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The Co-Cr-Si (Cobalt-Chromium-Silicon) System

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Introduction

The Co-Cr-Si system has been studied by several investigators. Isothermal sections at four different temperatures have been established. Several ternary intermediate phases exist in the ternary system.

Binary Systems

The Co-Cr system [Massalski2] in Fig. 1 is a simple eutectic system at the higher temperatures. The eutectic reaction $L \leftrightarrow \alpha + \gamma$ occurs at 1395 °C, where α and γ are the terminal solid solutions (Cr) and (γCo), respectively. At 1283 °C a σ phase forms through a congruent transformation from the α phase. A eutectoid reaction $\alpha \leftrightarrow \gamma + \sigma$ occurs at ~1260 °C and at 967 °C a peritectoid reaction $\gamma + \sigma \leftrightarrow \varepsilon$ occurs, where ε is the terminal solid solution (εCo). At the Co-end a paramagnetic to ferromagnetic transition occurs, and it is proposed that a eutectoid-type reaction $\gamma_p \leftrightarrow \gamma_f + \varepsilon$ occurs at ~860 °C. In the wide ε-phase field, formation of three intermediate phases Co_3Cr (ν), Co_2Cr (ξ), and Co_2Cr_3 (ϕ) have been reported by [1961Gri] with congruent transformation temperatures of ~620, ~640, and ~625 °C, respectively. While the existence of the Co_3Cr phase has been confirmed by [1969Sin], no confirmation exists for the Co_2Cr and Co_2Cr_3 phases.

The Co-Si system [Massalski2] in Fig. 2 has five intermediate phases, Co_3Si (ι), αCo_2Si (ρ_1), βCo_2Si (ρ_2), CoSi (ζ), and $CoSi_2$ (π), of which the ρ_2, ζ and π phases melt congruently at 1334, 1460, and 1326 °C, respectively. The ι and ρ_1 phases form through peritectic reactions: $L + \rho_1 \leftrightarrow \iota$ at 1214 °C and $L + \rho_2 \leftrightarrow \rho_1$ at ~1320 °C. On addition of Si to Co the cph ε-phase is stabilized to high temperatures and at 1250 °C a peritectic reaction $L + \gamma \leftrightarrow \varepsilon$ occurs. The ι and ρ_2 phases exist only at high temperature and decompose through eutectoid reactions $\iota \leftrightarrow \varepsilon + \rho_1$ at 1193 °C and $\rho_2 \leftrightarrow \rho_1 + \zeta$ at 1286 °C. Four eutectic reactions $L \leftrightarrow \varepsilon + \iota$, $L \leftrightarrow \rho_2 + \zeta$, $\lambda \leftrightarrow \zeta + \pi$ and $L \leftrightarrow \pi$ + (Si) occur at 1204, 1286, 1310, and 1259 °C, respectively. The π phase is of invariant composition.

The Cr-Si system [Massalski2] in Fig. 3 has four intermediate phases, Cr_3Si (β), (γ), Cr_5Si_3, CrSi (ζ), and $CrSi_2$ (δ), of which the β and βCr_5Si_3 (λ_1), and δ phases melt congruently at 1770, 1680, and 1490 °C, respectively.

