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The Ni-Pd-Si (Nickel-Palladium-Silicon) System

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Introduction

Only one isothermal section for the Ni-Pd-Si system has been established and is reported here.

Binary Systems

The Ni-Pd system [Massalski2] (Fig. 1) is an isomorphous system with a minimum of 1237 °C at ~45 at.% Pd.

The Ni-Si system [Massalski2] (Fig. 2) has eight intermediate phases—Ni_3Si (β_1), Ni_3Si (β_2 and β_3), $Ni_{31}Si_{12}$ (γ'), Ni_2Si (δ), Ni_2Si (θ), Ni_3Si_2 (ϵ and ϵ'), NiSi (ξ), and $NiSi_2$ (α and β)—of which several phases, Ni_3Si (β_2 and β_3), Ni_3Si_2 (ϵ and ϵ'), and $NiSi_2$ (α and β) exist in polymorphic forms with polymorphic transition temperatures of ~1165, 830, and 981 °C, respectively. The γ', θ, and ξ phases melt congruently at 1242, 1306, and 992 °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, $\gamma + \beta_2 \leftrightarrow \beta_1$ at 1035 °C, and $\theta + \xi \leftrightarrow \epsilon$ at 845 °C. γ is the fcc terminal solid solution (Ni). There are nine eutectic or eutectoid reactions in the Ni-Si system: $L \leftrightarrow \gamma + \beta_3$ at 1145 °C, $L \leftrightarrow \gamma' + \delta$ at 1215 °C, $L \leftrightarrow \theta + \xi$ at 964 °C, $L \leftrightarrow \zeta + \xi$ at 966 °C, $\beta_2 \leftrightarrow \beta_1 + \gamma'$ at 990 °C, $\theta \leftrightarrow \delta + \epsilon$ at 825 °C, $\epsilon' \leftrightarrow \delta + \epsilon$ at 820 °C, $\epsilon \leftrightarrow \epsilon' + \xi$ at 800 °C, and $\epsilon \leftrightarrow \epsilon' + \delta$ at 820 °C. The γ', δ, ξ, and ζ phases are single composition phases.

The Pd-Si system [Massalski2] (Fig. 3) has five intermediate phases—PdSi (ξ), Pd_2Si (ρ), Pd_3Si (π), Pd_9Si_2 (κ), and Pd_5Si (η). The ρ, π, and η phases melt congruently at 1394, 1070, and 835 °C, respectively. A polymorphic form of Pd_2Si phase, Pd_2Si' (ρ'), forms through a peritectic reaction $\rho + L \leftrightarrow \rho'$ at 1090 °C. The PdSi (ξ) and Pd_9Si_2 (κ) phases form through peritectic reactions $L + \rho \leftrightarrow \xi$ at 900 °C and $L + \xi \leftrightarrow \kappa$ at 823 °C. The ξ, κ, and η phases exist only at the high temperatures and undergo eutectoid transformations: $\xi \leftrightarrow \rho' + (Si)$ at 824 °C, $\kappa \leftrightarrow \eta + \pi$ at 772 °C, and $\eta \leftrightarrow \pi + (Pd)$ at 727 °C. There are four eutectic reactions: $L \leftrightarrow (Pd) + \eta$ at 821 °C, $L \leftrightarrow \eta + \kappa$ at ≃820 °C, $L \leftrightarrow \pi + \rho$ at 1050 °C, and $L \leftrightarrow \xi + (Si)$ at 892 °C.

Binary and Ternary Phases

The three binary systems Ni-Pd, Pd-Si, and Ni-Si have 11 intermediate phases with several phases of the Ni-Si system having polymorphic forms. In the Ni-Pd-Si system, existence of two ternary intermediate phases, $Ni_{18}Pd_7Si_9$ and $NiPd_2Si$, have been reported. The binary and ternary phases of the Ni-Pd-Si system and their structure data are given in Table 1.

