JPEDAV (2006) 27:523–528
DOI: 10.1361/154770306X136511
1547-7037/$19.00 ©ASM International

The Cr-Ni-Si (Chromium-Nickel-Silicon) System

K.P. Gupta, The Indian Institute of Metals

The Cr-Ni-Si system has been studied by several investigators, and two partial isothermal sections and a complete isothermal section have been established at three different temperatures. Several ternary intermediate phases exist in the Cr-Ni-Si system.

Binary Systems

The Cr-Ni system [Massalski2] (Fig. 1) is a simple eutectic system with the eutectic reaction L $\leftrightarrow$ α + γ occurring at 1345 °C. The α and γ phases are the body-centered cubic (bcc) terminal solid solution (Cr) and face-centered cubic (fcc) terminal solid solution (Ni), respectively. Beyond the wide γ phase region a peritectic reaction forms the structurally related $CrNi_2$ (γ'') phase at $T < 600$ °C.

The Ni-Si system [Massalski2] (Fig. 2) has eight intermediate phases. Ni_3Si (β_1), Ni_3Si (β_2/β_3), $Ni_{31}Si_{12}$ (γ'), Ni_2Si (δ), Ni_2Si (θ), Ni_3Si_2 (ϵ/ϵ'), NiSi (η), and $NiSi_2$ (ζ/ζ'), of which several phase β_2 and β_3, ϵ and ϵ' and ξ and ζ' are polymorphic forms of Ni_3Si, Ni_3Si_2, and $NiSi_2$ phases with polymorphic transformation temperatures of ~1165, 830, and 981 °C, respectively. The γ', θ, and η phases melt congruently at 1242, 1306, and 992 °C, respectively. The β_3, δ, and ζ' phases form through peritectic reactions: L + γ' $\leftrightarrow$ β_3 at 1178 °C, L + θ $\leftrightarrow$ δ' at 1255 °C, L + (Si) $\leftrightarrow$ ζ' at 993 °C, and the β_1 and ϵ' phases form through peritectoid reactions. (Ni) + β_2 $\leftrightarrow$ β_1 at 1035 °C and θ + η $\leftrightarrow$ ϵ' at 845 °C. There are four eutectic reactions in the Ni-Si system: L $\leftrightarrow$ γ + β_3 at 1143 °C, L $\leftrightarrow$ γ' + δ at 1215 °C, L $\leftrightarrow$ θ + η at 964 °C, L $\leftrightarrow$ η + ζ at 966 °C, and four eutectoid reactions forming the β_2, θ, ϵ', and ϵ phases: β_2 $\leftrightarrow$ β_1 + γ' at 990 °C, θ $\leftrightarrow$ δ + ϵ at 825 °C, ϵ' $\leftrightarrow$ δ + ϵ at 820 °C, and ϵ $\leftrightarrow$ ϵ' + η at 800 °C. The γ', δ, η, and ζ phases are single-composition phases.

The Cr-Si system [Massalski2] (Fig. 3) has four intermediate phases, Cr_3Si, Cr_5Si_3, CrSi, and $CrSi_2$, of which the Cr_3Si, βCr_5Si_3, and $CrSi_2$ phases melt congruently at 1770, 1680, and 1490 °C, respectively. βCr_5Si_3 transforms to αCr_5Si_3 at ~1505 °C. The CrSi phase forms through a peritectic reaction L + αCr_5Si_3 $\leftrightarrow$ CrSi at 1413 °C. Four eutectic reactions—L $\leftrightarrow$ (Cr) + Cr_3Si, L $\leftrightarrow$ Cr_3Si + βCr_5Si_3, L $\leftrightarrow$ CrSi + $CrSi_2$, and L $\leftrightarrow$ $CrSi_2$ + (Si)—occur at 1705, 1660, 1390, and 1305 °C, respectively.

