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The Mn-Ni-Si (Manganese-Nickel-Silicon) System

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The Mn-Ni-Si system has been studied at two different temperatures, 800 and 1000 °C, to establish isothermal sections. A relatively large number of ternary intermediates phases were found in this system.

The Boundary Binary Systems

The binary Mn-Ni system in Fig.1 [Massalski2] has five intermediate phases of differing stoichiometries: $Mn_3Ni(\phi)$, $Mn_2Ni(\pi)$, $MnNi(\eta/\eta'/\eta'')$, $MnNi_2(\alpha_1/\alpha_2)$, and $MnNi_3(\gamma_1)$ with MnNi having three crystallographic forms and $MnNi_2$ having two. A peritectic reaction, L + (δMn) ↔ (γMn), occurs at 1164 °C on the Mn-rich side of the system. At elevated temperatures γMn and Ni form a continuous series of solid solutions, γ(Mn,Ni) and exhibit a congruent solidus/liquidus minimum at 1020 °C and 38 at.% Mn. At the pure Mn terminus, (βMn) and (αMn) are stable below 1100 and 727 °C, respectively. The π, η, and α_1 phases form from the face-centered cubic (fcc) γ(Mn,Ni) phase through congruent transformations, respectively, at 720, 911, and 710 °C. There are five peritectoid reactions: γ + η ↔ η′ at 775 °C, γ + (αMn) ↔ γ_1 at 520 °C, (αMn) + η″ ↔ ϕ at 430 °C, γ_1 + (αMn) ↔ η″ at 480 °C, and η″ + γ_1 ↔ α_2 at 440 °C. There are also five eutectoid reactions: π ↔ γ + (αMn) at 560 °C, η ↔ γ + η′ at 675 °C, η′ ↔ π + α_1 at 620 °C, α_1 ↔ π + γ at 580 °C, and γ ↔ η′ + α_1 at 655 °C.

The binary Mn-Si system in Fig. 2 [Massalski2] has seven intermediate phases: $Mn_6Si(R)$, ν, Mn_3Si, Mn_5Si_2, Mn_5Si_3, MnSi, and $MnSi_{1.75-x}$, with Mn_3Si having two polymorphic forms. Two intermediate phase melt congruently: Mn_5Si_3 at 1300 °C and MnSi at 1276 °C. Three peritectic reactions occur: L + (βMn) ↔ ν at 1060 °C, L + Mn_5Si_3 ↔ Mn_3Si at 1155 °C, and L + MnSi ↔ $MnSi_{1.75-x}$. The R and Mn_5Si_2 phases form by peritectoid reactions: (βMn) + ν ↔ R at 880 °C and $\beta Mn_3Si + Mn_5Si_3 \leftrightarrow Mn_5Si_2$ at 850 °C. The polymorphic transition from αMn_3Si to βMn_3Si occurs at $T \leq 667$ °C. The (γMn) and (βMn) terminal solutions are formed by peritectic reactions: L + (δMn) ↔ (γMn) at 1205 °C and L + (γMn) ↔ (βMn) at 1155 °C. The (βMn) phase transforms eutectoidally to (αMn) through the reaction (βMn) ↔ (αMn) + R at ~635 °C.

The binary Ni-Si system in Fig. 3 [Massalski2] shows eight intermediate binary phases with differing stoichiometries: Ni_3Si (β_1), Ni_3-Si (β_2/β_3), $Ni_{31}Si_{12}$ (γ′), Ni_2Si (δ′), Ni_3Si (θ), Ni_3Si_2 (ϵ,ϵ′), NiSi (ξ), and $NiSi_2$ (ζ,ζ′), with Ni_3-Si, Ni_3Si_2, and $NiSi_2$ having polymorphic transitions, respectively, at ~1163, 830, and 981 °C. The most Ni-rich

