JPEDAV (2005) 26:379-384
DOI: 10.1361/154770305X56872
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The Mo-Ni-Si (Molybdenum-Nickel-Silicon) System

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Introduction

The Mo-Ni-Si system has been studied by several investigators. Several isothermal sections have been established and are reported here.

Binary Systems

The Mo-Ni System [1991Nas] (Fig. 1) has three intermediate phases: δ (MoNi); $MoNi_3$; and $MoNi_4$. All of these phases form through peritectic or peritectoid reactions: L + (Mo) ↔ δ at 1362 °C; (Ni) + δ ↔ $MoNi_3$ at 910 °C; and (Ni) + $MoNi_3$ ↔ $MoNi_4$ at 870 °C. Only one eutectic reaction, L ↔ δ + (Ni), occurs at 1317 °C.

The Mo-Si system [Massalski 2] (Fig. 2) has three intermediate phases, Mo_3Si, Mo_5Si_3, and $MoSi_2$, of which Mo_3Si and $MoSi_2$ are single-composition phases. Although the Mo_5Si_3 and $MoSi_2$ phases melt congruently at ~2180 and ~2050 °C, respectively, the Mo_3Si phase forms through a peritectic reaction, L + (Mo) ↔ Mo_3Si at ~2025 °C. The $MoSi_2$ phase exists in two polymorphic forms, β$MoSi_2$ above 1900 °C and α$MoSi_2$ below 1900 °C. Three eutectic reactions, L ↔ Mo_3Si + Mo_5Si_3, L ↔ Mo_5Si_3 + α$MoSi_2$, and L ↔ $MoSi_2$ + (Si), occur at 2020, ~1900, and ~1480 °C, respectively.

The Ni-Si system [1991Nas] (Fig. 3) has eight intermediate phases, Ni_3Si (β), 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 $NiSi_2$ (ζ and ζ′), of which several phases have polymorphic forms: β_2 and β_3 at ~25 at.% Si, ϵ and ϵ′ at ~46 at.% Si, and α and β at ~66.7 at.% Si. These polymorphic transitions occur, respectively, at ~1165, a 830°, and 981 °C. 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 + γ′ ↔ β_3 at 1178 °C; L + θ ↔ δ′ at 1255 °C; L + (Si) ↔ ζ′ at 993 °C; (Ni) + β_2 ↔ β_1 at 1035 °C; and θ + ξ ↔ ϵ′ at 845 °C. There are eight eutectic or eutectoid reactions in the Ni-Si system: L ↔ γ + β_3 at 1145 °C; L ↔ γ′ + δ′ at 1215 °C; L ↔ θ + ξ at 964 °C; L ↔ ξ + ζ at 966 °C; β_2 ↔ β_1 + γ′ at 990 °C; θ ↔ δ′ + ϵ at 825 °C; ϵ′ ↔ δ′ + ϵ at 820 °C; ϵ ↔ ϵ′ + ξ at 800 °C; and ϵ ↔ ϵ′ + δ′ at 820 °C. The γ′, δ′, ξ, and ζ phases are single-composition phases.

Binary and Ternary Phases

There are 14 binary intermediate phases in the Mo-Ni-Si system. Several of them, however, exist in two polymorphic forms. Four ternary intermediate phases have been found to exist in the Mo-Ni-Si system. The structure data for all of the binary and ternary phases are given in Table 1.

