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The Co-Nb-Si (Cobalt-Niobium-Silicon) System

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Introduction

The Co-Nb-Si system has been investigated in the temperature range of 800-1300 °C and three isothermal sections have been established. The existence of seven ternary intermediate phases has been reported.

Binary Systems

The Co-Nb system [Massalski2] shows the presence of three intermediate phases Co_3Nb (λ_3), Co_2Nb, and Co_6Nb_7 (μ), of which the Co_6Nb_7 and Co_2Nb phases melt congruently at 1402 and 1480 °C, respectively. The Co_2Nb phase is known to have two polymorphic forms, Co_2Nb (λ_2), a Cu_2Mg type Laves phase and Co_2Nb (λ_1), a $MgZn_2$ type Laves phase, the latter phase has been reported to exist above 1225 °C [1964Kuz2]. The λ_3 phase, a $MgNi_2$ type Laves phase, forms through a peritectic reaction $L + Co_2Nb \leftrightarrow \lambda_3$ at 1247 °C. Three eutectic reactions $L \leftrightarrow \alpha + \mu$, $L \leftrightarrow \mu + Co_2Nb$ and $L \leftrightarrow \gamma + \lambda_3$ occur at 1374, 1378, and 1237 °C, respectively. The α and γ phases are the terminal solid solutions (Nb) and (αCo), respectively.

The Co-Si system [Massalski2] has five intermediate phases, Co_3Si (ϕ), αCo_2Si (ρ_1), βCo_2Si (ρ_2), CoSi (ζ), and $CoSi_2$ (π) 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 $L + \alpha Co_2Si \leftrightarrow Co_3Si$ at 1214 °C and $L + \beta Co_2Si \leftrightarrow \alpha Co_2Si$ 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 and the βCo_2Si phases exist only at higher temperatures and decompose through eutectoid reactions $Co_3Si \leftrightarrow (\varepsilon Co) + \alpha Co_2Si$ at 1193 °C and $\beta Co_2Si \leftrightarrow$

Table 1 Binary and ternary intermediate phases of the Co-Nb-Si system and their structure data

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameter, nm		
					a	*b*	*c*
γ	(αCo)	*cF*4	$Fm\bar{3}m$	Cu	···	···	···
ε	(εCo)	*hP*2	$P6_3/mmc$	Mg	···	···	···
α	(Nb)	*cI*2	$Im\bar{3}m$	W	···	···	···
Si	(Si)	*cF*8	$Fd\bar{3}m$	C (diamond)	···	···	···
λ_3	Co_3Nb	*hP*24	$P6_3/mmc$	$MgNi_2$	0.47407	···	1.54525
λ_2	αCo_2Nb	*cF*24	$Fd\bar{3}m$	Cu_2Mg	0.6758	···	···
λ_1	βCo_2Nb	*hP*12	$P6_3/mmc$	$MgZn_2$	0.4834	···	0.7853
μ	Co_7Nb_6	*hR*13	$R\bar{3}m$	Fe_7W_6	0.492	···	2.628
ϕ	Co_3Si	*t*	···	···	···	···	···
ρ_1	αCo_2Si (32-34)	*oP*12	*Pnma*	Co_2Si	0.7109	0.4918	0.3738
ρ_2	βCo_2Si (32-35.8)	···	···	···	···	···	···
ζ	CoSi	*cP*8	$P2_13$	FeSi	0.4447	···	···
π	$CoSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5376	···	···
κ	Nb_3Si	*tP*32	$P4_2/n$	PTi_3	···	···	···
ν_2	βNb_5Si_3	*tI*32	*I*4/*mcm*	Si_3W_5	1.002	···	0.507
ν_1	αNb_5Si_3	*tI*32	*I*4/*mcm*	B_3Cr_5	0.657	···	1.188
η	$NbSi_2$	*h*P9	$P6_222$	$CrSi_2$	0.4795	···	0.6589
θ	$CoNb_4Si$	*tP*12	*P*4/*mcc*	$CoNb_4Si$ (1)	0.6189	···	0.5053
E	CoNbSi	*oP*12	*Pnma*	Co_2Si	0.6231	0.3660	0.7070
H	Co_2Nb_3Si (2)	*cF*96	$Fd\bar{3}m$	$NiTi_2$	1.1196	···	···
λ_1	Co_3Nb_2Si	*hP*12	$P6_3/mmc$	$MgZn_2$	0.4794	···	0.7760
ψ, V	$Co_4Nb_4Si_7$	*tI*60	*I*4/*mmm*	$Co_4Ge_7Zr_4$	1.2557	···	0.4981
Φ	Co_4NbSi_3	*hP*168	*P*6/*mmm*	···	1.7182	···	0.7918
T (G)	$Co_{16}Nb_6Si_7$	*cF*116	$Fm\bar{3}m$	$Mn_{23}Th_6$	1.1251	···	···

