and ε phases. Since [1982Bor] did not find the ζ and ξ phases in their study of the Ge-In-Ni phase diagram, it may be assumed that the ζ and ξ phases do not extend far into the ternary. As a result of the shift of the high Ge side of the ε phase boundary (Fig. 4)

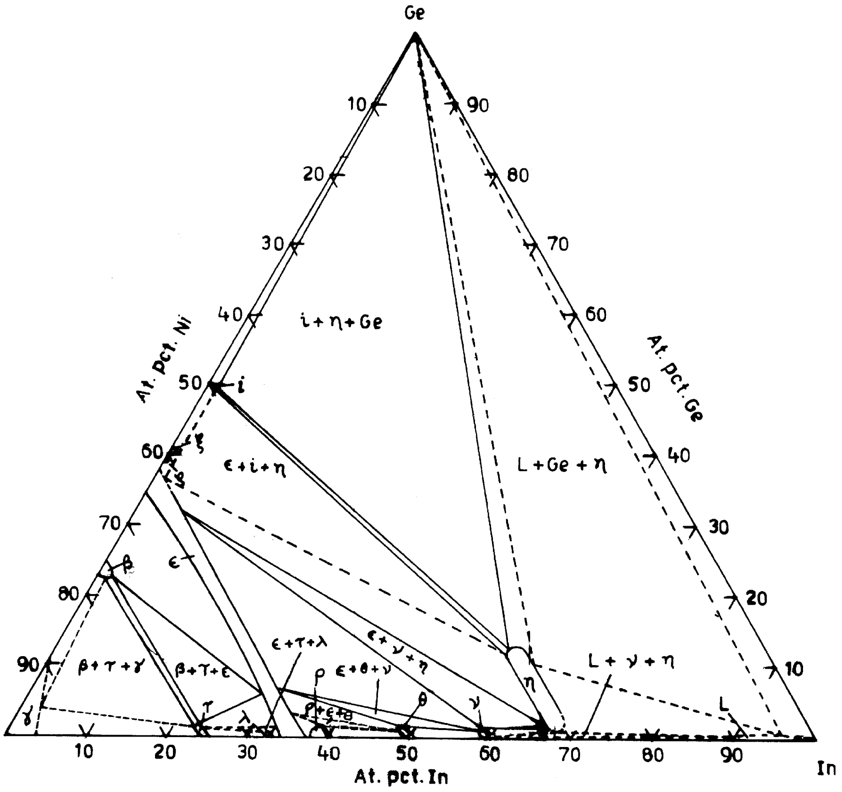

Fig. 4 An isothermal section of the Ge-In-Ni system at 650 °C [1982Bor]

and the possible presence of the ζ and ξ phases, the boundaries of the three-phase region ε + ι + η had to be shifted slightly (shown schematically by dashed lines) from that given by [1982Bor]. Because of these small adjustments made in the 650 °C isothermal section of the Ge-In-Ni system, and because the phase boundaries given in Fig. 1 are sometimes based on only one or two alloys using XRD only, it will be necessary to determine proper phase boundaries using various other techniques.

References

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# indicates presence of phase diagram.

Ge-In-Ni 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.