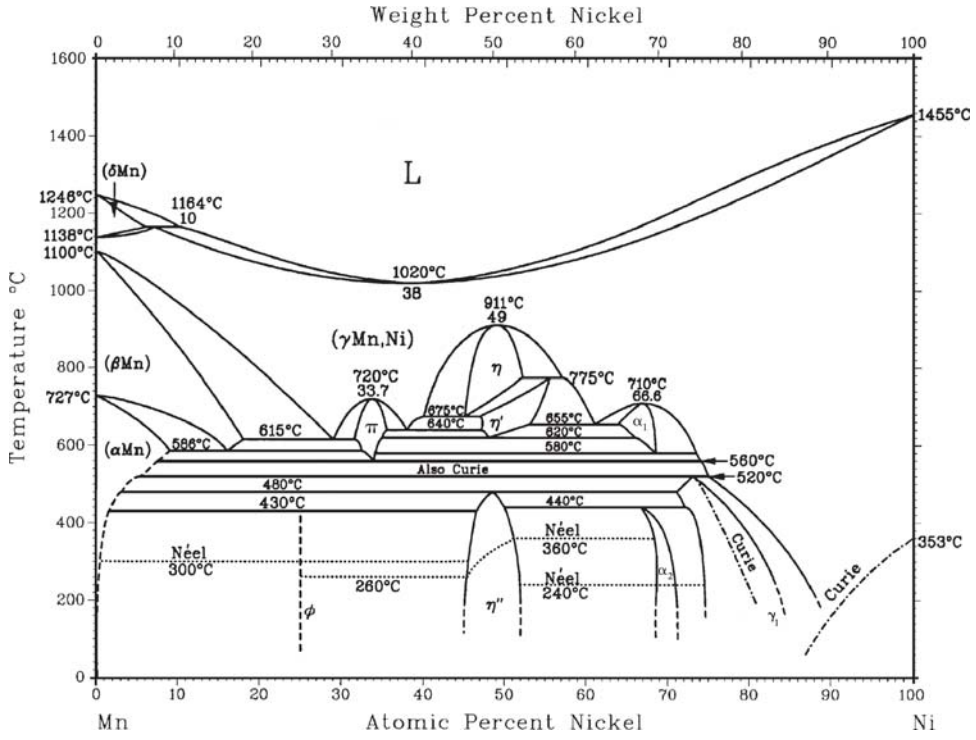

Fig. 1 Binary Mn-Ni diagram [Massalski2]

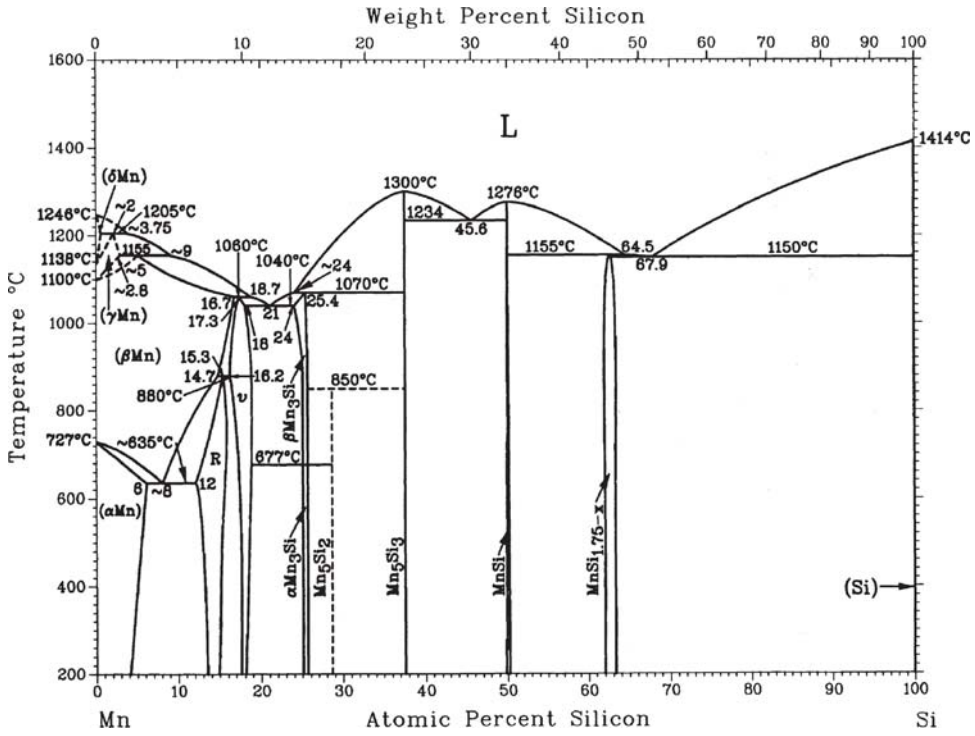

Fig. 2 Binary Mn-Si diagram [Massalski2]