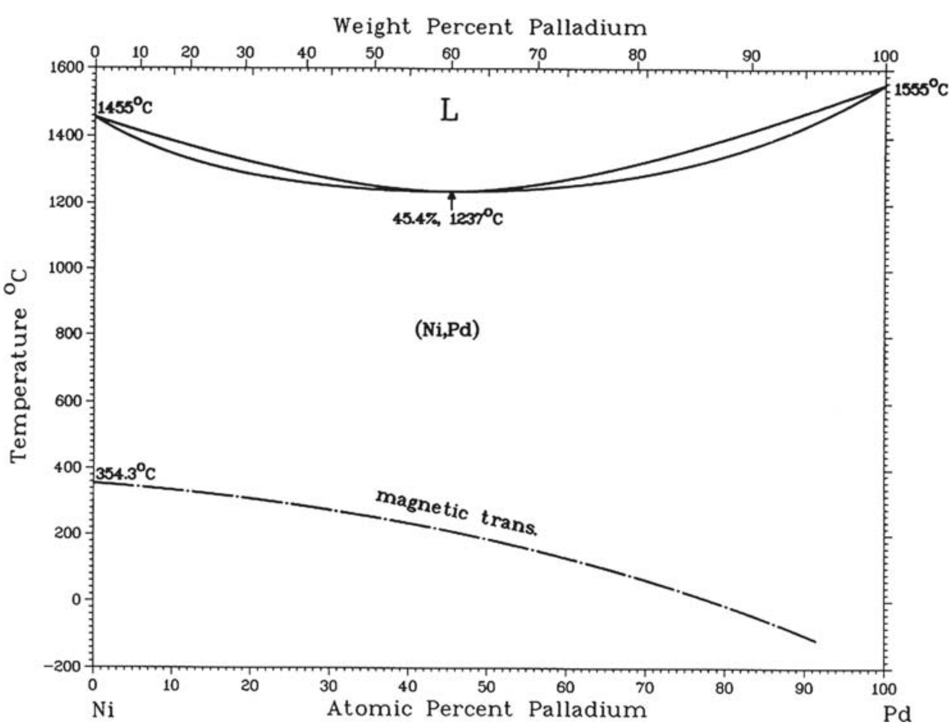

Fig. 1 Ni-Pd binary phase diagram [Massalski2]

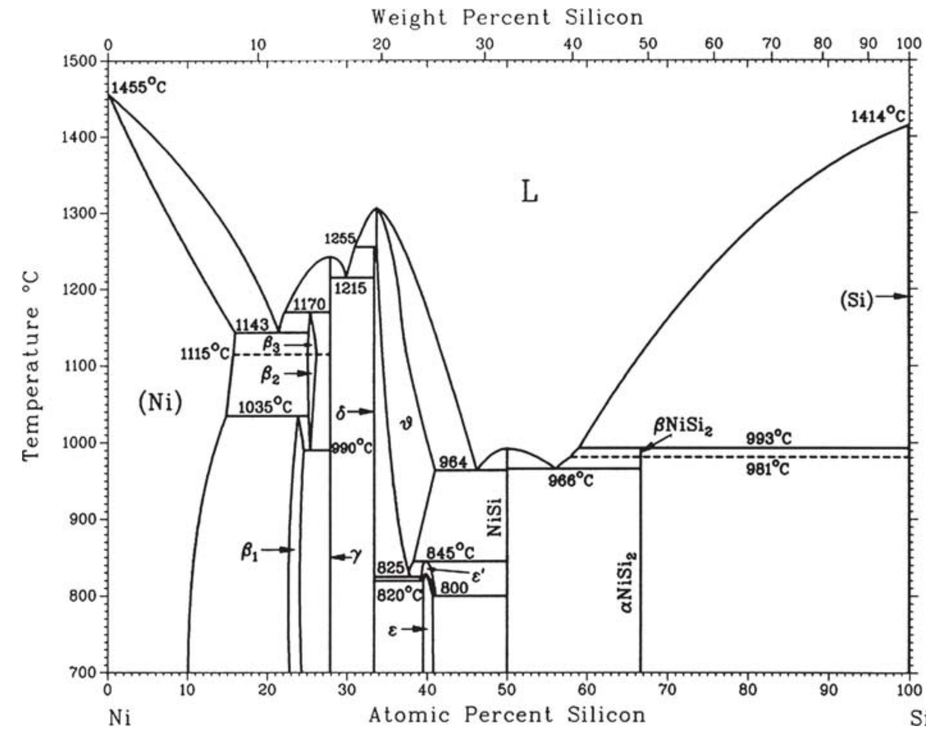

Fig. 2 Ni-Si binary phase diagram [Massalski2]