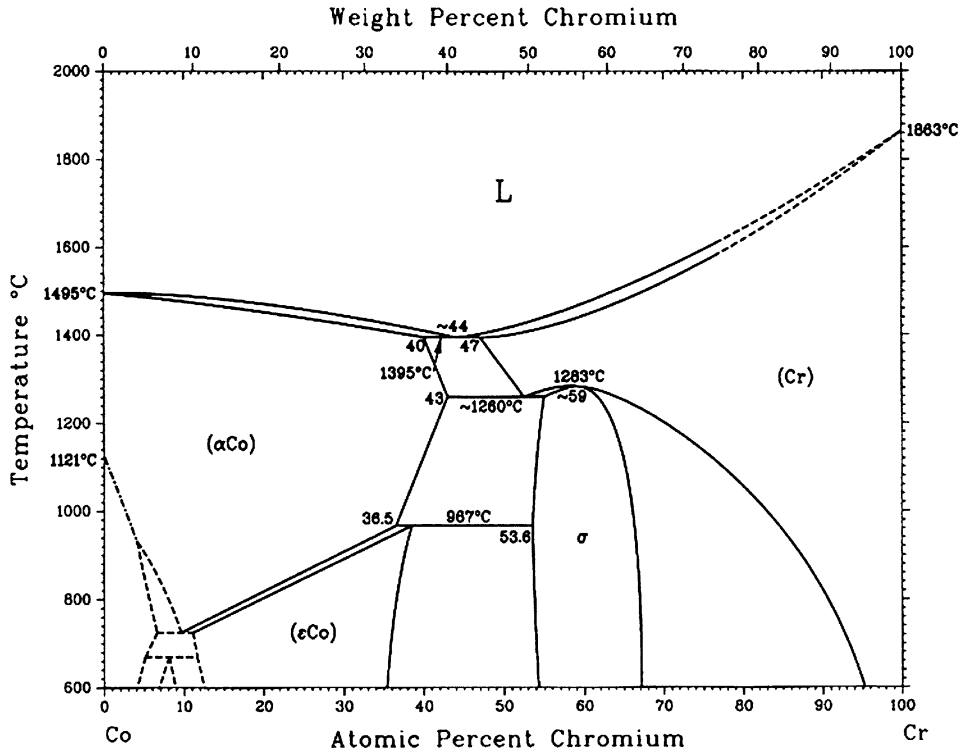

Fig. 1 Binary Co-Cr system [Massalski 2]

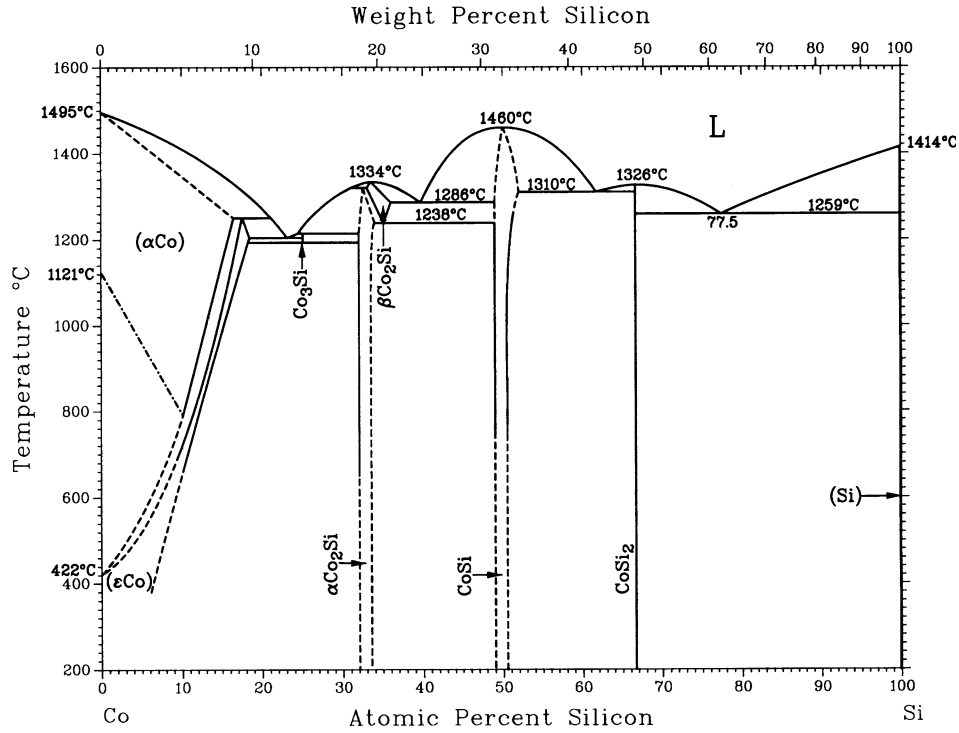

Fig. 2 Binary Co-Si system [Massalski 2]