Binary and Ternary Phases

In the three binary systems, Cr-Ni, Cr-Si, and Ni-Si, 13 intermediate phases form; some of them also exist in polymorphic forms. Seven ternary intermediate phases have been reported in the Cr-Ni-Si system. The binary and ternary phases of the Cr-Ni-Si system are given in Table 1.

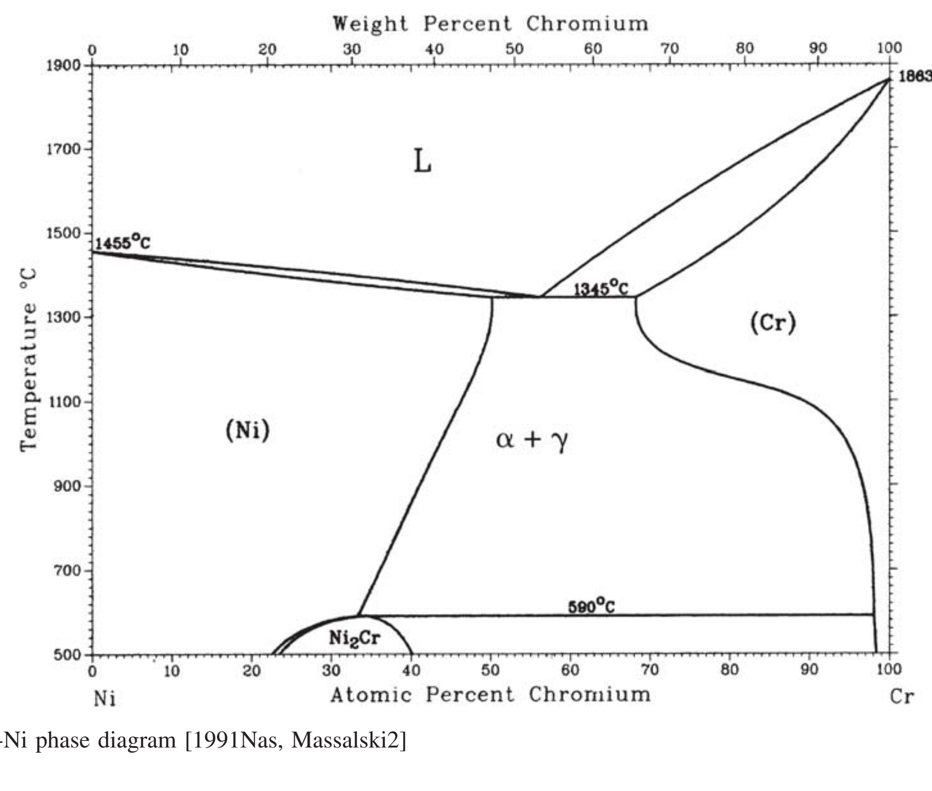

Fig. 1 Binary Cr-Ni phase diagram [1991Nas, Massalski2]