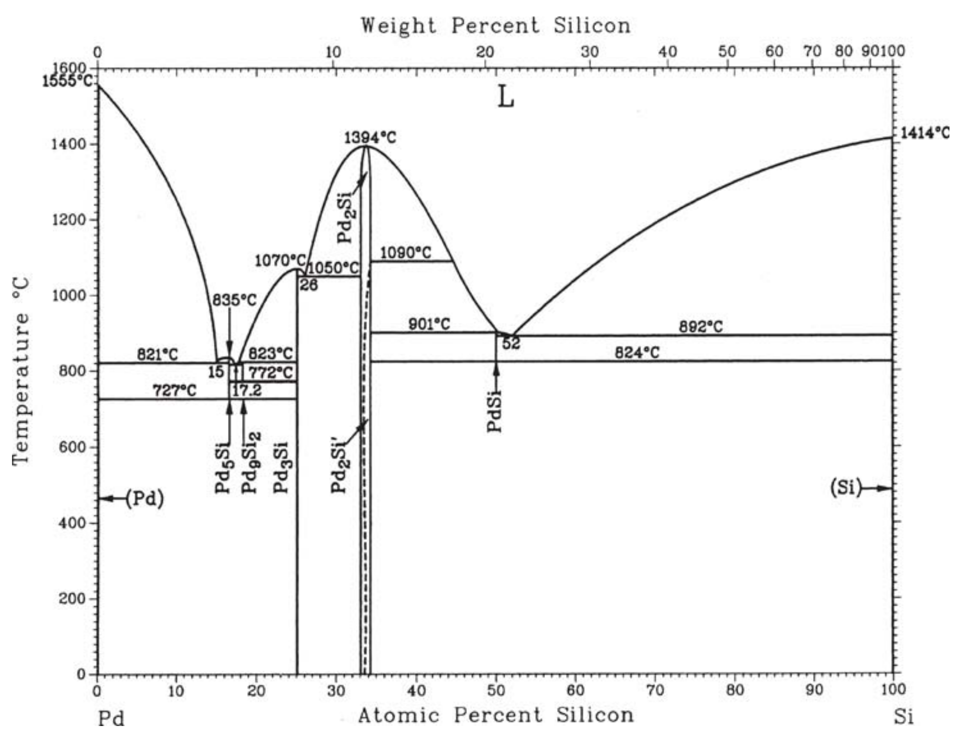

Fig. 3 Pd-Si binary phase diagram [Massalski2]

