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The Co-Ni-Si (Cobalt-Nickel-Silicon) System

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Introduction

The Co-Ni-Si system has been investigated recently to establish proper phase equilibria in this system. An isothermal section has been established and is reported here.

Binary Systems

The Co-Ni system [Massalski2] (Fig. 1) is a simple isomorphous system with liquidus and solidus temperatures very close to each other. The face centered cubic (fcc) solid solution of (αCo, Ni), designated here as γ phase, possibly has a short range ordering reaction at the $CoNi_3$ composition. At the Co-end, the fcc αCo transforms to close packed hexagonal (cph) εCo phase at $T \leq 422\,^{\circ}C$.

The Co-Si system [Massalski2] (Fig. 2) has five intermediate phases, $Co_3Si(\iota)$, $\alpha Co_2Si(\delta)$, $\beta Co_2Si(\rho)$, $CoSi(\eta)$, and $CoSi_2$ (ζ), of which the βCo_2Si, CoSi, and $CoSi_2$ phases melt congruently at 1334, 1460, and 1326 °C, respectively. The Co_3Si and αCo_2Si phases form through peritectic reactions, $L + \delta \leftrightarrow \iota$ at 1214 °C and $L + \rho \leftrightarrow \delta$ at ~ 1320 °C. The cph (εCo) phase is stabilized to higher temperatures with addition of Si to Co and at 1250 °C a peritectic reaction, $L + (\alpha Co) \leftrightarrow (\varepsilon Co)$, occurs. The $Co_3Si(\iota)$ and βCo_2Si (ρ) phases exist only at higher temperatures and decompose through eutectoid reactions, $\iota \leftrightarrow (\varepsilon Co) + \delta$ at 1193 °C and $\rho \leftrightarrow \delta + \eta$ at 1286 °C. The four eutectic reactions $L \leftrightarrow (\varepsilon Co) + \iota, L \leftrightarrow \rho + \eta, L \leftrightarrow \eta + \zeta$, and $L \leftrightarrow \zeta$ + (Si) occur at 1204, 1286, 1310, and 1259 °C, respectively. The $CoSi_2$ phase is of invariant composition.

The Ni-Si system [Massalski2] (Fig. 3) has eight intermediate phases, Ni_3Si (β_1), Ni_3Si (β_2 and β_3), $Ni_{31}Si_{12}(\gamma')$, $Ni_2Si(\delta)$, $Ni_2Si(\theta)$, Ni_3Si_2(ε and ε′), NiSi(ξ), and $NiSi_2$(ζ and ζ′), of which several phases, β_2 and β_3, ε and ε′ and ζ and ζ′, exist in polymorphic forms with polymorphic transformation temperatures of ~1115, 830, and 981 °C, respectively. The β_1, β_3, δ, ε′, and ζ′ phases form through peritectic or peritectoid reactions: $L + \gamma' \leftrightarrow \beta_3$ at 1178 °C, $L + \theta \leftrightarrow \delta$ at 1255 °C, $L + (Si) \leftrightarrow \zeta'$ at 993 °C, $(Ni) + \beta_2 \leftrightarrow \beta_1$ at 1035 °C, and $\theta + \xi \leftrightarrow \varepsilon'$ at 845 °C. There are eight eutectic or eutectoid reactions in the Ni-Si system: $L \leftrightarrow (Ni) + \beta_3$ at 1145 °C, $L \leftrightarrow \gamma' + \delta$ at 1215 °C, $L \leftrightarrow \theta + \xi$ at 964 °C, $L \leftrightarrow \xi + \zeta$ at 966 °C, $\beta_2 \leftrightarrow \beta_1 + \gamma'$ at 990 °C, $\theta \leftrightarrow \delta + \varepsilon'$ at 825 °C, $\varepsilon' \leftrightarrow \delta + \varepsilon$ at 820 °C, and $\varepsilon' \leftrightarrow \varepsilon + \xi$ at 800 °C. The γ', δ, ξ and ζ phases are single composition phases.