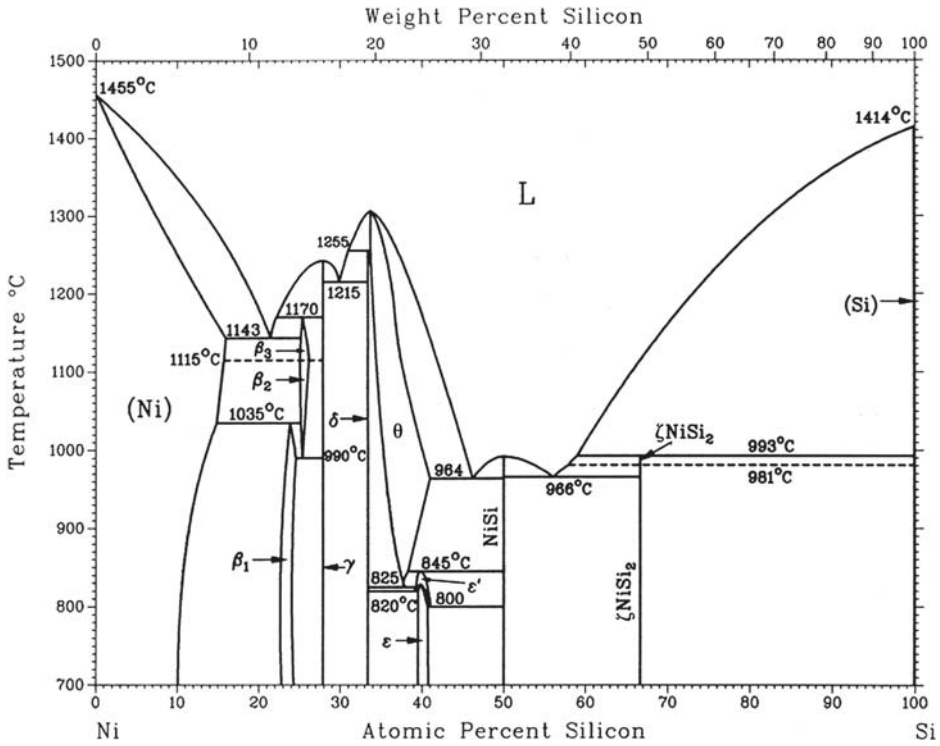

Fig. 3 Binary Ni-Si diagram [Massalski2]

phase is near a stoichiometry of Ni_3Si and is designated the β_1 phase, This phase participates in two invariant reactions with a neighboring phase; one invariant is a peritectoid reaction and the other is a eutectoid reaction. The stoichiometry of the neighboring phase is only slightly more Si-rich than β_1 with composition approximated as Ni_3-Si. This phase has been designated β_2 below its crystallographic transition and β_3 above the transition. The γ', θ, and ξ

Table 1 Binary and ternary phases in the Mn-Ni-Si system and their structure data