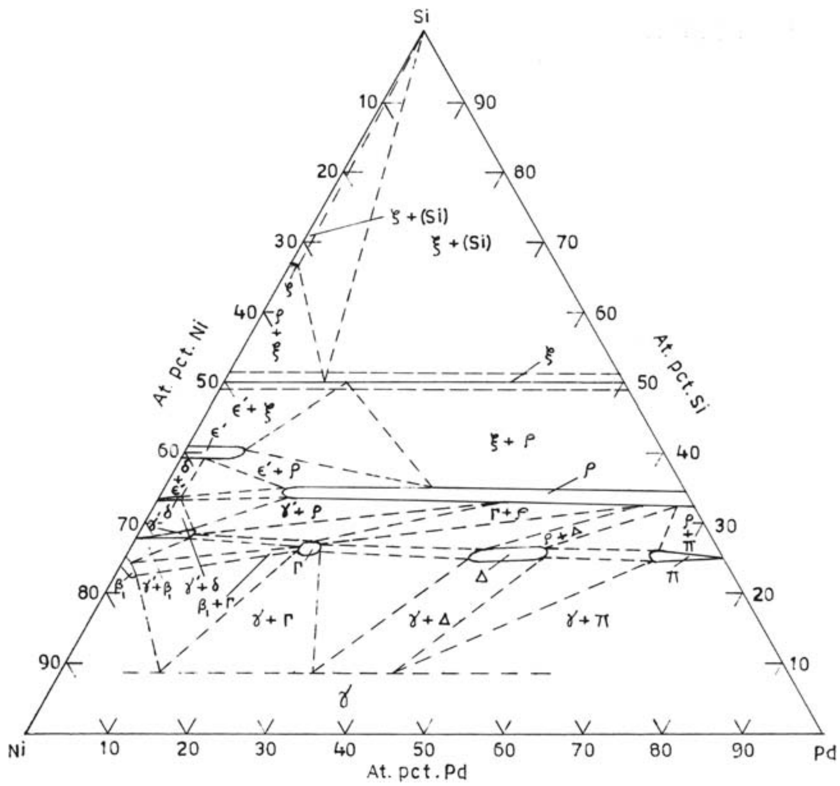

Fig. 4 800 °C isothermal section of Ni-Pd-Si system

Table 1 Phases of the Ni-Pd-Si system and their structure data

Phase designation	Composition, at.%	Pearson's symbol	Space group	Type	Lattice parameter, nm *a*	*b*	*c*
γ	(Ni), (Pd) (Ni, Pd)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
(Si)	(Si)	*cF*8	$Fd\bar{3}m$	C (Diamond)	…	…	…
β_1	Ni_3Si (22.8-24.5)	*cP*4	$Pm\bar{3}m$	$AuCu_3$	0.350	…	…
β_2	Ni_3Si (24.5-25.5)	*mC*16	…	$GePt_3$	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
ϵ	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	$NiSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5406	…	…
ζ′	$NiSi_2$	…	…	…	…	…	…
η	Pd_sSi	…	…	…	…	…	…
κ	Pd_qSi_2	…	…	…	…	…	…
π	Pd_3Si	*oP*16	*Pnma*	cFe_3	0.5735	0.7555	0.5260
ρ	Pd_2Si	*hP*9	$P\bar{6}2m$	Fe_2P	0.6496	…	0.3433
ρ′	Pd_2Si'	…	…	…	…	…	…
ξ	PdSi	*oP*8	*Pnma*	MnP	0.56173	0.33909	0.61534
Δ	$NiPd_2Si$	…	…	…	…	…	…
Γ	$Ni_{18}Pd_7Si_9$	…	…	$Pd_{25}Ge$	0.6835	…	0.9916

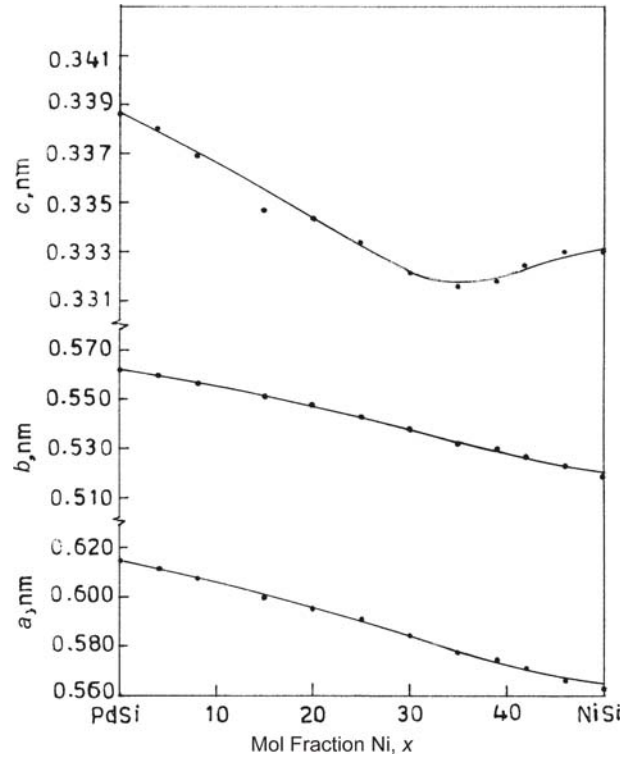

Fig. 5 Lattice parameter of $Pd_{50-x}Ni_xSi_{50}$ alloys (annealed at 900 °C) as a function of Ni content *x*

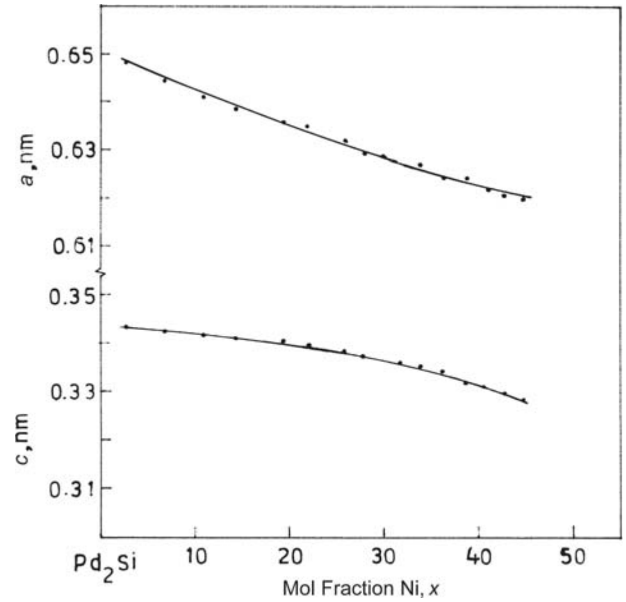

Fig. 6 Lattice parameter of $Pd_{66.7-x}Ni_xSi_{33.3}$ alloys (annealed at 900 °C) as a function of Ni content *X*