(1) Related to Al_2Cu type
(2) This phase is stabilized by carbon [1967Sko]

$\alpha Co_2Si + CoSi$ at 1286 °C. The four eutectic reactions $L \leftrightarrow (\varepsilon Co) + Co_3Si$, $L \leftrightarrow \beta Co_2Si + CoSi$, $L \leftrightarrow CoSi + CoSi_2$ and $L \leftrightarrow CoSi_2 + (Si)$ occur at 1204, 1286, 1310, and 1259 °C, respectively. The $CoSi_2$ phase is of invariant composition.

The Nb-Si system [Massalski2] has four intermediate phases, Nb_3Si (κ), αNb_5Si_3 (ν_1), βNb_5Si_3 (ν_2), and $NbSi_2$ (η), of which the βNb_5Si_3 and $NbSi_2$ phases melt congruently at 2520 and 1940 °C, respectively. The Nb_3Si phase forms through a peritectic reaction $L + \beta Nb_5Si_3 \leftrightarrow Nb_3Si$ at 1980 °C. The αNb_5Si_3 phase forms through a peritectoid reaction $Nb_3Si + \beta Nb_5Si_3 \leftrightarrow \alpha Nb_5Si_3$ at 1940 °C. The Nb_3Si and the βNb_5Si_3 phases undergo eutectoid transformations: $Nb_3Si \leftrightarrow \alpha + \alpha Nb_5Si_3$ and $\beta Nb_5Si_3 \leftrightarrow \alpha Nb_5Si_3 + NbSi_2$ at 1770 and 1650 °C, respectively. Three eutectic reactions $L \leftrightarrow \alpha + Nb_3Si$, $L \leftrightarrow \beta Nb_5Si_3 + NbSi_2$ and $L \leftrightarrow NbSi_2 + (Si)$ occur at 1920, 1900, and 1400 °C, respectively.

Binary and Ternary Phases

There are 12 binary intermediate phases in the three binary systems Co-Nb, Co-Si, and Nb-Si. Seven ternary intermediate phases have been reported to form in the Co-Nb-Si ternary system. The binary and ternary phases and their structure data are given in Table 1.

Ternary System

In search of ternary silicides [1964Kuz1] studied the Co-Nb-Si system. [1964Kuz1] used 99.3 mass% Nb, 99.26 mass% Co, and 99.99 mass% Si to melt alloys in alumina crucibles under hydrogen gas atmosphere. The alloys were sealed in evacuated quartz capsules and annealed at 800 °C to 750 h. Thirty-five alloys up to ~40 at.% Si were studied using x-ray diffraction (XRD) and metallography. Six ternary intermediate phases were reported to be present in the investigated composition region of the Co-Nb-Si system. These phases are: a T phase at $Co_{16}Nb_6Si_7$ composition, a λ_1 phase at 33.3 at.% Nb, and between 15 and 20 at.% Si, and H phase at around the Co_2Nb_3Si composition, a ψ phase at 15 at.% Co, 45 at.% Nb, and 40 at.% Si, a Φ phase in the composition range of 40-50 at.% Co, 20-33 at.% Nb, and 30-35 at.% Si and a θ phase at 15 at.% Co and 15-20 at.% Si. The Co_2Nb_3Si phase with lattice parameter a = 1.196 nm was identified as the Mn_3Ni_2Si type phase with a superstructure of $NiTi_2$ phase. The λ_1 phase was identified as the $MgZn_2$ type Laves phase with lattice parameters a = 0.4794 nm and c = 0.7760 nm. The $Co_{16}Nb_6Si_7$ phase (T) was identified as the $Mg_6Cu_{16}Si_7$ type phase with Th_6Mn_{23} type structure and with lattice parameter a = 1.1251 nm. The T phase was reported to be in equilibrium with the Co_2Si, Co_3Nb, λ_1, and Φ phases. The λ_1 phase was found in equilibrium with the Co_3Nb, Co_2Nb, Φ and H phases. [1964Kuz2] studied the