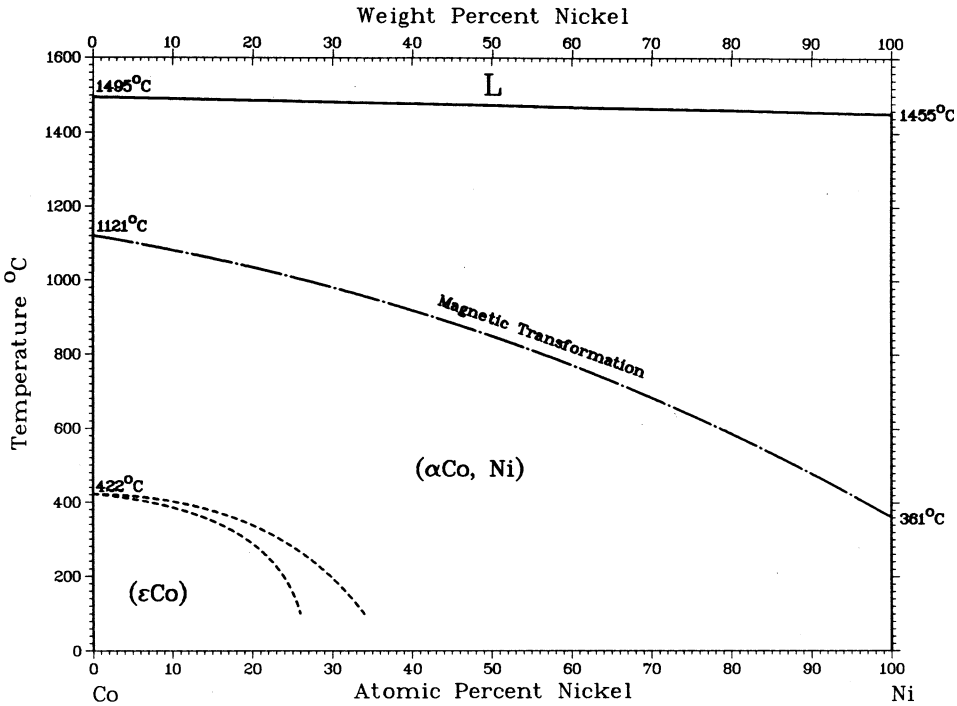

Fig. 1 Binary Co-Ni system [Massalski2]

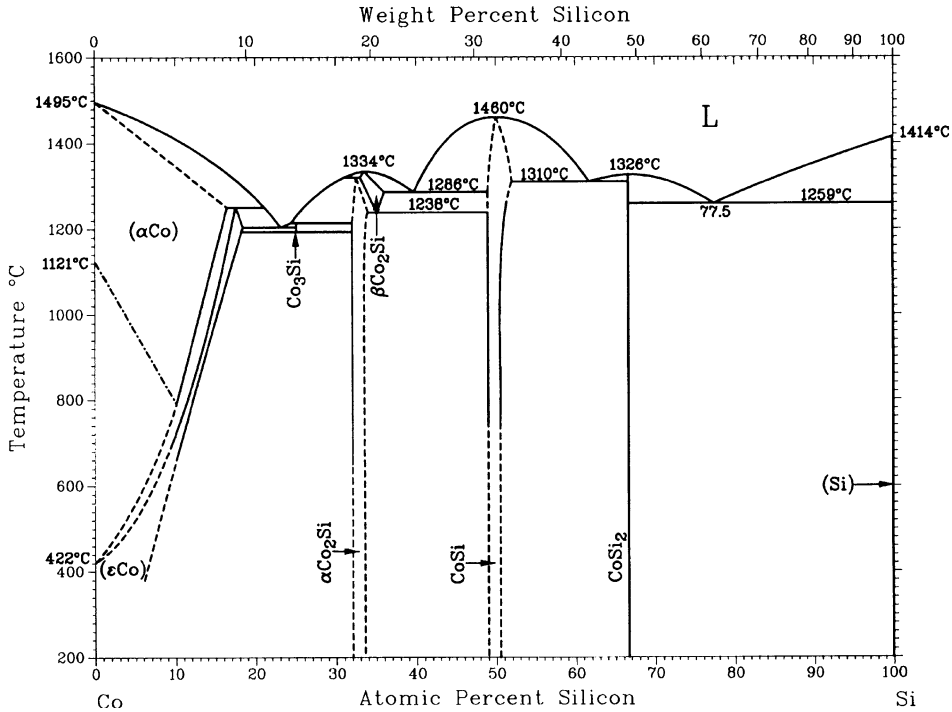

Fig. 2 Binary Co-Si system [Massalski2]