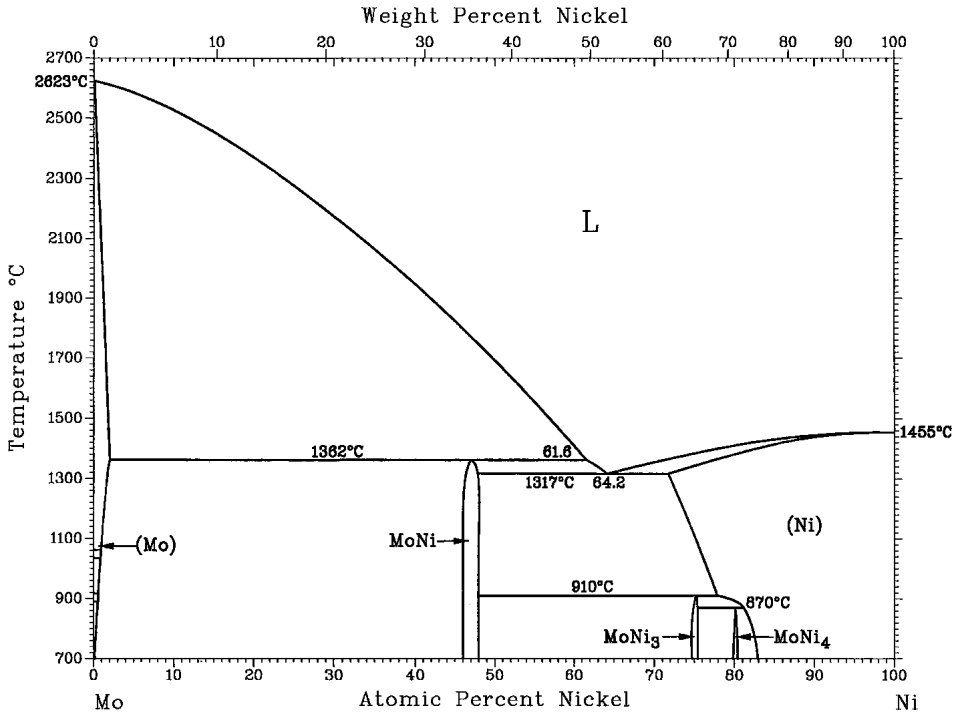

Fig. 1 Mo-Ni phase diagram [1991Nas]

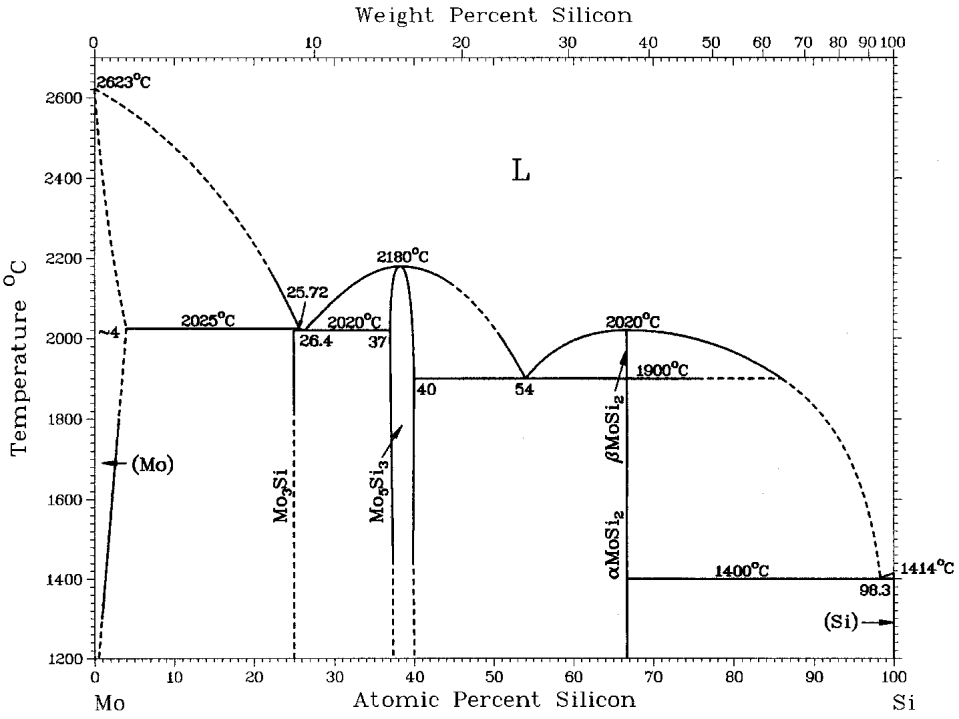

Fig. 2 Mo-Si phase diagram [Massalski 2]