Ternary System

An isothermal section of the Ni-Pd-Si system has been established at 800 °C by [1976Wop]. Pure component elements, (99.9 mass %), sealed in evacuated quartz capsules, were melted in a high-frequency induction furnace. Alloys with >40 at.% Si were, however, arc melted. The alloys were prepared between 20 and 65 at.% Si. The alloys sealed in evacuated quartz capsules were annealed for 2 d at 800 °C and water quenched. The annealed alloys were crushed to prepare powder for x-ray diffraction (XRD) work. The powder of the alloys was again annealed at 800 °C for 1 d before taking XRD patterns. The phase analysis of the alloys was done using an XRD method only.

The 800 °C isothermal section of the Ni-Pd-Si system, in a slightly modified form, is shown in Fig. 4. The alloys along the NiSi-PdSi line showed complete solid solubility of the NiSi and PdSi phases (ξ) in each other, characteristic of an isomorphous pseudobinary system. Lattice parameter data are shown in Fig. 5.

The Pd_2Si (ρ) phase was found to extend into the ternary up to ~50 at.% Ni along the A_2B stoichiometric line. Lattice parameter data are shown in Fig. 6. Along the Pd_3Si (π) and $Ni_{31}Si_{12}$ (γ′) line two ternary intermediate phases, $NiPd_2Si$ (Δ) and $Ni_{18}Pd_7Si_9$ (Γ), were found to exist as small regions. The Pd_3Si and $Ni_{31}Si_{12}$ phases were found to extend up to ~9 at.% Ni and ~7 at.% Pd, respectively. The Ni_3Si_2 (ϵ) phase was also found to extend into the ternary up to ~7 at.% Pd. All the other phases Ni_3Si (β_1), Ni_2Si (δ), and $NiSi_2$ (ζ) were found to have only very limited extensions (<3 at.% Pd) into the ternary. The Γ phase was found in equilibrium with the γ, β, γ′, ρ, and Δ phases. The Δ phase was found in equilibrium with the γ, Γ, ρ, and π phases.

[1976Wop] have shown in their isothermal section that the binary phases have a solubility range of 2 to 3 at.%. For example, the NiSi and the PdSi phases are single composition (MSi) phases, but are shown to be within ~2 at.% solubility range, and accordingly the ξ phase region in the ternary has been shown to be ~2 at.% wide. Because all the ξ phase alloys were melted along the stoichiometric line between NiSi and PdSi and only XRD was used for phase identification, the ξ phase boundary given by [1976Wop] (dash-dot line in Fig. 4) is rather doubtful. Hence, in Fig. 4 the ξ phase is shown only as a single line joining the NiSi and PdSi phases. Similarly, the other binary phases that are single composition phases are shown accordingly in Fig. 4, and the location of the binary phase region adjusted according to the accepted binary data. Further work has to be done to determine the phase boundaries and the proper locations of the three-phase and two-phase regions. Because Pd_4Si and Pd_5Si phases do not exist in the accepted Pd-Si system, these phases are not shown in Fig. 4.

Lattice parameters of ρ and ξ phases have been determined as a function of Ni content and are given in Fig. 5 and 6.

The amorphous state of an $Ni_{15}Pd_{65}Si_{20}$ alloy was produced by the piston and anvil technique [1966Tsu]. On heating the amorphous alloy at >20 °C/min, sudden heat evolution of ~1000 cal/g · mole was noticed at 420 °C. Below this temperature the alloy was found to transform by a process of nucleation and growth.

References

1966Tsu: C.C. Tsuci and P. Duwez, Metastable Amorphous Ferromagnetic Phases in Pd-Base Alloys, *J. Appl. Phys.,* 1966, **37,** p 435 (Amorphous state)

1976Wop: W. Wopersnow and K. Schubert, Nickel-Palladium-Silicon Alloys, *Z. Metallkd.,* 1976, **67,** p 807-810, in German (Phase equilibria; #[1])

# indicates presence of a phase diagram.

Ni-Pd-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 Program Co-Category Editor for ternary nickel alloys.