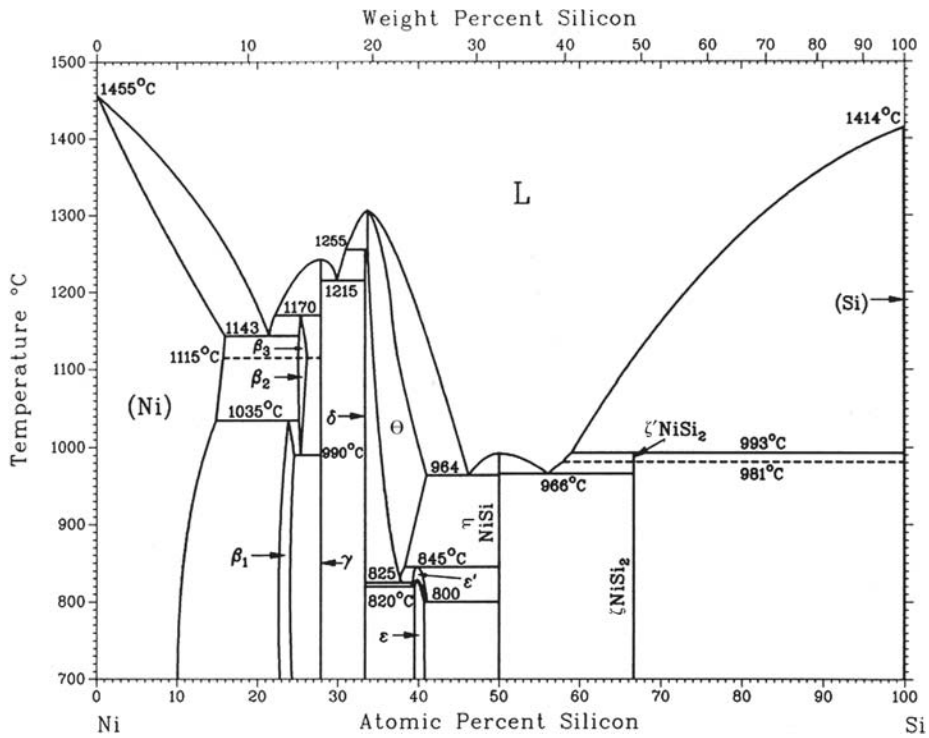

Fig. 2 Binary Ni-Si phase diagram [1991Nas, Massalski2]

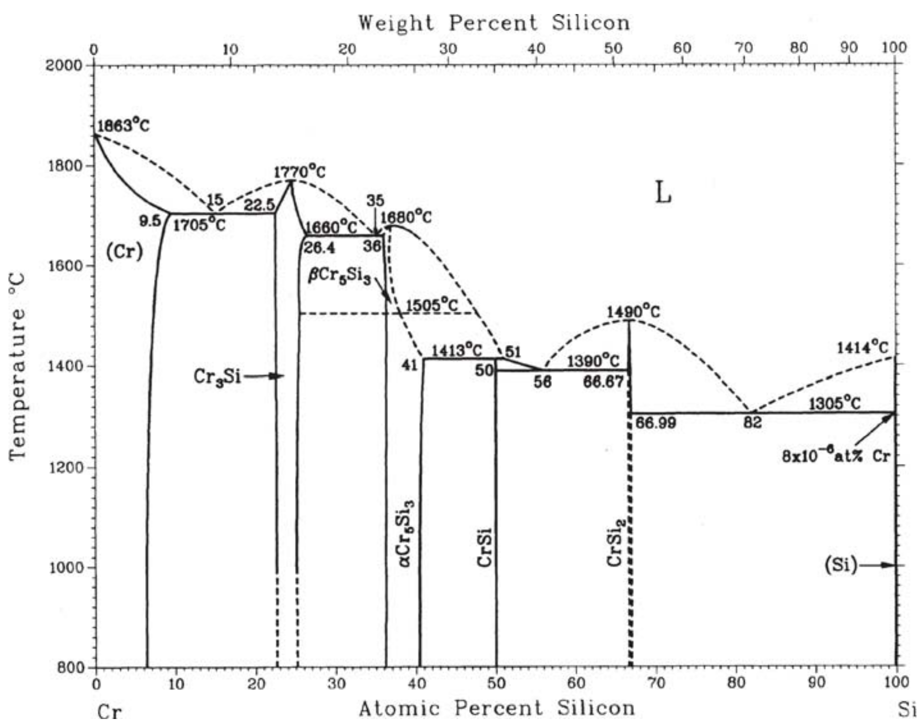

Fig. 3 Binary Cr-Si phase diagram [Massalski2]

Ternary System

[1960Gua] studied the Cr-Ni-Si system at the Ni corner up to 50 at.% Cr and 50 at.% Si. Carbonyl Ni with <0.1 mass% impurity, Cr of 99.25 mass% purity containing ~0.5 mass% C, and 99.8 mass% Si were used for arc melting the alloys. The alloys were annealed in dry hydrogen at 1050 °C for 100 h and cooled in a cooling chamber. A few alloys

Table 1 Binary and ternary phases of the Cr-Ni-Si system and their structure data