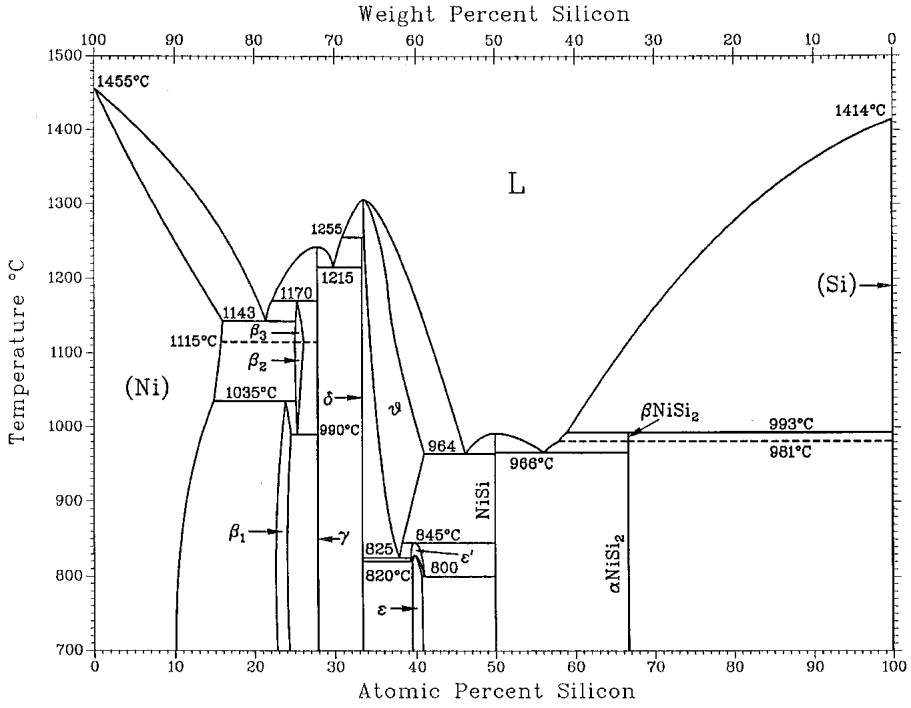

Fig. 3 Ni-Si phase diagram [1991Nas]

Ternary System

An early investigation [1925Pfa] of the high Ni region of the Mo-Ni-Si system at 700 °C has been quoted by several later investigators [1959Gua, 1969Vir]. The existence of a ternary intermediate phase was reported by [1925Pfa]. However, [1959Gua] suggested that the Ni solid-solution boundary line as well as the position of the reported ternary intermediate phase were not determined accurately. Hence, [1959Gua] studied the Ni-rich region of the Mo-Ni-Si sys-

Table 1 Structure data of binary and ternary phases of the Mo-Ni-Si system

Phase designation	Composition(a)	Pearson symbol	Space group	Type	Lattice parameter, nm		
					a	*b*	*c*
γ	(Ni)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
α	(Mo)	*cI*2	$Im\bar{3}m$	W	…	…	…
Si	(Si)	*cF*8	$Fd\bar{3}m$	C(diamond)	…	…	…
ν	$MoNi_4$	*tI*10	*I*4/*m*	$MoNi_4$	0.5720	…	0.3564
κ	$MoNi_3$	*oP*8	*Pmnn*	βCu_3Ti	0.5064	0.4224	0.4448
δ	MoNi	*oP*56	$P2_12_12_1$	δ(MoNi)	0.9108	0.9108	0.8852
ρ	Mo_3Si	*cP*8	$Pm\bar{3}m$	Cr_3Si	0.489	…	…
τ	Mo_5Si_3	*tI*38	*I*4/*mcn*	W_5Si_3	0.728	…	0.500
π	$\alpha MoSi_2$	*tI*6	*I*4/*mmm*	$MoSi_2$	0.320	…	0.787
π′	$\beta MoSi_2$	…	$C6_22$	…	…	…	…
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	0.507
						β = 48.74°	
β_3	Ni_3Si(24.5-25.5)	*mC*16	…	…	0.704	0.626	0.508
						β = 48.84°	
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	$NiSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5406	…	…
ζ′	$NiSi_2$	…	…	…	…	…	…
Γ_1	$Mo_{33.3}Ni_{50}Si_{16.7}$	*hP*12	$P6_3/mmc$	$MgZn_2$	0.4709	…	0.7655
Γ_1'	$Mo_{32}Ni_{50.5}Si_{17.5}$	…	…	(b)	…	…	…
Γ_1''	$Mo_{32}Ni_{38}Si_{30}$	…	…	(b)	…	…	…
μ	$Mo_{50}Ni_{40}Si_{10}$	*R*13	$R\bar{3}m$	W_6Fe_7	0.4731	…	2.570(c)(d)
R	$Mo_{55}Ni_{42}Si_3$	*R*53	$R\bar{3}$	R(Mo,Co,Cr)	1.102	…	1.963(c)(d)

(a) Composition of phases in at.%. (b) Possibly closely related to the $MgZn_2$-type Laves phase. (c) Lattice parameters from [1969Vir]. (d) Lattice parameters for hexagonal cell

tem in the composition region Ni-MoNi-NiSi. Alloys were prepared by arc melting high-purity component elements (Mo 99.92 mass% purity, Si 99.98 mass% purity, and carbonyl Ni containing ≤0.1 mass% impurity) and homogenized at 1100 °C for 72 h in dry hydrogen. At the Ni corner, the alloys were also annealed at 900 °C for 144 h to determine the phase boundary of the Ni solid-solution region. Phase analysis was done by x-ray diffraction (XRD) and metallography.