Phase designation	Composition	Pearsons symbol	Space group	Type	Lattice parameters, nm		
					a	*b*	*c*
γ	(γMn),(Ni),(Mn,Ni)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
δ	(δMn)	*cI*2	$Im\bar{3}m$	W	…	…	…
βMn	(βMn)	*cP*20	$P4_132$	βMn	…	…	…
αMn	(αMn)	*cI*58	$I\bar{4}3m$	αMn	…	…	…
Si	(Si)	*cF*8	$Fd\bar{3}m$	*C*(diamond)	…	…	…
γ_1	$MnNi_3$	*CP*4	*Pm*3*m*	$AuCu_3$	0.3589	…	…
α_1	$MnNi_2$ (H)	…	…	…	…	…	…
α_2	$MnNi_2$ (L)	…	…	…	…	…	…
η	MnNi (H)	*cP*2	$Pm\bar{3}m$	CsCl	0.29743	…	…
η′	MnNi (M)	*tF*4	*P*4/*mmm*	AuCu	0.37218	…	0.35295
η″	MnNi (L)	…	…	…	…	…	…
π	Mn_2Ni	…	…	…	…	…	…
ϕ	Mn_3Ni	…	…	…	…	…	…
R	Mn_6Si	*hR*53	$R\bar{3}$	R(Co,Cr,Mo)	1.0874	…	1.9177
ν	$Mn_{4.5}Si$	*oI*186	*Immm*	…	…	…	…
β′	βMn_3Si	*cF*16	$Fm\bar{3}m$	BiF_3	…	…	…
β'_1	αMn_3Si	…	…	…	…	…	…
κ	Mn_5Si_2	*tP*56	$P4_12_12_1$	…	…	…	…
ϕ	Mn_5Si_3	*hP*16	$P6_3/mcm$	Mn_5Si_3	0.6912	…	0.4812
τ	MnSi	*cP*8	$P2_13$	FeSi	0.4557	…	…
σ_1	$MnSi_{1.75-x}$	*tP*120	*P*4*m*2	…	…	…	…
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
σ	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	$Fm\bar{3}m$	CaP_2	0.5406	…	…
ζ′	$NiSi_2$	…	…	…	…	…	…
N	$Mn_{15}Ni_{40}Si_{45}$	…	…	…	…	…	…
Φ	$Mn_{15}Ni_{50}Si_{35}$	…	…	…	…	…	…
T/G (a)	$Mn_6Ni_{16}Si_7$	*cF*116	$Fm\bar{3}m$	$Mg_6Cu_{16}Si_7$	1.1158	…	…
E	MnNiSi	*oP*12	*Pnma*	$PbCl_2$	0.58967	0.36124	0.69162
Γ_1	$Mn_3Ni_3Si_2$	*hP*12	$P6_3/mmc$	$MgZn_2$	0.4762	…	0.7507
Γ_2	$M_2Ni_3Si_2$	*cF*24	$Fd\bar{3}m$	Cu_2Mg	0.6687	…	…
Ω	Mn_3Ni_2Si	*cF*96	$Fd\bar{3}m$	$NiTi_2$	1.0757	…	…
S	$Mn_{51}Ni_{23.5}Si_{25.5}$	*cF*16	$Fm\bar{3}m$	BiF_3(b)	…	…	…
R	$Mn_{16}Ni_{12}Si_{27}$	*hR*53	$R\bar{3}$	R(Co,Cr,Mo)	1.081	…	1.928
U	$Mn_{66}Ni_4Si_{30}$	…	…	…	…	…	…
W	$Mn_{51}Ni_{30}Si_{15}$	…	…	…	…	…	…
I	$Mn_{45}Ni_{28}Si_{27}$	…	…	…	…	…	. . .

(a)The T phase is more commonly known as the G phase [1963Spi]. (b) As identified in the Co-Mn-Si system S phase

phases melt congruently at 1242, 830, and 981 °C, respectively, There are four eutectic reactions: L ↔ (Ni) + β_3 at 1170 °C, L ↔ γ′ + δ′ at 1215 °C, L ↔ θ + ξ at 964 °C, and L ↔ ξ + ζ at 966 °C. The β_3, δ′, and ζ′ phases form by peritectic reactions: L + γ′ ↔ β_3 at 1170 °C, L + θ ↔ δ′ at 1255 °C, and L + (Si) ↔ ζ′ at 993 °C. Peritectoid reactions occur as: (Ni) + β_2 ↔ β_1 at 1035 °C and θ + ξ ↔ ϵ′ at 845 °C. Two eutectoid reactions occur: β_2 ↔ β_1 + δ′ at 990 °C and θ ↔ δ′ + ϵ at 825 °C. The somewhat unusual ranges of homogeneity involving the β_1, β_2, and β_3 and the ϵ, ϵ′, and θ′ phases are likely to make thermodynamic modeling of this system difficult.