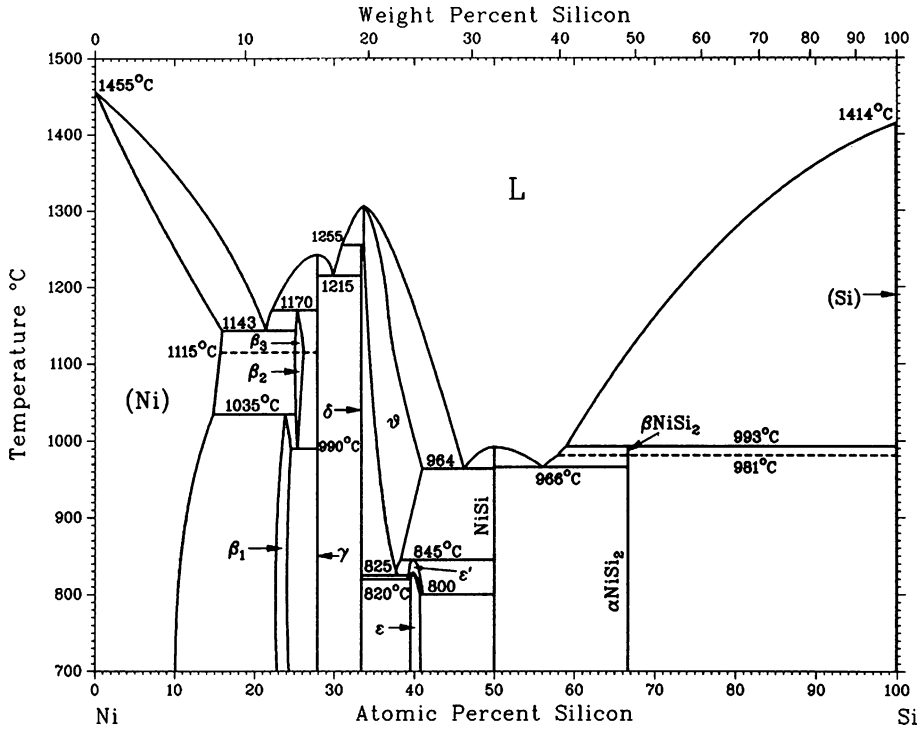

Fig. 3 Binary Ni-Si system [Massalski2]

Binary and Ternary Phases

In the three binary systems Co-Ni, Co-Si, and Ni-Si there are eight intermediate phases. Several intermediate phases of the Ni-Si system, however, have polymorphic transformations. No ternary intermediate phase has been reported in the Co-Ni-Si system. The binary phases and their structure data are given in Table 1.

Table 1 Phases of the binary systems Co-Ni$_7$, Co-Si, and Ni-Si and their structure data