Phase designation	Composition(a)	Pearson symbol	Space group	Type	Lattice parameters, nm a	b	c
α	(Cr)	*cI*2	$Im\bar{3}m$	W	…	…	…
γ	(Ni)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
Si	(Si)	*cF*8	$Fd\bar{3}m$	C(diamond)	…	…	…
γ″	$CrNi_2$	*oI*6	*Immm*	$MoPt_2$	…	…	…
β	Cr_3Si	*cP*8	$Pm\bar{3}n$	Cr_3Si	0.4564	…	…
α′	$\alpha(Cr_5Si_3)$	*tI*38	*I4/mcm*	W_5Si_3	0.918	…	0.465
β′	$\beta(Cr_5Si_3)$	…	…	…	…	…	…
ϕ	CrSi	*cP*8	$P2_13$	FeSi	0.4629		
π	$CrSi_2$	*hP*9	$P6_222$	$CrSi_2$	0.4431	…	0.6364
β_1	β_1Ni_3Si(22.8-25.4)	*cP*4	$Pm\bar{3}m$	$AuCu_3$	0.350	…	…
β_2	β_2Ni_3Si (24.5-25.5)	*mC*16	…	$GePt_3$	0.697	0.625 β = 48.74	0.507
β_3	β_3Ni_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	…	…	…	…	…	…
η	NiSi	*oP*8	*Pnma*	MnP	0.562	0.518	0.334
ζ′	$\zeta'NiSi_2$	…	…	…	…	…	…
ζ	$\zeta NiSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5406	…	…
Ψ	Cr_2Ni_3Si(b)	…	…	…	…	…	…
σ	$Cr_{60}Ni_{30}Si_{10}$	*tP*30	$P4_2/mnm$	σ(Cr,Fe)	0.8787	…	0.4570
T	$Cr_6Ni_{16}Si_7$(c)	*cF*116	$Fm\bar{3}m$	$Mg_6Cu_{16}Si_7$	1.110	…	…
T_1	Cr_2Ni_2Si	…	…	…	…	…	…
T_2	$Cr_3Ni_3Si_4$	…	…	…	…	…	…
Δ	$Cr_3Ni_5Si_2$(b)	*cP*20	$P2_13$	$AlAu_4$	0.6120	…	…
Z	Cr_3Ni_2Si(d)	*cF*112	$Fd\bar{3}m$	CFe_3W_3	1.062	…	…

(a) Compositions of several phases are given in at.%. (b) The Ψ phase occurs close to the Δ phase composition region. (c) Homogeneous T phase occurs with >1 at.% Ta. (d) The Z phase occurs only with ~1 wt.% C in the alloy

close to the fcc γ phase boundary were also annealed at 900 °C, time of anneal not mentioned, to determine the γ phase boundary at 900 °C. X-ray diffraction (XRD) and metallography were used for phase identification and phase boundary determination. Figure 4 gives the partial isothermal section of the Cr-Ni-Si system at 1050 °C and also shows the fcc γ phase boundary at 900 °C. The presence of a ternary intermediate phase Ψ was found close to the Cr_2Ni_3Si composition, but its crystal structure was not determined. Of the binary phases of the Ni-Si system only the Ni_3Si phase was found to extend into the ternary to ~6 at.% Cr, extending approximately along the 75 at.% Ni line. The extension into the Cr-Ni-Si ternary system of all other binary phases of the Ni-Si system was found to be quite small. The Ψ phase was found in equilibrium with the fcc γ, NiSi (η), Ni_2Si (θ), Ni_2Si (δ), and $Ni_{31}Si_{12}$ (γ′) phases, but not with the Ni_3Si phase. The Ni_3Si (β_2) phase was found in equilibrium with the γ and γ′ phases. The phase boundary of the γ phase was determined at 1050 and 900 °C. These γ phase boundaries, however, do not agree with the accepted binary diagrams of the Cr-Ni and Ni-Si systems. The probable phase boundaries at 1050 and 900 °C are indicated in Fig. 4 by dash-dot lines. The γ phase boundaries at the Cr-Ni and Ni-Si binaries should be redetermined.