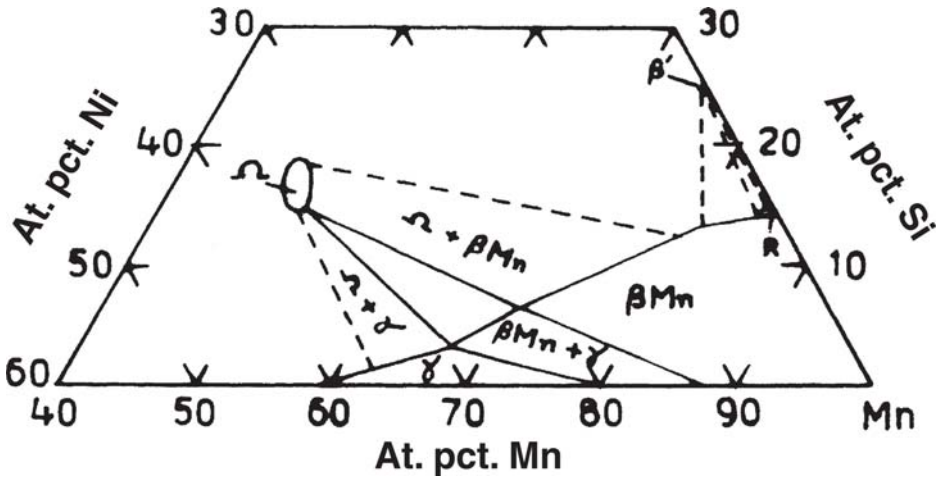

Fig. 4 Partial isothermal section of the Mn-Ni-Si system at 800 °C [1962Kuz]

Binary and Ternary Phases

The three binary systems Mn-Ni, Mn-Si, and Ni-Si have 21 binary intermediate phases, of which a few also have polymorphic forms. In the Mn-Ni-Si system, the existence of 12 ternary intermediate phases have been reported. The phases and their structure data are given in Table 1.

Ternary System

In search of ternary intermediate phases in various transition metal and nontransition metal systems, [1958Che] made a cursory study of the Mn-Ni-Si system. Electrolytic grade Mn and Ni plus Si (purity not specified) were used to melt alloys in porcelain crucibles under a layer of a KCl + NaCl mixture. The alloys were annealed at 400 °C for 10 days in sealed quartz capsules and x-ray diffraction (XRD) was used for phase identification. Two ternary intermediate phases were reported in this investigation—a $MgZn_2$-type Laves phase (Γ_1) of variable composition around the composition $Mn_3Ni_3Si_2$ and another phase of composition near MnNiSi, the XRD pattern of which matched well with that of the phase CoMnSi. The lattice parameter of the Laves phase was reported to be $a = 0.4792$ nm and $c = 0.7507$ nm, very close to those given in Table 1.

Two more ternary intermediate phases were reported in the Mn-Ni-Si system, a Cu_2Mg-type cubic Laves phase Γ_2 at the $MnNi_{1.55}Si_{0.45}$ by [1960Kuz] and a T phase at $Mn_6Ni_{16}Si_7$ composition [1961Gla] with $Mg_6Cu_{16}Si_7$-type structure. Phases with $Mg_6Cu_{16}Si_7$-type structure are now more commonly known as the G phase [1963Spi].

A more detailed investigation of the Mn-Ni-Si system was done by [1962Kuz] at the Mn corner. Seventy-seven alloys were prepared with Ni up to 40 at.% and Si up to 20 at.%. Alloys were prepared with 99.9 mass% Mn and Ni and 99.5 mass% Si by melting in porcelain crucibles under hydrogen with use of a high-frequency furnace. The alloys were sealed in quartz capsules, annealed at 800 °C for 120 h, and were then quenched in water. Phase analysis, phase identification and phase boundary determination were done using metallography and XRD. A partial isothermal section