The partial isothermal section at 1100 °C established by [1959Gua] is given in Fig. 4. The presence of a ternary intermediate phase, ϕ, was reported along the line joining MoNi and NiSi at ~28 at.% Si. The ϕ-phase was not identified. The ϕ-phase was reported to be in equilibrium with the δ, γ, β_1, γ′, δ′, θ, and ξ-phases. At 900 °C, the Ni solid-solution phase γ was found to have smaller solubility of Mo and Si than at 1100 °C, which is to be expected on the basis of Mo-Ni and Ni-Si binary data. The dash-dot line in Fig. 4 indicates the region of high Si content at which the alloys melted at 1100 °C. The phase equilibria shown in this region correspond to a lower temperature, possibly 900 °C.

The ϕ phase was later identified by [1960Gla] to be a $MgZn_2$-type Laves phase. In search of Laves phases stabilized by Si, [1961Bar] found the alloy Mo_2Ni_3Si to be of $MgZn_2$-type Laves phase at 1200 °C, indicating that the Laves phase is stable at high temperatures. The lattice parameters of the Mo_2Ni_3Si Laves phase were found to be $a = 0.47$ nm and $c = 0.747$ nm.

A more complete investigation of the Mo-Ni-Si system was done by [1969Vir]. High-purity Ni (purity not indicated), 99.9^+ mass% Mo and 99.9999 mass% Si were arc-melted in argon to prepare the alloys. The alloys were wrapped in Mo foil and sealed in evacuated quartz capsules, and were annealed for 1 week at 950 °C, the capsules were then cooled in air. Only XRD was used for the characterization of the alloys. The isothermal section of the Mo-Ni-Si system at 950 °C is given in Fig. 5. Fig. 5 shows the presence of three ternary intermediate phases Γ_1, μ, and R. The presence of the R and μ phases in the Mo-Ni-Si system was reported earlier by [1965Sko] and [1966Sko], respectively. The Γ_1 phase, an $MgZn_2$-type Laves phase, was found to be a narrow (~2–3 at.% wide) region extending along the 33.3 at.% Mo line from ~15 to ~35 at.% Si. The μ-phase was found to be a very narrow V-shaped region, and the R-phase region was found to be an inverted triangular region ~7 at.% Mo wide and extending from about 2 to ~16 at.% Si. The