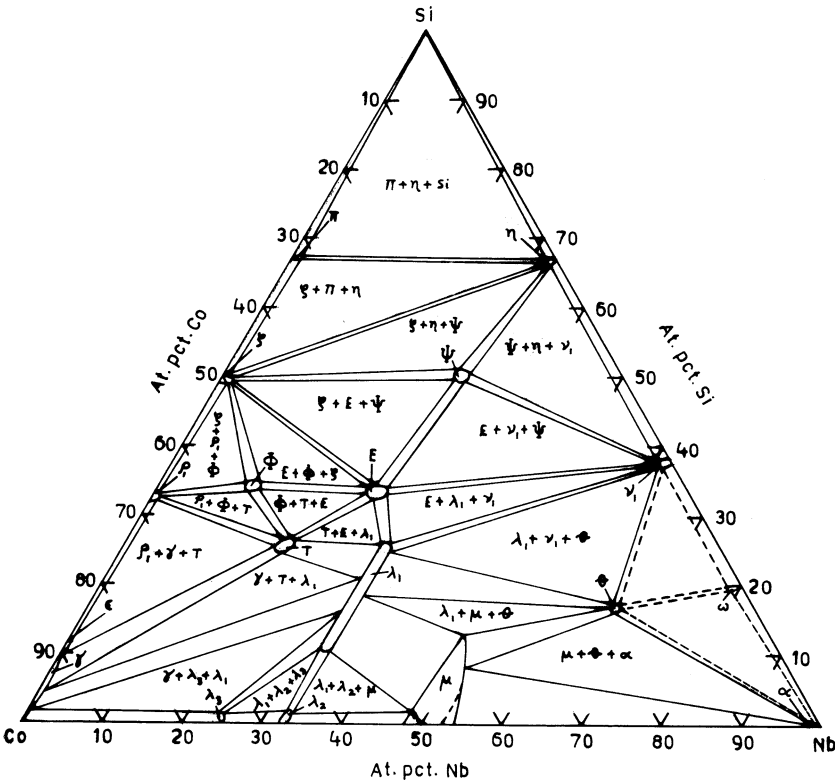

Fig. 1 An isothermal section of the Co-Nb-Si system at 800 °C [1967Sko]

Co-Nb system at the Co_2Nb composition and observed that the Co_2Nb phase is of $MgCu_2$ type cubic Laves phase up to about 1200 °C and above 1225 °C the Co_2Nb phase is of hexagonal $MgZn_2$ type Laves phase with lattice parameters a = 0.4834 nm and c = 0.7853 nm. On addition of Si to Co_2Nb phase, annealed at 1300 °C for 2 h showed that the $MgZn_2$ type phase extends into the ternary Co-Nb-Si system, i.e., the high temperature $MgZn_2$ type Laves phase is stabilized by Si. The λ_1 phase found by [1964Kuz1] in the Co-Nb-Si system thus appears to be an extension of the high temperature $MgZn_2$ type Laves phase stabilized to lower temperatures due to addition of Si and is not truly a ternary intermediate phase. [1965Gla] used a slightly higher purity component elements to melt alloys near the 66.7 at.% Nb and 15-20 at.% Si, i.e., in the composition range in which the θ phase was reported by [1964Kuz1] and annealed the alloys at 1100 °C for 90 h followed by annealing at 800 °C for 750 h. The θ phase composition was found to be $CoNb_4Si$, with $CuAl_2$ type structure, and the lattice parameters were reported to be a = 0.6189 nm and c = 0.5053 nm.