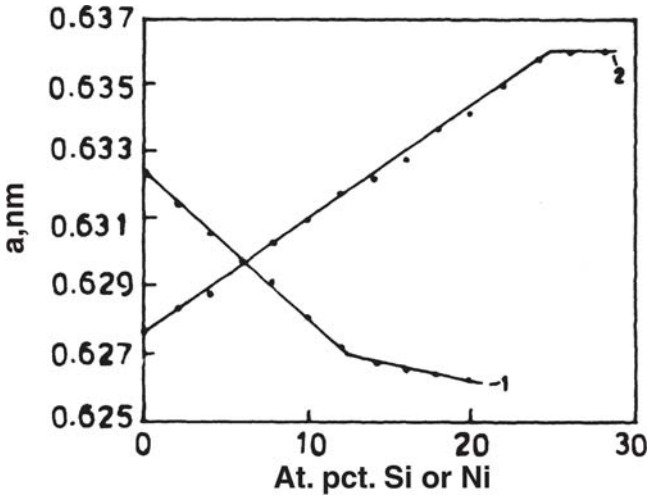

Fig. 5 Lattice parameter of βMn phase, (1) along 6 at.% Ni line and (2) along 6 at.% Si line [1962Kuz]

at the Mn corner of the Mn-Ni-Si system was proposed (Fig. 4). The lattice parameters of the βMn phase were measured along lines of 6 at.% Ni with variable Si/Mn ratio and of 6 at.% Si with variable Ni/Mn ratio. The results are shown in Fig. 5 and were used to locate the βMn phase boundaries. Along those composition lines the βMn was found to extend into the Mn-Ni-Si ternary system to approximately 25 at.% Ni and to approximately 12 at.% Si. A ternary intermediate phase Ω, was found to exist near the composition Mn_3Ni_2Si. The Ω phase was identified as a $NiTi_2$-type phase with lattice parameter $a = 1.0784$ nm, close to that given in Table 1. The Ω phase was found in equilibrium with the βMn phase and the fcc γ (Mn,Ni) phase.

[1964Kuz] subsequently proposed a complete 800 °C isothermal section through use of 240 alloys. Alloy preparation, heat treatment, and phase analysis methods were the same as those used by [1962Kuz]. This 800 °C isothermal section is given in Fig. 6. The solubilities of Ni in the Mn-Si binary phases and of Mn in the Ni-Si binary phases have been found to be very small. Exceptions occur for the $NiSi_2$

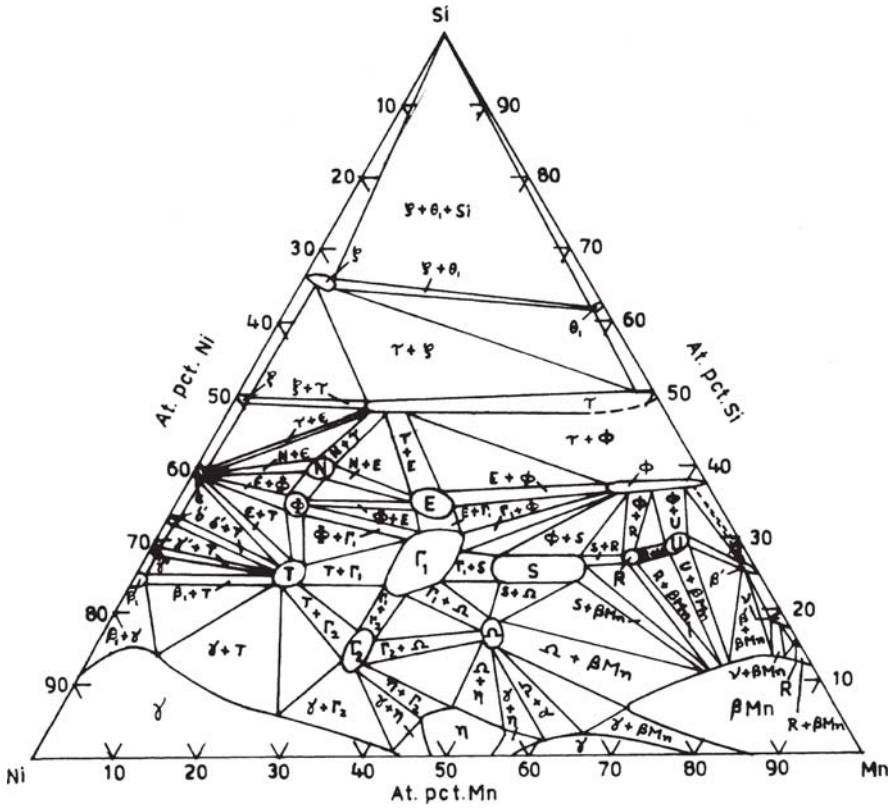

Fig. 6 Isothermal section of the Mn-Ni-Si system at 800 °C [1964Kuz]