In a study of stabilization of the σ phase in various ternary systems of transition metals and Si, [1960Gup] studied the Cr-Ni-Si system at the Cr end. Electrolytic grade Cr and Ni and high-purity Si were used for arc melting of alloys under He atmosphere. The alloys were annealed in evacuated and sealed silica capsules at 1175 °C for 72 h and water quenched. XRD and metallography were used for phase identification and phase-boundary determination. Figure 5 shows the partial isothermal section of Cr-Ni-Si at 1175 °C. A ternary σ phase was found to exist in the Cr-Ni-Si system even though no σ phase forms in the Cr-Ni binary. The σ phase region exists close to the Cr-Ni binary in the composition region of 58 to 67 at.% Cr, 22 to 33 at.% Ni and 7 to 14 at.% Si. The σ phase was found in equilibrium with the Cr_3Si, bcc α, fcc γ, and a liquid phase; the latter exists in the Ni-Si system at 1175 °C and possibly extends far into the Cr-Ni-Si ternary. The two-phase alloys in the σ + Cr_3Si region suggest a large extension of the Cr_3Si phase, up to ~18 at.% Ni, into the Cr-Ni-Si ternary system.

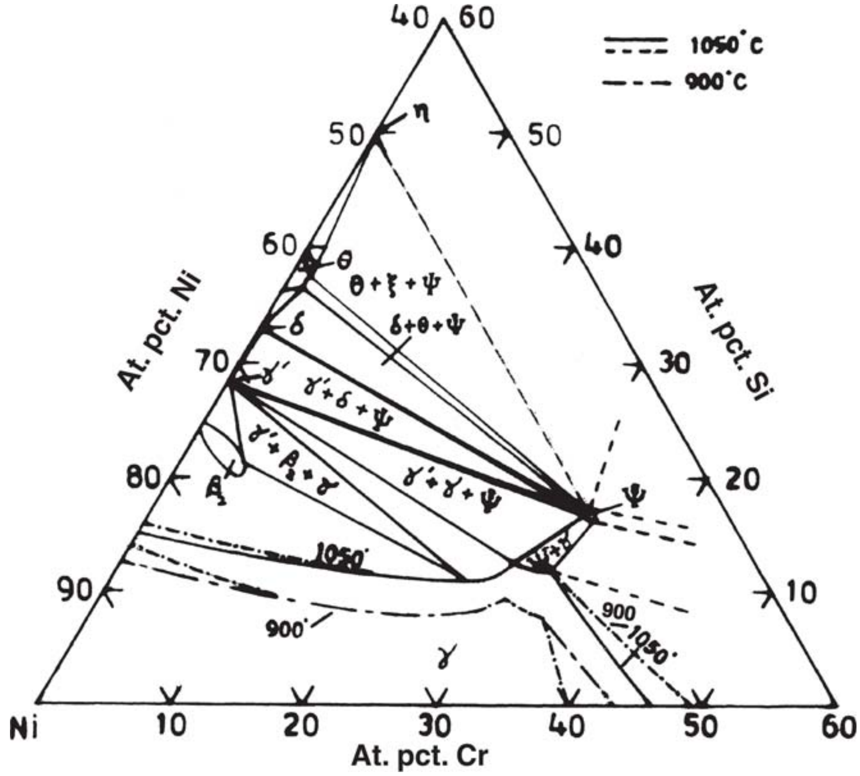

Fig. 4 Partial isothermal section of the Cr-Ni-Si system at the Ni-corner at 1050 °C [1960Gua]. The dash-dot (— · — · —) lines indicate the probable solubility limit of the fcc γ phase.