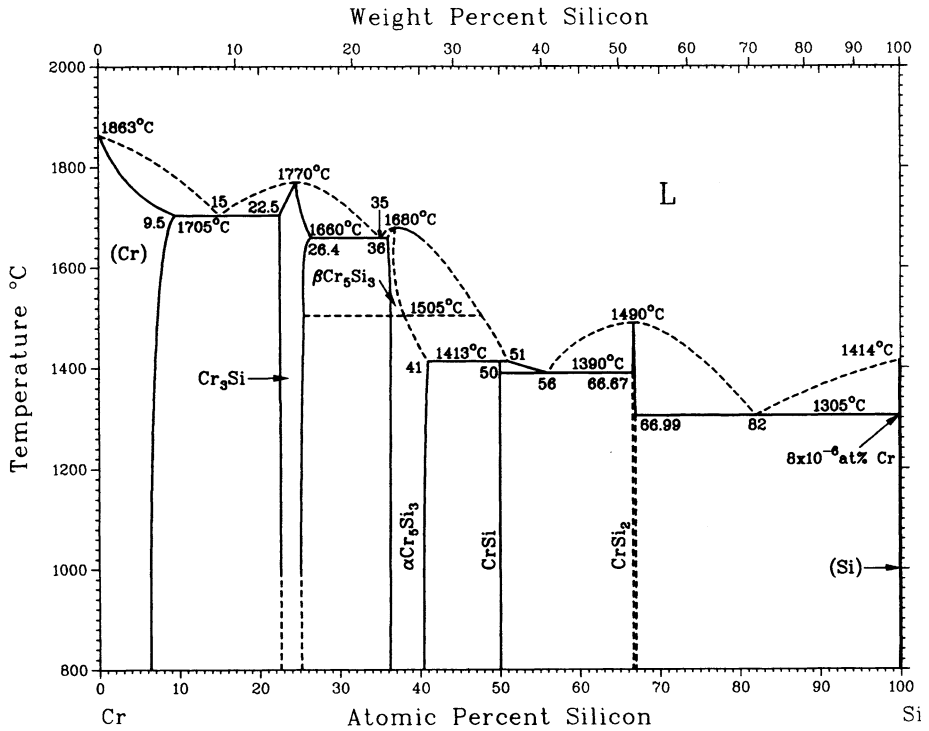

Fig. 3 Binary Cr-Si system [Massalski 2]

The polymorphic transformation βCr_5Si_3 (λ_1) $\leftrightarrow$ αCr_5Si_3 (λ) occurs at ~1505 °C. The ζ phase forms through a peritectic reaction $L + \lambda \leftrightarrow \zeta$ at 1413 °C. Four eutectic reactions $L \leftrightarrow \alpha + \beta$, $L \leftrightarrow \beta + \lambda$, $L \leftrightarrow \zeta + \delta$, and $L \leftrightarrow \delta$+ (Si) occur at 1705, 1660, 1390, and 1305 °C, respectively. The ζ phase is of invariant composition.

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

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameter, nm		
					a	*b*	*c*
α	(Cr)	*cI*2	$Im\bar{3}m$	W	...	...	...
γ	(γCo)	*cF*4	$Fm\bar{3}m$	Cu	...	...	...
ε	(εCo)	*hP*2	$P6_3/mmc$	Mg	...	...	...
Si	(Si)	*cF*8	$Fd\bar{3}m$	C (diamond)	...	...	...
ν	Co_3Cr	*hP*8	$P6_3/mmc$	Ni_3Sn	0.5028	...	0.4034
ξ	Co_2Cr	...	...	...	...	...	...
ϕ	Co_2Cr_3	...	...	...	...	...	...
σ	Co_7Cr_8	*tP*30	$P4_2/mnm$	σ (Cr,Fe)	0.8758	...	0.4536
ι	Co_3Si	t**	...	...	...	...	...
$ρ_1$	αCo_2Si	*oP*12	*Pnma*	Co_2Si	0.7109	0.4918	0.3738
$ρ_2$	βCo_2Si	...	...	...	...	...	...
ζ	CoSi	*cP*8	$P2_13$	FeSi	0.4447	...	...
π	$CoSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5376	...	...
β	Cr_3Si	*cP*8	$Pm\bar{3}m$	Cr_3Si	0.4564	...	...
λ	αCr_5Si_3	*tI*38	*I*4/*mcm*	W_5Si_3	0.918	...	0.465
$λ_1$	βCr_5Si_3	...	...	...	...		...
ζ	CrSi	*cP*8	$P2_13$	FeSi	0.4629	...	...
δ	$CrSi_2$	*hP*9	$P6_222$	$CrSi_2$	0.4431	...	0.6364
χ	Co_5Cr_3Si	*cI*58	$I\bar{4}3m$	αMn	0.8705	...	...
R	$Co_3Cr_3Si_2$	*hR*53	$R\bar{3}$	R (Co,Cr,Mo)	1.0587	...	1.8730
N	$Co_{2.5}Cr_{2.5}Si_3$	...	...	Mn_5Si_3(a)	...	...	...
T	$Co_{70}Cr_6Si_{24}$	...	...	...	...	...	...