(ζ), MnSi (γ), and Mn_5Si_3 (ϕ) phases. Above 50 at.% Si no ternary intermediate phase forms. The Ni_2Si phase, which was found to extend to ~4 at.% Mn, was found in equilibrium with the Mn $Si_{1.75-x}$ phase, and Si and the NiSi(gkt) phase were found in equilibrium with the MnSi phase. The MnSi phase was found to extend far into the ternary. Lattice parameters of the MnSi phase were measured as a function of Ni content (Fig. 7), and the results indicate the solubility of Ni in the MnSi phase to be ~35 at.%. Below 50 at.% Si 10 ternary intermediate phases were reported to be present in the Mn-Ni-Si system at 800 °C. The MnNiSi phase region was found in the composition region of ~28 to 33 at.% Mn and ~35 to 38 at.% Si. The MnNiSi phase has been identified as the E phase by [1969Jei] with lattice parameters $a = 0.5895$ nm, $b = 0.3611$ nm, and $c = 0.6898$ nm. A ternary phase N of unknown crystal structure was found to exist near the composition $Mn_{15}Ni_{40}Si_{45}$. Another phase Φ of unknown crystal structure was found near the composition $Mn_{15}Ni_{50}Si_{35}$. The N phase was found to be in equilibrium with the E, Φ, τ, and ϵ phases whereas the Φ phase was found in equilibrium with the ϵ, N, G, Γ_1, and E phases. The Φ phase diffraction pattern of an 800 °C annealed alloy was found to be diffuse, suggesting the possibility of instability of the Φ phase at 800 °C. The Φ phase alloy on annealing at 500 °C for 1000 h did not show many of the Φ phase diffraction lines, whereas new diffraction lines appeared that could not be identified. The T phase (i.e., the G phase) was found in equilibrium with the ϵ, δ′, γ′, β, γ, Γ_2, and Γ_1 phases. The Γ_2 phase exists along the 33.3 at.% Mn line from ~11 to 16 at.% Si and is about 2 at.% Mn wide.

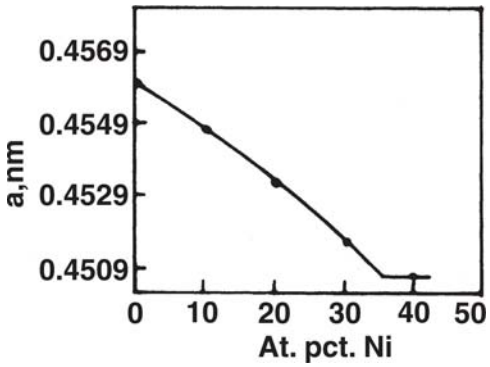

Fig. 7 Lattice parameter of MnSi phase as a function of Ni content [1964Kuz]

The lattice parameter of the Γ_2 phase was reported to be $a = 0.6668$ nm at 11 at.% Si and and $a = 0.6673$ nm at 15 at.% Si. The Γ_2 phase was found in equilibrium with T (or G), γ, η, Ω, and Γ_1 phases. The Γ_1 phase extends from 33 to 39 at.% Mn and 22 to 30 at.% Si. The lattice parameter of the Γ_1 phase at the lowest Si content was found to be $a = 0.4750$ nm and $c = 0.7500$ nm and for the maximum Si content $a = 0.4787$ nm and $c = 0.7428$ nm. The Γ_1 phase was found in equilibrium with the T (or G), Γ_2, Ω, S, Φ, E, and Φ phases. The Ω phase was found at around the composition Mn_3Ni_2Si, a small region, in equilibrium with the Γ_1, Γ_2, η, γ, βMn, and S phases. The Ω phase appeared to form in the solid state as this phase was not found in the as-cast nor in the 1000 °C annealed condition. The S phase,