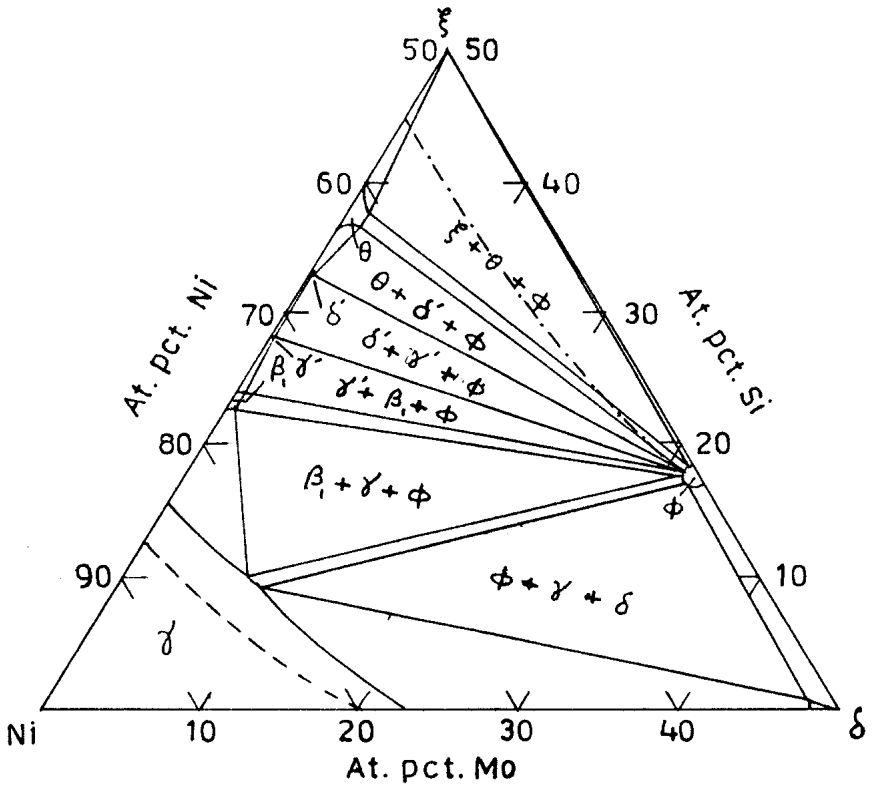

Fig. 4 A partial isothermal section of the Mo-Ni-Si system at the Ni-δ (MoNi) – ξ (NiSi) region at 1100 °C. The dash-dot line indicates the composition region of high Si content in which the alloys melted at 1100 °C. The dashed line shows the γ phase boundary at 900 °C [1959Gua].

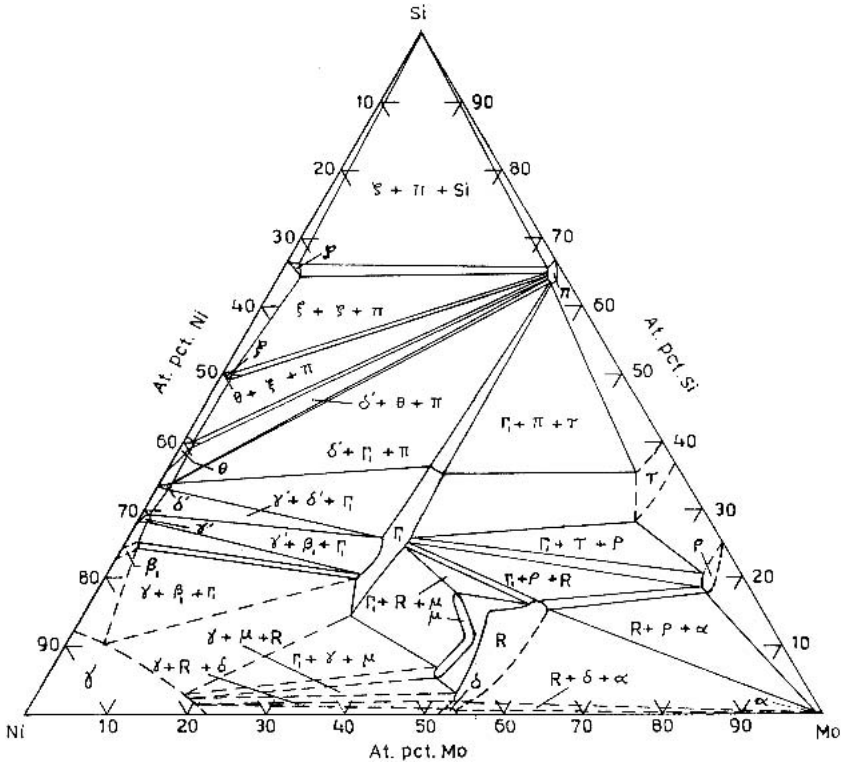

Fig. 5 The 950 °C isothermal section of the Mo-Ni-Si system [1969Vir]