(a) Probably Mn_5Si_3 type [1965Bor]

Binary and Ternary Phases

There are 13 binary intermediate phases in the three binary systems Co-Cr, Co-Si, and Cr-Si. Four ternary intermediate phases form in the Co-Cr-Si system. The binary and ternary phases and their structure data are given in Table 1.

Ternary System

The Co-Cr-Si system was studied by [1960Gup] with a limited goal of determining the extension of the σ phase from the Co-Cr system into the ternary. The alloys were arc melted under argon using electrolytic grade Co and Cr and pure Si. The alloys were annealed at 1175 °C for 72 h in evacuated and sealed silica capsules, water quenched, and phase analysis and phase boundary determination were made with x-ray diffraction (XRD) and metallographic methods. Only a partial isothermal section was established and is given in Fig. 4. The maximum solubility of Si in the σ phase was found to be ~17 at.% and the σ phase was found in equilibrium with the bcc α phase, fcc γ phase, the β phase, and an unidentified phase X. The β phase appeared to extend far into the ternary; the extension was estimated to be ~20 at.% Co. The α, γ, and β phase boundaries were not determined but are shown schematically in Fig. 4 by dashed lines.

Complete isothermal sections of the Co-Cr-Si system were established at 800 and 1000 °C by [1965Bor] using 150 alloys. Electrolytic Cr (99.9 mass% pure) and Co (99.99 mass% pure) and Si of 99.96 mass% purity were melted in corundum crucibles under argon atmosphere. The alloys were annealed at 800 and 1000 °C, time of anneal was not mentioned, and phase boundary determination and phase analysis were done using XRD and metallography. The isothermal sections at 800 and 1000 °C established by [1965Bor] are given in Fig. 5 and 6, respectively. The solid lines in the two diagrams are from [1965Bor], and the dashed lines give the probable phase boundaries that conform to the accepted binary data.

At 800 °C (Fig. 5) the σ phase region was found to extend up to ~16 at.% Si, and the σ phase was found in equilibrium with the β, α, and ε phases, the latter phase being stable at 800 °C in both Co-Cr and Co-Si systems. The existence of two ternary intermediate phases R and χ were found around the compositions $Co_3Cr_3Si_2$ and $Co_5Cr_3Si_2$, respectively. The χ phases at the $Co_5Cr_3Si_2$ composition was earlier reported to exist in the Co-Cr-Si system by [1962Gla]; the lattice parameter was reported to be 0.87045 nm. The χ phase was found in equilibrium with the σ, R, ε, and $ρ_1$ phases. The R phase was found in equilibrium with the σ, β, and $ρ_1$ phases. The extension of the β phase into the ternary was found to be small, ~5 at.% Co. The isostructural CoSi and CrSi phases formed a continuous solid solution region extending from

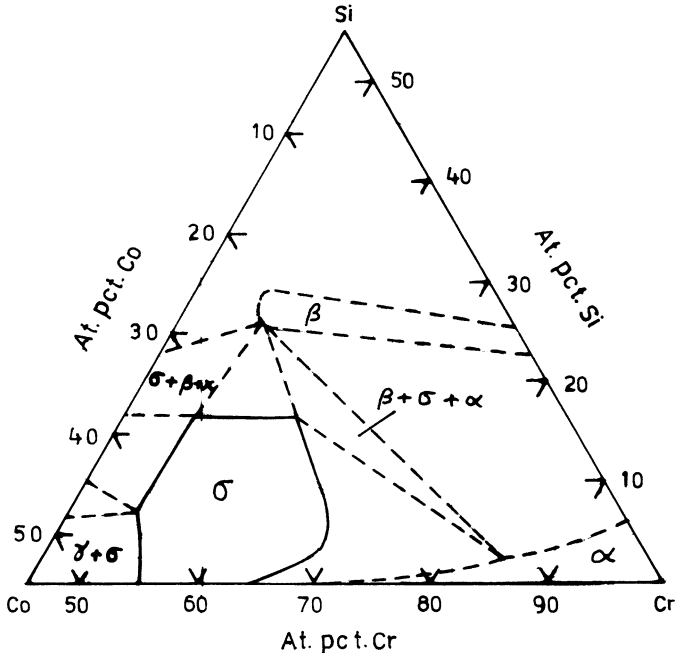

Fig. 4 A partial isothermal section of the Co-Cr-Si system [1960Gup]