Phase designation	Composition (a)	Pearson's symbol	Space group	Type	Lattice parameter, nm		
					a	*b*	*c*
γ	(Ni), (αCo) (αCo,Ni)	*cF*4	$Pm\bar{3}m$	Cu	…	…	…
ε	(εCo)	*hP*2	$P6_3/mmc$	Mg	…	…	…
Si	(Si)	*cF*8	$Fd\bar{3}m$	C (diamond)	…	…	…
ι	Co_3Si	…	…	…	…	…	…
δ	αCo_2Si (32-34)	*oP*12	*Pnma*	Co_2Si	0.7109	0.4918	0.3738
ρ	βCo_2Si (~32-35.8)	…	…	…	…	…	…
η	CoSi	*cP*8	$P2_13$	FeSi	0.4447	…	…
ζ	$CoSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5376	…	…
$β_1$	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′	$Ni_{31}Si_{12}$	*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	Ni_2Si (33.4-41.0)	*hP*6	$P6_3/m$	Ni_2Si	0.3805	…	0.489
ε	Ni_3Si_2	*oP*8	…	…	…	…	…
ε′	Ni_3Si_2	…	…	…	…	…	…
ξ	NiSi	*oP*8	*Pnma*	MnP	0.562	0.518	0.334
ζ	α$NiSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5406	…	…
ζ′	β$NiSi_2$	…	…	…	…	…	…

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

Ternary System

The Co-Ni-Si system has been investigated by [2000Bee] using arc melted alloys as well as using diffusion couples. Purities of component elements used for this study are Co of 99.78 mass% purity and Ni and Si of 99.998 mass% purity. Binary and ternary alloys were arc melted under argon atmosphere. The alloys, sealed in evacuated quartz capsules, were annealed at 800 ± 3 °C for 900 h and quenched in water. The diffusion couples prepared with Si and Co and three Co-Ni alloys of compositions $Co_{70}Ni_{30}$, $Co_{50}Ni_{50}$, $Co_{30}Ni_{70}$ were annealed in a vacuum furnace at 800 °C for 64 to 400 h. The annealed binary and ternary alloys and the diffusion zones of the diffusion couples were investigated using polarized light microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) techniques. X-ray diffraction was used for phase identification. The 800 °C isothermal section of the Co-Ni-Si system, established by [2000Bee], is shown in Fig. 4.

This isothermal section at 800 °C shows continuous solid solubility between αCo_2Si and Ni_2Si phases (δ) and between $CoSi_2$ and $NiSi_2$ phases (ζ). The extensions of all the binary intermediate phases into the ternary occur along the respective stoichiometric lines of fixed Si contents. The solubility of Co in NiSi phase (ξ) was found to be ~12 at.% Co, and Ni in CoSi phase (η) was found to be ~21 at.% Ni. The ξ and η phases were found in equilibrium with each other and were found in equilibrium with the ε and ζ phases. The η phase was also found in equilibrium with the δ phase. The Ni_3Si_2 phase (ε) extends into the ternary up to ~5 at.% Co. The $Ni_{31}Si_{12}$ phase (γ′) extends far into the ternary, up to ~43 at.% Co and is found in equilibrium with the δ and γ phases. The Ni_3Si phase ($β_1$) extends into the ternary up to ~12 at.% Co and is in equilibrium with the fcc γ and γ′ phases. The fcc γ phase region extends from Co to Ni and the solubility of Si in the γ phase varies from ~11 at.% Si at the Ni-end and ~13 at.% Si at the Co-end. A small hcp (εCo) phase (ε) region was also detected at the Co-Si side of the ternary system and the ε phase was found in equilibrium with the γ and δ phases. All the binary intermediate phases have been shown by [2000Bee] with some solubility extended from the binary composition into the ternary region. The accepted binary data of Co-Si and Ni-Si systems, however, show that the ζ, ξ, δ, and γ′ phases are single composition phases and the $β_1$ phase region has a slightly wider phase field. Moreover, [2000Bee] shows the ε phase region at a slightly higher Si content than given by the accepted Co-Si binary diagram. The probable phase boundaries of all these phases are shown in Fig. 4 with dashed lines.