The Co-Nb-Si system has been studied in more detail by [1967Sko]. Eighty-three alloys were prepared using 99.9 mass% Co and Nb and 99.999 mass% Si, in an arc furnace under argon atmosphere. The alloys, sealed in evacuated quartz capsules, were annealed at 800 °C for 2400 h. Phase analysis of the alloys were carried out using XRD and metallographic methods. The 800 °C isothermal section by [1967Sko] is given in Fig. 1. The isothermal section at 800 °C shows the presence of six intermediate phases within the ternary: $Co_2Nb_3Si_5$ (ψ), a phase at $Co_{1.15}Nb_{0.85}Si$ composition (E), $Co_{16}Nb_6Si_7$ (T), Co_3Nb_2Si (λ_1), $CoNb_4Si$ (θ) and a phase at $Co_{54.7}Nb_{12.0}Si_{33.3}$(Φ). The T phase has been identified to be the G phase [1963Spi]. The Co_2Nb_3Si (H) phase, however, was not observed in the arc melted alloys and it was concluded that this phase gets stabilized by carbon during the process of melting used by [1964Kuz1]. The E phase, which has an ideal composition of AB Si [1963Spi, 1969Jei] was found with slightly shifted composition of higher Co content. The Co_3Nb_2Si (ψ) phase was found to be of tetragonal structure with lattice parameters a = 1.252 nm and c = 0.497 nm. The ψ phase was found in equilibrium with the $NbSi_2$ (η), CoSi (ζ), E, and αNb_5Si_3 (ν_1) phases. The Φ phase was found in equilibrium with the Co_2Si (ρ_1), ζ, T (G), and E phases. The existence of the $CoNb_4Si$ (θ) was confirmed by [1967Sko] and it was found in equilibrium with the α, μ, ν_1, and λ_1 phases. A probable equilibrium of the θ phase with a Nb_4Si (ω) also has been indicated by [1967Sko]. Since the accepted Nb-Si binary does not support the existence of the Nb_4Si phase and the Nb_3Si phase exists only above 1770 °C, the probable equilibrium of the θ phase with Nb_4Si or Nb_3Si is not possible at 800 °C. The λ_1 phase exists between ~10 and ~27 at.% along the 33.3 at.% Nb composition and is found in equilibrium with the E, T(G), γ, λ_2, μ, θ, and ν_1 phases. The binary phases λ_3, λ_2, ρ_1, ζ, π, η, ν_1, of the Co-Nb, Co-Si and Nb-Si systems extend only marginally into the ternary. Only the μ phase of the Co-Nb system was found to extend into the ternary up to ~12 at.% Si.

The Co-Nb-Si system was investigated by [1972Sin] in the composition range of 25-70 at.% Nb and up to ~25 at.% Si with a limited goal of finding the stabilization of the μ and the Laves phases of the Co-Nb system by Si. Pure metals 99.9 mass% Nb and Si and 99.5 mass% Co were used to prepare the alloys by arc melting under argon atmosphere. The alloys, sealed in evacuated silica capsules, were annealed at 1100 °C for 3 days and water quenched. Metallography and XRD methods were used for phase analysis. The partial isothermal section of the Co-Nb-Si system by [1972Sin] is given in Fig. 2. Figure 2 shows that the μ phase extends up to ~15 at.% Si and is found in equilibrium with the α, ν_1, and Laves phases. Two Laves phases λ_2 and λ_1 were observed. The Cu_2Mg type λ_2 phase extended from the Co-Nb binary only up to <5 at.% Si and the $MgZn_2$ type Laves phase λ_1 was found between 5 to 15 at.% Si. While at 1100 °C, the μ-phase extension into the ternary was found about the same as that reported by [1964Kuz1] and [1967Sko], the λ_1 phase extension was found smaller than that at 1300 and 800 °C.

[1974Ste1] investigated the Co-Nb-Si system between ~20 at.% Si and ~70 at.% Si. The alloys were prepared by reacting Co and Nb powders in the presence of tetrachloride of silicon, homogenized at the reaction temperature (not specified) for 120 h. The reaction products were then melted

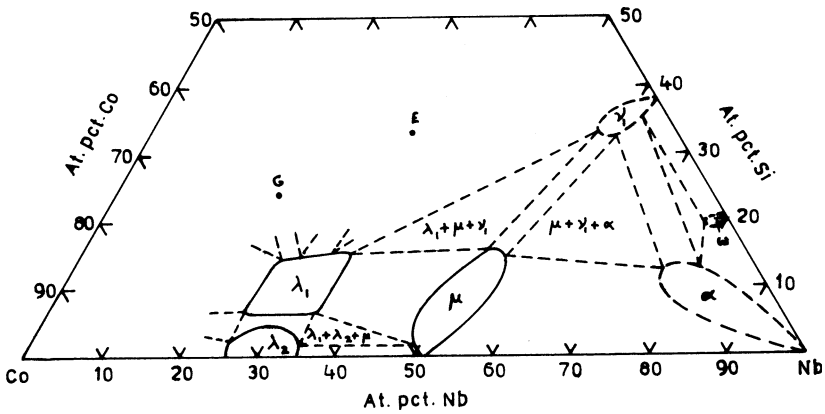

Fig. 2 A partial isothermal section of the Co-Nb-Si system at 1100 °C [1972Sin]