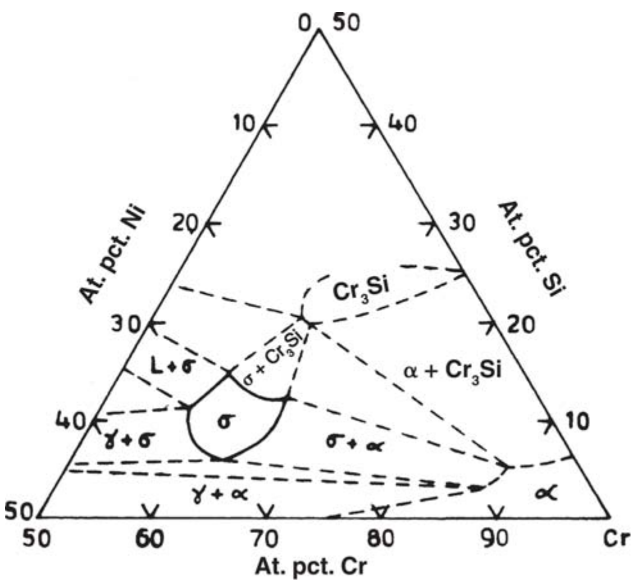

Fig. 5 Partial isothermal section of the Cr-Ni-Si system at the Cr-corner at 1175 °C [1960Gup]

[1963Gla] used 185 alloys to establish a complete isothermal section of the Cr-Ni-Si system at 850 °C. Pure metals, 99.95 mass% Ni, 99.9 mass% Cr, and >99.9 mass% Si, were used to induction melt the alloys in corundum crucibles. The alloys, vacuum sealed in quartz capsules, were annealed at 850 °C for 200 to 1000 h and quenched in water. Some of the alloys were also annealed at 800 and 600 °C. XRD and metallographic methods were used for phase identification and phase boundary determination. The isothermal section at 850 °C [1963Gla] is given in Fig. 6. Six ternary intermediate phase, T, T_1, T_2, Δ, σ, and Z, all existing at compositions <50 at.% Si were found to exist at 850 °C. The $CrSi_2$ and $NiSi_2$ (ζ) phases were found in equilibrium with each other and a three-phase equilibrium $CrSi_2 + \zeta$ + Si was found to exist above 67 at.% Si. At ~50 at.% Si, the NiSi (η) and CrSi phases were found in equilibrium. Also a three-phase equilibrium $\eta + CrSi_2 + \phi$ region was observed. The $CrSi_2$, ζ, and η phase extensions into the ternary system is quite small. The CrSi phase extended far into the ternary. Lattice parameters of the (Cr,Ni) Si solution region of this phase was measured as a function of Ni content (Fig. 7) after annealing at 850 °C, and the maximum solubility of Ni in CrSi phase was found to be 30 at.% Ni. The (Cr,Ni)Si solution phase, however, was found to be unstable at and below 800 °C. The (Cr,Ni)Si alloys were found to transform to yield two phases, one high in Ni content and the other low in Ni content. Lattice parameter data of the high Ni (Cr,Ni) Si phase (Fig. 7) indicated that it exists between 20 and 25 at.% Ni, whereas the low Ni(Cr,Ni) Si phase exists up to 4 at.% Ni. At 600 °C, the solubility of Ni in the low Ni (Cr,Ni) Si phase was found to decrease to <2 at.% Ni. However, [1963Gla] do not mention what happens to the solubility of Ni in the high Ni (Cr,Ni) Si phase of 600 °C. The T_2 phase exists at 40 at.% Si at the