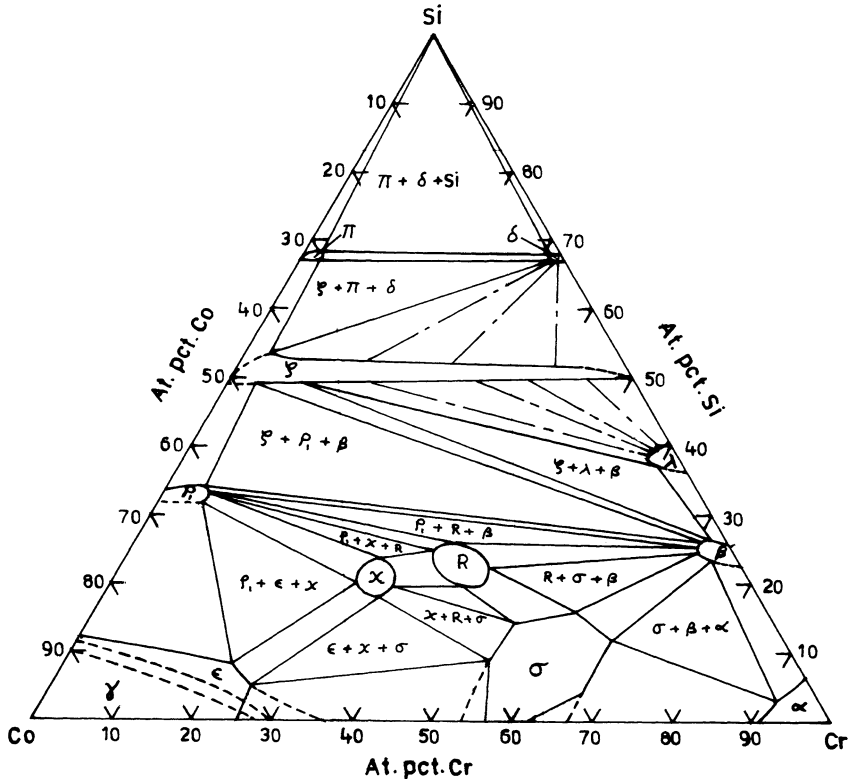

Fig. 5 Isothermal section of the Co-Cr-Si system at 800 °C [1965Bor]

the Co-Si system to the Cr-Si system, and the ζ-phase region was found in equilibrium with the ρ_1, β, λ, π, and δ phases.

The isothermal section at 1000 °C (Fig. 6) shows somewhat different phase equilibrium than at 800 °C. The σ phase region extended up to ~16 at.% Si and was found