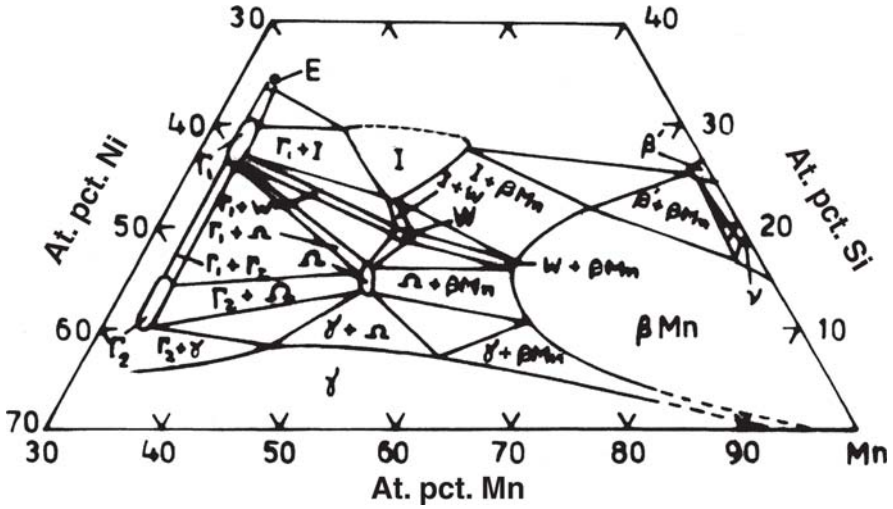

Fig. 8 Partial isothermal section of the Mn-Ni-Si system at 1000 °C [1966Bar]

which is isostructural with the S phase of the Co-Mn-Si system, was found to extend along the 25 at.% Si line from ~42 to 54 at.% Mn.

The S phase was found in equilibrium with the Γ, Ω, βMn, R, and ϕ phases. The ternary R phase occurs near the $Mn_{61}Ni_{12}Si_{27}$ composition and is isostructural with the R (Co, Cr, Mo) and R (Mn_6Si) phases. Whether the ternary R phase is an extension of the binary R (Mn_6Si) phase is not known and should be investigated. The U phase exists at the $Mn_{66}Ni_4Si_{30}$ composition and is isostructural with the U phase of the Co-Mn-Si system. Both the ternary R phase and the U phase were found in equilibrium with the ϕ and βMn phases and the latter phase was found in equilibrium with the β′ phase.

A partial isothermal section at the Mn corner of the Mn-Ni-Si system was proposed by [1966Bar] at 1000 °C. Electrolytic Mn and Ni of 99.9 mass% purity and Si of 99.98 mass% purity were melted in an induction furnace in recrystallized alumina crucibles, annealed in argon- or He-filled silica capsules at 1000 °C (annealing time not given), and quenched in water. Metallography and XRD were used for phase analysis, phase-boundary determination, and phase identification. The partial isothermal section of the Mn-Ni-Si system at 1000 °C is given in Fig. 8. The existence of six ternary intermediate phases, E, Γ_1, Γ_2, Ω, W, and I are included in this partial section. The E phase region was not determined and is shown in the diagram by a dashed line. The Γ_1 phase region was found to be much smaller in size than at 800 °C and extended along the 33.3 at.% Mn line from ~37 to 40 at.% Si and is ~2 at.% Mn wide. The Γ_2 phase region is about the same size at both 800 and 1000 °C. Unlike the reported absence of the Ω phase at 1000 °C by [1964Kuz], a small Ω phase region was found to exist at 1000 °C [1966Bar] at a slightly lower Si content of ~14 at.% Si and ~50 at.% Mn.

The S phase was not found at 1000 °C, but in the same composition region of the S phase a new phase I was found. The I phase extends from ~42 to 52 at.% Mn and ~24 to 30 at.% Si. The I phase was also found in the Co-Mn-Si system at 1000 °C. Between the I and Ω phase regions a new phase W was found near the composition $Mn_{51}Ni_{30}Si_{19}$. The R phase and U phase were not detected at 1000 °C in the composition region of this investigation of the Mn-Ni-Si system.

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*indicates key paper.
#indicates presence of a phase diagram.

Mn-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 alloys.