The Co-Ni-Si ternary system at 800 °C shows continuous solid solution regions δ and ζ between the Co_2Si and Ni_2Si phases and between the $CoSi_2$ and $NiSi_2$ phases, respectively. The Co-Si and Ni-Si binaries show that both the αCo_2Si and Ni_2Si phases form through peritectic reactions. The solid solution region δ between the αCo_2Si and Ni_2Si phases thus suggest that a pseudobinary may exist between these two phases. A probable αCo_2Si-Ni_2Si

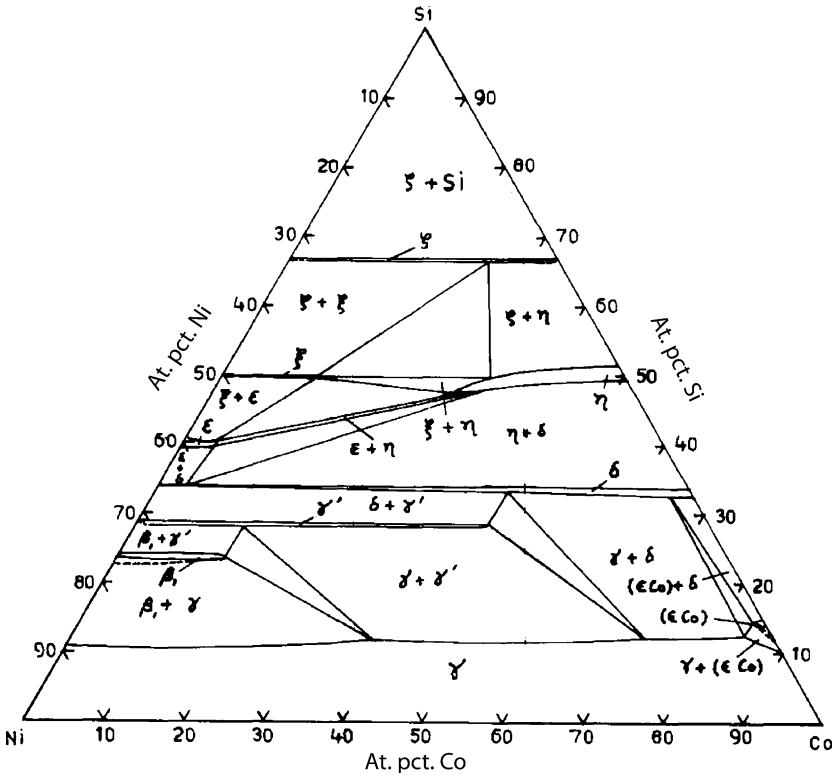

Fig. 4 An isothermal section of the Co-Ni-Si system at 800 °C [2000Bee]

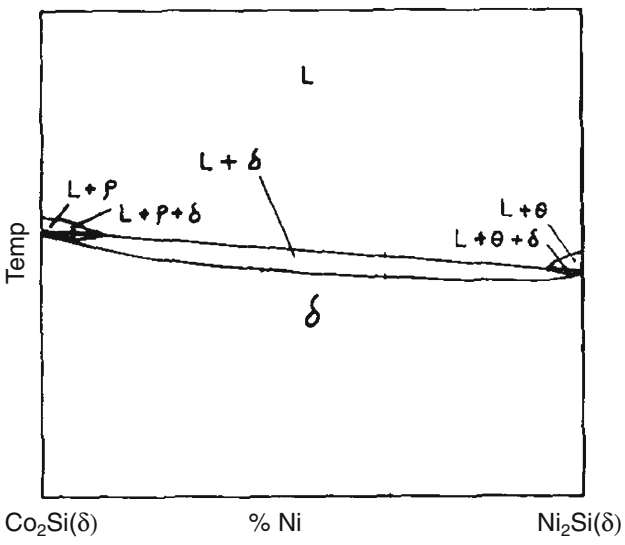

Fig. 5 A probable pseudobinary section (schematic) of the αCo_2Si-Ni_2Si system

pseudobinary section is shown schematically in Fig. 5. The $CoSi_2$ phase melts congruently at 1326 °C and the $NiSi_2$ (ζ′) phase forms through a peritectic reaction at 993 °C and the $NiSi_2$ (ζ′) phase undergoes a polymorphic transformation to $NiSi_2$ (ξ) phase at 981 °C. The $CoSi_2$ (ζ) and $NiSi_2$ (ζ) form the continuous solid solution region between these phases at 800 °C. In this case a more complex pseudobinary system may also exist between the $CoSi_2$ and $NiSi_2$ phases. The CoSi (η) and NiSi (ξ) phases melt congruently at 1460 °C and 992 °C, respectively. The two phases are of different crystal structures and are found in equilibrium with each other with a two phase field η + ξ between them. It is possible that a eutectic type pseudobinary may exist between the CoSi and NiSi phases. Further work in the Co-Ni-Si system is needed to see whether or not the suggested pseudobinaries exist in the ternary system.