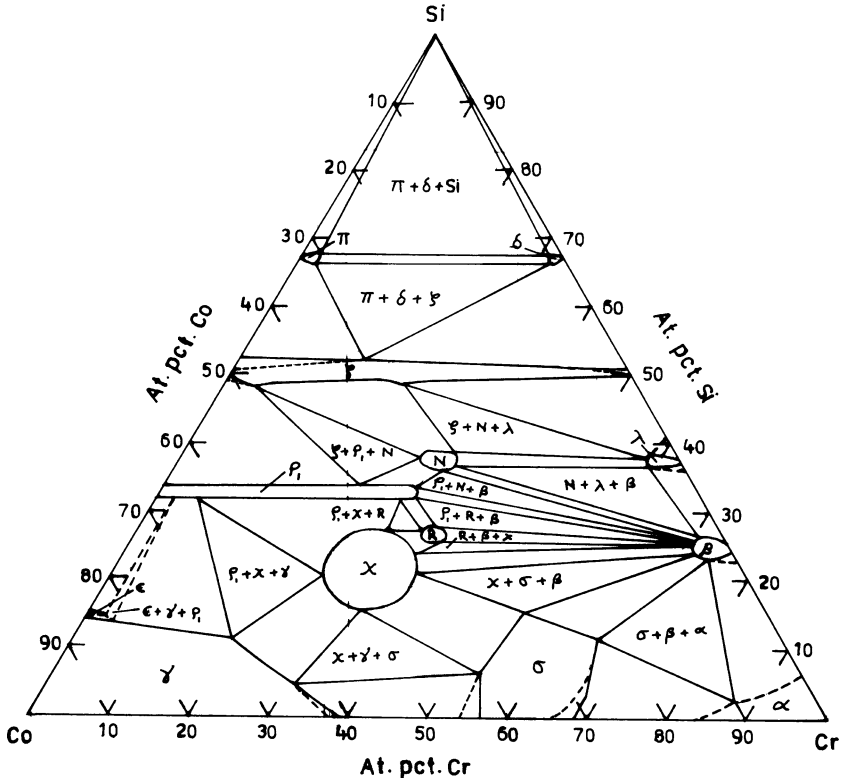

Fig. 6 Isothermal section of the Co-Cr-Si system at 1000 °C [1965Bor]

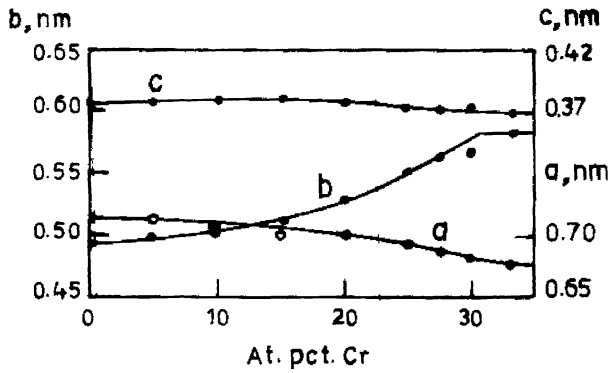

Fig. 7 Lattice parameter of the αCo_2Si (ρ_1) phase as a function of Cr content [1965Bor]

in equilibrium with the α, γ, χ, and β phases but not in equilibrium with the R phase. The χ-phase region was found to be larger in size than at 800 °C and the R-phase region was found smaller in size. A new ternary intermediate phase N was found at around the composition of $Co_{2.5}Cr_{2.5}Si$. The crystal structure of the N phase is reported to be of Mn_5Si_3 type but the lattice parameter of the N phase was not reported. The χ phase was found to be in equilibrium with the γ, ρ_1, R, β, and σ phases. Comparing Fig. 4 with the Fig. 5 and 6, it appears that the X phase in Fig. 4 is possibly the χ phase. The N phase was found in equilibrium with the ρ_1, ζ, λ, and β phases. As at 800 °C, the CoSi phases were found to form a continuous solid-solution region ζ. The phase equilibrium above 50 at.% Si was the same as that at 800 °C. The ρ_1 phase extended far into the ternary. Lattice parameters of the ρ_1 phase as a function of Cr content (Fig. 7) show the extension of the ρ_1 phase is up to ~30 at.% Cr.

An isothermal section at 1150 °C was established by [1996Kun]. Two binary Co-Si alloys with 20 at.% Si and 80 at.% Si were arc melted under argon using electrolytic 99.9 mass% purity Cr, and 99.99 mass% purity Co, and 99.99 mass% purity Si. Alloys were annealed in evacuated and sealed quartz capsules for 100 h at 1150 °C. These alloys were used to prepare two diffusion couples with pure Cr, diffusion annealed at 1150 °C for 300 h, and the diffusion zones were analyzed using electron probe micro-analysis (EPMA). EPMA of the diffusion zones of the two diffusion couples $Co_{80}Si_{20}$/Cr and $Co_{20}Si_{80}$/Cr showed the presence of the following sequence of phases: α, σ, χ, γ, an unknown phase (designated as the T phase), and ρ_1 phases in Co-rich alloy and α, β, λ, ζ, π and Si phases in the Si-rich alloy. Additionally, 30 alloys with less than 50 at.% Si were arc melted and annealed at 1150 °C for 300 h. Phase analysis of these alloys was done by EPMA only. The isothermal section at 1150 °C of the Co-Cr-Si system was established and is given in Fig. 8. Figure 8 shows the presence of four ternary intermediate phases, χ, R, N, and T. The ternary intermediate phase T was found close to the Co-Si binary, extending from 24 to 29 at.% Si and 3 to