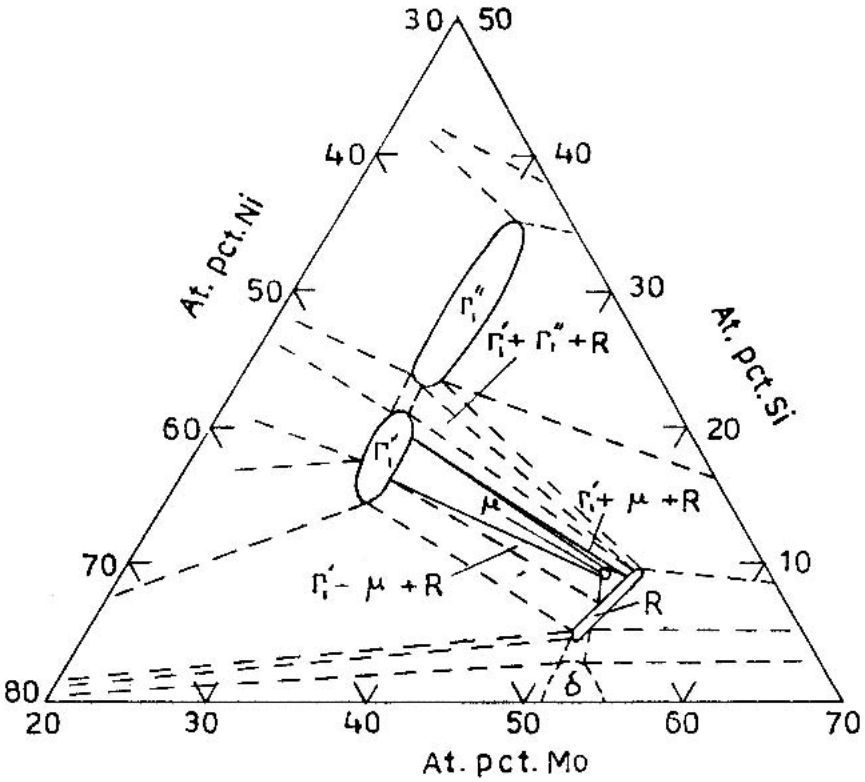

Fig. 6 A partial isothermal section of the Mo-Ni-Si system at 1280 °C [1979Sin]

MoNi δ phase did not extend to more than ~1 at.% Si. The lattice parameters of the μ and R phases were determined from two-phase alloys and are given in Table 1. The lattice parameters for the alloy with Mo_2Ni_3Si composition was found to be $a = 0.4709$ nm and $c = 0.7655$ nm, which is in reasonable agreement with [1961Bar]. Unlike [1959Gua], [1969Vir] showed that at lower temperatures the Γ_1 phase is in equilibrium with γ, β_1, γ′, δ, θ, π, τ, and ρ phases but is not in equilibrium with the ξ on Mo solid-solution phase α. In the low-Si content region, the three phase boundaries were not determined accurately, and the γ phase boundary was also not determined. The R phase was found to be in equilibrium with the γ, δ, α, μ, Γ_1, and ρ phases, and the μ phase was found to be in equilibrium with the γ, Γ_1, and R phases. [1969Vir] showed that all of the binary phases had some solid solubility, whereas the accepted binary data show that some of the phases are single-composition phases. Hence, in Fig. 5 the phase boundaries of some of the intermediate phases have been adjusted to conform to the binary data.

[1979Sin], in their study of crystal chemistry of complex phases present in the Mo-(Fe, Co, Ni)-Si systems, determined a partial isothermal section of the Mo-Ni-Si system at 1280 °C. The alloys were arc-melted using 99.9 mass% pure component elements near the MoNi δ phase region, up to ~40 at.% Si. The alloys were annealed at 1280 °C for 4 days in evaeuated quartz capsules and quenched in cold water. Characterization of the alloys was done using metallography and x-ray diffraction. Figure 6 shows the partial isothermal section of the No-Ni-Si system at 1280 °C. At 1280 °C, the R-phase was found to be a very narrow (~1 at.% wide) lens-shaped region extending from ~5 to ~9 at.% Si, and the μ phase was found to be a very small region. Two other intermediate phases, Γ_1' and Γ_1'', were detected around the alloy compositions $Mo_{33}Ni_{50.5}Si_{17.5}$ (Γ_1') and $Mo_{32}Ni_{38}Si_{30}$ (Γ_1'') extending from ~16 to 21 at.% Si and ~23 to ~35 at.% Si, respectively. The XRD patterns of both the phases resembled closely the XRD pattern of the $MgZn_2$-type Laves phase but had many extra diffraction lines that could not be accounted for on the basis of $MgNi_2$-type Laves phase. Thus, the Γ_1' and Γ_1'' phases appear to be closely related to the $MgZn_2$-type Laves phase. The results of [1969Vir] and [1979Sin] indicate that both the R and μ-phase regions become small as the temperature increases and suggest that these phases possibly form through peritectic reactions or they melt congruently. The $MgZn_2$ Laves phase was found to be stable between 900 and 1200 °C, but above 1200 °C the two $MgZn_2$-related Laves phases form. Further investigation of the Mo-Ni-Si system should be done to determine how the μ and R phases form, up to what temperature the $MgZn_2$ and its related Laves phases remain stable, and how they form.

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