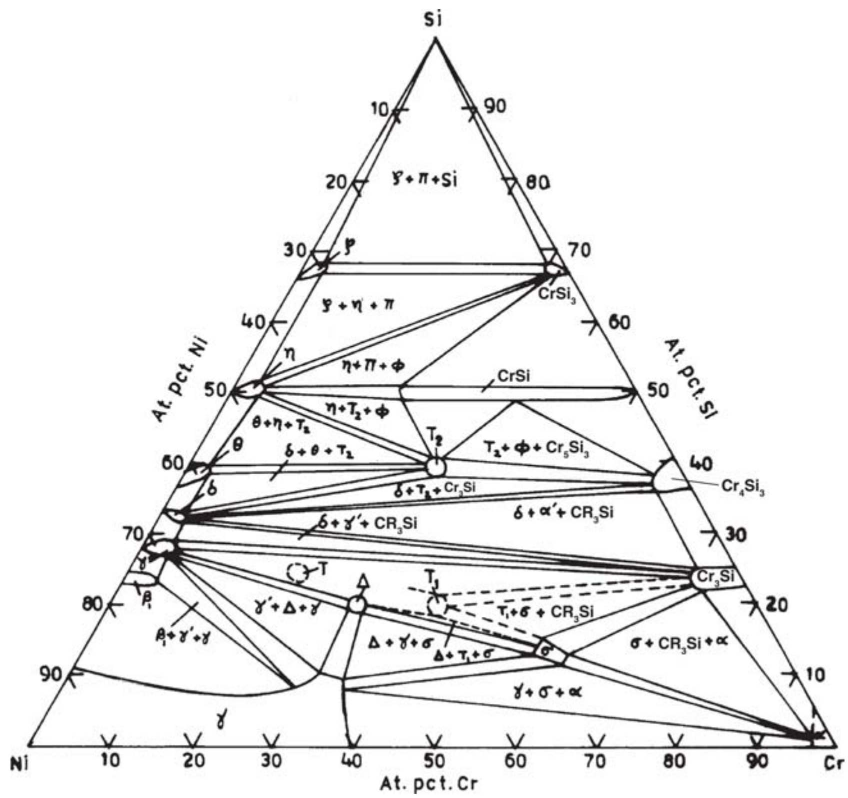

Fig. 6 The 850 °C isothermal section of the Cr-Ni-Si system [1963Gla]

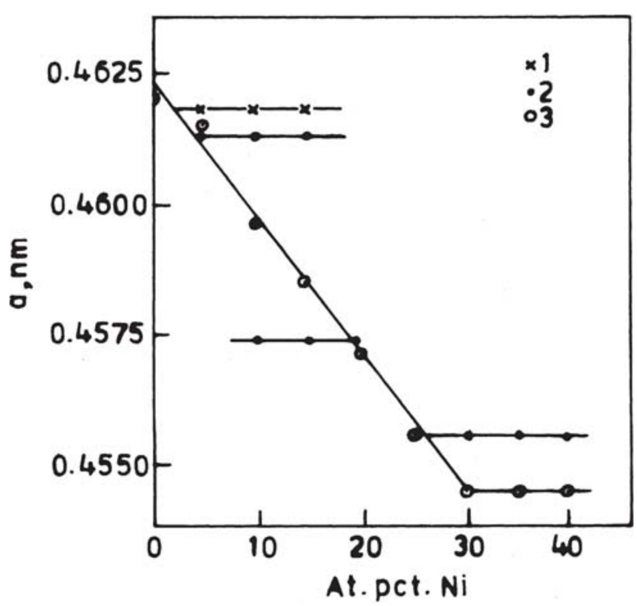

Fig. 7 Dependence of the lattice parameter of (Cr,Ni) Si phase at (1) 600 °C, (2) 800 °C, and (3) 850 °C [1963Gla]

composition $Cr_3Ni_3Si_4$. The crystal structure of the T_2 phase was not determined. The T_2 phase was found in equilibrium with the η, CrSi, Cr_5Si_3 (α′), θ, and δ phases.