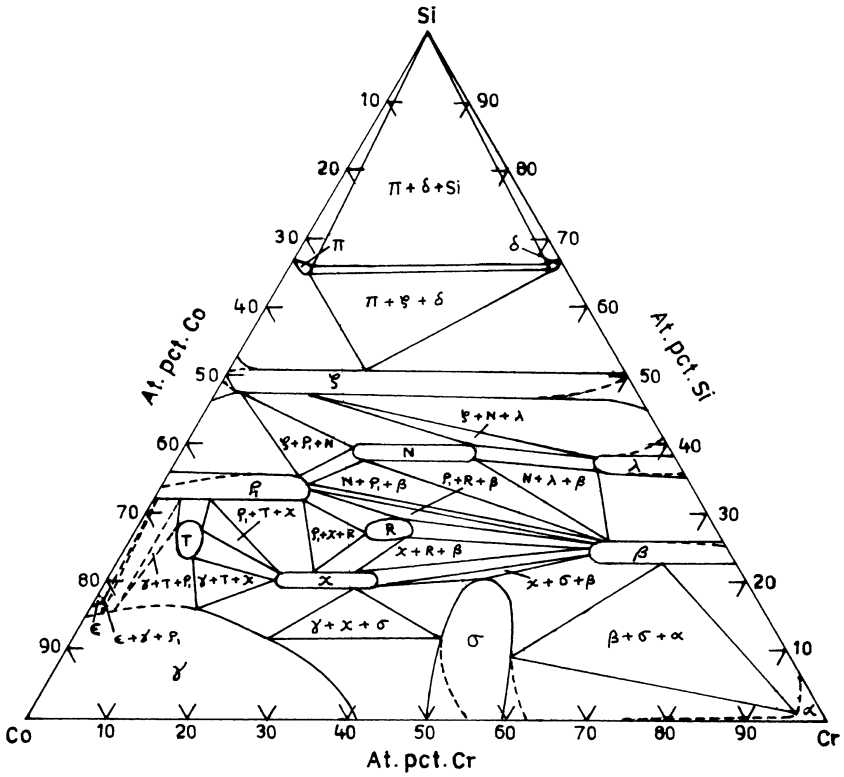

Fig. 8 Isothermal section of the Co-Cr-Si system at 1150 °C [1996Kun]

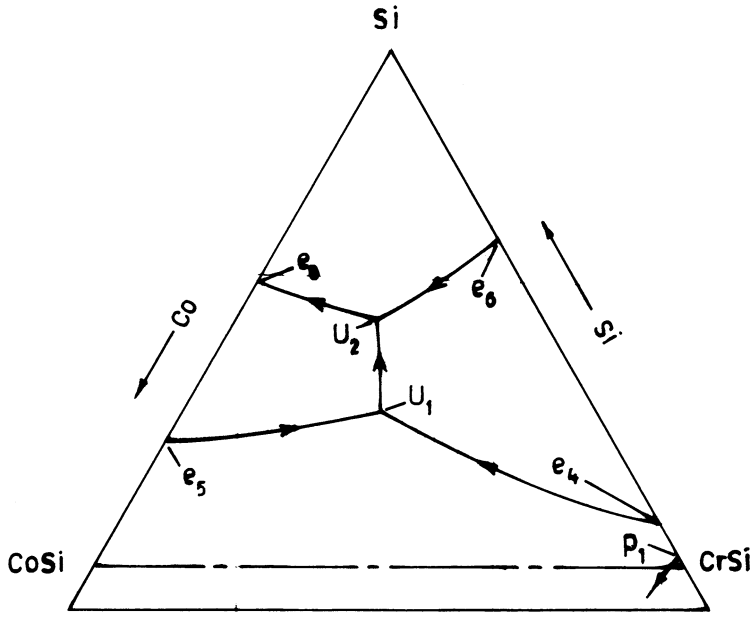

Fig. 9 A probable partial liquidus projection for the Co-Cr-Si system above 50 at.% Si

7 at.% Cr. The σ phase was found to extend up to ~20 at.% Si. Unlike the 800 and 1000 °C results, the β phase at 1150 °C was found to extend up to ~20 at.% Co, in agreement with that reported by [1960Gup] at 1175 °C. At 1150 °C the σ phase was found in equilibrium with the γ, α, χ, and β phases but not in equilibrium with the R phase, in agreement with the data of [1965Bor] at 1000 °C. The T phase was found in equilibrium with the γ, χ, and ρ_1 phases.