to prepare the solid alloys. The solid alloys were annealed at 1200 °C (time of anneal not given) and characterized by using metallographic, XRD, and electro probe microanalysis (EPMA) methods. The partial isothermal section established by [1974Ste1] at 1200 °C is given in Fig. 3. The binary phases in the investigated composition region, i.e., ρ_1, ζ, π, η, and ν_1 phases, were found to extend marginally into the ternary system. The ψ, Φ, E and λ_1, intermediate phases were detected within the ternary system. Unlike [1967Sko], the ψ phase was found at a composition of $Co_4Nb_4Si_7$ and not at $Co_2Nb_3Si_5$ composition. The $Co_4Nb_4Si_7$ phase has been identified by [1969Jei] as the V phase. The ψ (or V) phase was found in equilibrium with the E, ζ, η, and ν_1 phases. The E phase was found at the composition of $Co_{1.15}Nb_{0.85}Si$. The E phase was found in equilibrium with the λ_1, ψ and ν_1 phases. The Φ phase was initially reported to be present around the composition of $Co_7Nb_2Si_5$ but later the composition of the phase was given as Co_4NbSi_3 [1974Ste2]. The Φ phase was reported to have lattice parameters a = 1.7182 nm and c = 0.7918 nm. Unlike [1967Sko], the Φ phase at 1200 °C was found in equilibrium with the ρ_1, ζ, and E phases but not with the T(G) phase. The T phase was found in equilibrium with the ρ_1, ζ and λ_1 phases. Since the investigation was not carried out below 20 at.% Si the θ phase was not reported. The λ_1 phase was reported to extend up to ~27 at.% Si which agrees with that reported by [1967Sko] at 800 °C but does not agree with that reported by [1972Sin] at 1100 °C which is ~15 at.% Si.

The lattice parameters of the $MgZn_2$ type Laves phase λ_1 of the Co-Nb-Si system, annealed at 1300 °C, was measured as a function of Si content [1964Kuz2] and is given in Fig. 4. The lattice parameter a was found to initially decrease with addition of Si but from ~10 at.% Si it increased linearly up to 25 at.% Si, the limit of solubility of Si in the λ_1 phase. The c parameter, however, decreased with addition of Si, initially at a slower rate and then from ~10 at.% Si linearly up to 25 at.% Si. The lattice parameters of the λ_1 phase was also measured by [1972Sin] for alloys containing 30 at.% Nb content and by [1986Bla] for alloys with 66.7 at.% Co content. At 10 at.% Si content the lattice parameters of the λ_1 phase was reported to be a = 0.4785 nm and c = 0.7773 nm by [1972Sin] and a = 0.474 nm and c = 0.7707 nm by [1986Bla]. The lattice parameter of the λ_1 phase at 33.3 at.% Nb and 10 at.% Si from Fig. 4 is a = 0.4813 nm and c = 0.7825 nm which are somewhat higher than those by [1972Sin] and [1986Bla]. The somewhat higher values of a and c parameters reported

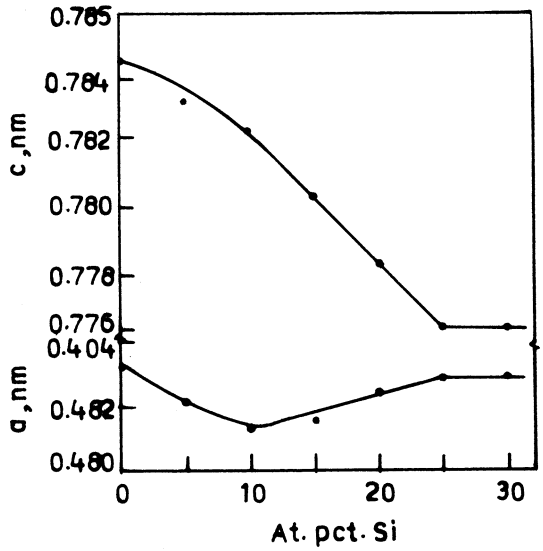

Fig. 4 Lattice parameters of $MgZn_2$ type Laves phase of the Co-Nb-Si system. [1964Kuz2]