The δ and ζ phases extend from the Co-Si to the Ni-Si system. [2000Bee] did not report any lattice parameter data for these phases. The lattice parameter of NiSi phase ξ has been measured by [1969Pan] as a function of Co content. The alloys were arc melted under argon atmosphere using 99.5^{+} mass% pure component elements. The alloys and the alloy powders were annealed at 900 °C for 10 days, quenched in water and lattice parameters were measured for the $(Co_xNi_{50-x})Si_{50}$ alloys as a function of cobalt content. The variation of lattice parameters as a function of x for the (Co,Ni)Si ξ phase are given in Fig. 6. The lattice parameters are given by [1969Pan] up to ~8 at.% Co. Whether at 900 °C this is the limit of solubility of Co in NiSi phase is, however, is not known. At 800 °C the solubility of Co in NiSi phase has been reported to be ~12 at.% Co [2000Bee]. It is possible that the solubility of Co in NiSi phase increases with decrease in temperature.

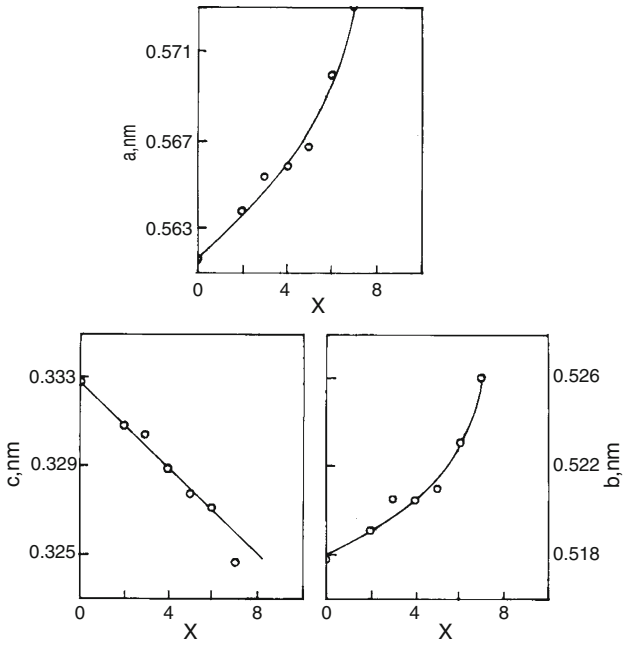

Fig. 6 Lattice parameters *a*, *b*, and *c* of $Co_xNi_{50-x}Si_{50}$ alloys as a function of cobalt content *x* [1969Pan]

The $CoSi_2$ and $NiSi_2$ phases both have the CaF_2 type structure, show metallic behavior, and have good oxidation resistant properties; hence, these phases are important as contact materials for Si. The diffusion couple studies were made to find the phases formed and the morphologies of the formed phases. In the Co/Si and (Co,Ni)/Si couples the predominant phase found in the diffusion zone is the CoSi phase and the (Co,Ni)Si phase, respectively. The CoSi phase was found to have columnar structure whereas the (Co,Ni)Si phase was equiaxed. The phase found next to the Si substrate was $CoSi_2$ for the Co/Si couple but $NiSi_2$ followed by NiSi phase for the (Co,Ni) Si couples. The $CoSi_2$ phase was found to form in the $(Co_{70}Ni_{30})$/Si couple between NiSi and (Co,Ni)Si phases, but for the higher Ni alloys no Co_2Si phase formed in the diffusion zone. The $CoSi_2$ phase is not in contact with the Si substrate in the (Co,Ni)/Si couples.

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# indicates presence of phase diagram.

Co-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.