All the other ternary intermediate phases—T, T_1, Δ, σ, and Z phases—exist between 14 and 25 at.% Si. The T phase occurs at the $Cr_6Ni_{16}Si_7$ composition and is of the $Mg_6Cu_{16}Si_7$-type structure (more commonly now called the G phase [1963Spi]) with lattice parameter $a = 1.110$ nm. However, the alloys around this composition region as well as at the ideal composition were found to be heterogeneous. Only with some impurities, especially transition metals of large atomic radius such as Ta, could a homogeneous T phase be obtained. Because of this behavior, a compositional range of stability for the T phase in the pure ternary system could not be established, if indeed it exists. The Δ ($Cr_3Ni_5Si_2$) phase exists at 20 at.% Si and ~30 at.% Cr, and the T_1 (Cr_2Ni_2Si) phase exists at 20 at.% Si and 40 at.% Cr. The crystal structure of the Δ phase at one time was reported to be of the βMn type [1959Gla], but later it was found to be of $AlAu_4$ type [1962Gla]. The crystal structure of the T_1 phase was not determined. The XRD pattern of the T_1 phase showed some similarity with the σ and R phase diffraction patterns. The phase equilibria involving the T_1 phase could not be properly established because of the uncertainty about the existence of the T phase as an equilibrium phase. The probable phase equilibrium of the T_1 phase with the other phases is indicated in Fig. 7. The Δ phase was found in equilibrium with the γ′, γ, σ, and T_1 phases. The Δ phase appears in the same composition region as the Ψ, but it is not known whether the two phases are the same. The σ phase region was found to be small at ~15 at.% Si, extending from ~56 to 60 at.% Cr, quite small compared to the σ phase region at 1175 °C [1960Gup]. On prolonged annealing of σ phase alloys at 600 °C, the σ phase vanished and the alloy was found to contain two phases $\gamma' + \alpha$. Thus, the σ phase appears to exist only at high temperatures, and possibly it forms directly from the liquid. This has to be verified through proper study of the Cr-Ni-Si system. As found by [1960Gua], the Ni_3Si phase was found in equilibrium with the γ' and γ phases. Unlike results at 1175 °C, the Cr_3Si phase region at 850 °C is small and extends only to ~5 at.% Ni. The Ni_3Si phase at 850 °C is, however, the β_1 phase and not the β_2 phase that is stable only above ~970 °C. The Z phase region, reported near the Cr_3Ni_2Si composition, is not indicated in Fig. 7 because it was observed that this phase is stable in Cr-Ni-Si system when some C (~1 wt.% C) is present as an impurity. The Cr_3Ni_2Si (C) Z phase was found to be of the W_3Fe_3C-type phase with lattice parameter a = 1.062 nm. The Cr-Ni-Si system should be studied in the composition region between 14 and 25 at.% Si to establish proper phase equilibrium.

References

1959Gla: E.I. Gladyshevskii, P.I. Kripyakevich, and Yu.B. Kuzma, in *Fedorovskaya Sessiya po Kristallografii: Tezisy Dokladov,* Leningrad, 1952, p 32, in Russian. (Quoted by [1963Gla])

1960Gua: R.W. Guard and E.A. Smith, Constitution of Ni-base Ternary Alloys, V. Nickel-Chromium-Silicon System. *J. Inst. Met.* 1959-1960, **88,** p 373-374. (Phase equilibrium. #)

1960Gup: K.P. Gupta, N.S. Rajan, and P.A. Beck, Effect of Si and Al on the Stability of Certain Sigma Phases. *Trans. TMS-AIME,* 1960. **218,** p 617-624. (Phase equilibria, #).

1962Gla: E.I. Gladyshevskii, P.I. Kripyakevich, and Yu.B. Kuzma, *Zh. Strukt. Khim.,* 1962, **3,** p 414, in Russian. (Quoted by [1963Gla])

1963Gla: E.I. Gladyshevskii and L.K. Borusevich, The Cr-Ni-Si Ternary System, *Russian J. Inorg. Chem.,* 1963, **8**(8), p 997-999. (Phase equilibria, #)

1963Spi: F.X. Spiegel, D. Bardos, and P.A. Beck, Ternary G and E Silicides and Germanides of Transition Elements, *Trans. TMS-AIME,* 1963, **227,** p 575-579. (Crys structure)

1991Nas: P. Nash, *Phase Diagrams of Binary Nickel Alloys,* ASM International, 1991. (Review)

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

Cr-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 1997. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary alloys.