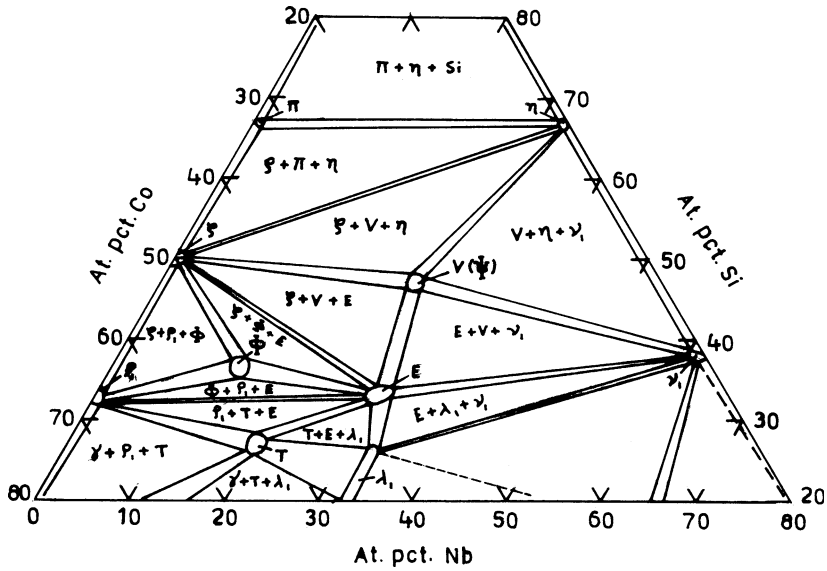

Fig. 3 A partial isothermal section of the Co-Nb-Si system at 1200 °C [1974Ste1]

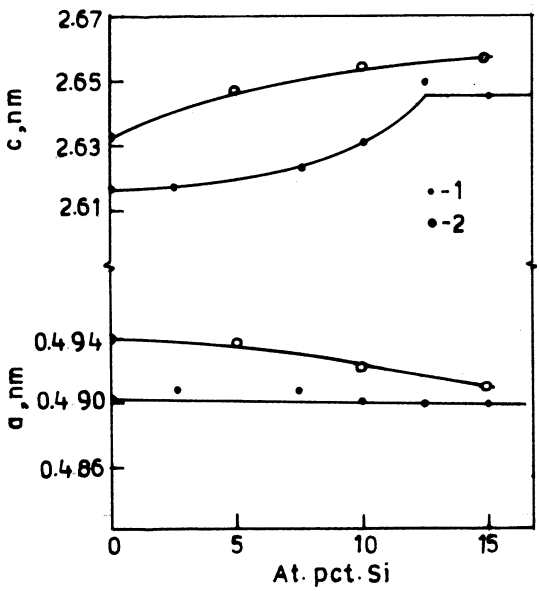

Fig. 5 Lattice parameters of μ phase of the Co-Nb-Si system. 1 [1967Sko]. 2 [1972Sin]

by [1964Kuz2] could be due to the slightly higher Nb content of the alloys or may also be due to carbon contamination of alloys during melting [1967Sko].

The lattice parameters of the μ phase as a function of Si content and is given in Fig. 5. The *a* parameter of the μ phase with 50 at.% Nb content [1967Sko] was found to remain more or less constant with increase in Si content but the *c* parameter increased up to 12.5 at.% Si, the limit of solubility of Si in the μ phase at 800 °C. The lattice parameters of the μ phase at 52 at.% Nb content was also measured by [1972Sin] which shows (Fig. 5) the *a* parameter to decrease slightly with increase in Si content and the *c* parameter increases with increase in Si content up to ~15 at.% Si; the rate of increase in *c* parameter was found quite different than reported by [1967Sko]. While the slightly higher lattice parameters of the μ phase by [1972Sin] is possibly due to the increase in Nb content of the alloys compared to those by [1967Sko], but there is no apparent reason for the different rates of increase in the *c* parameters of the μ phase with increase in Si content. This should be checked by further investigation.

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# indicates presence of phase diagram.

Co-Nb-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.