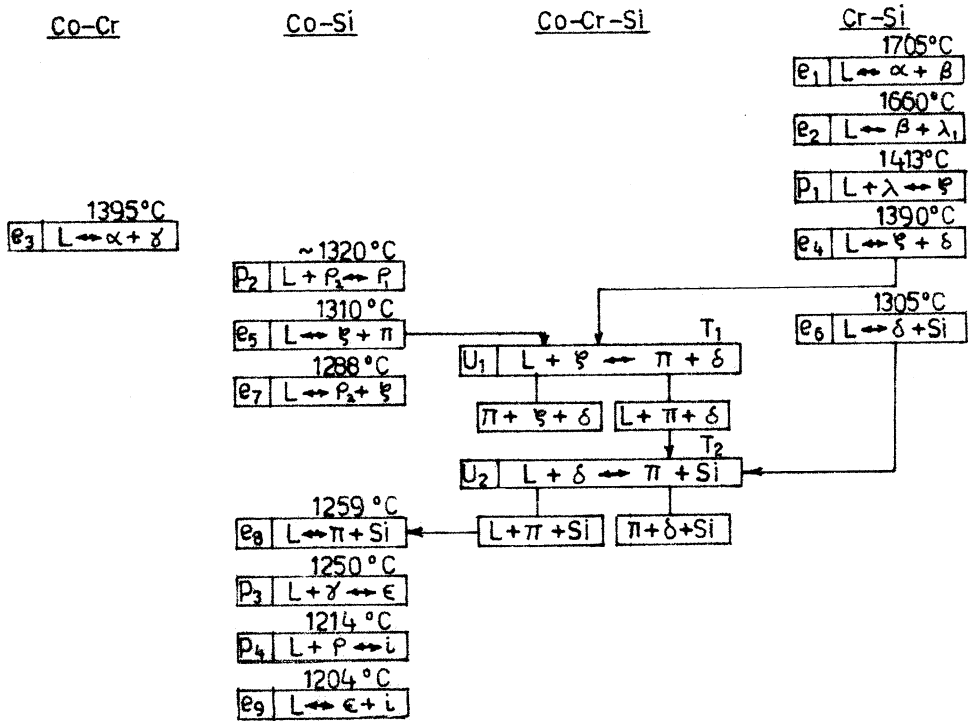

Fig. 10 A partial reaction scheme for the Co-Cr-Si system

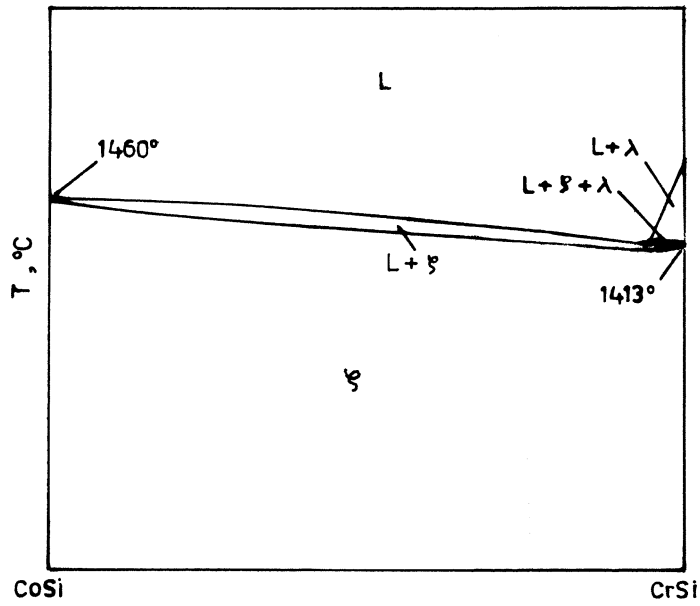

Fig. 11 A probable CoSi-CrSi pseudobinary system

The N-, R-, and χ-phase regions were found to be narrow (~2 at.% Si wide) and elongated phase regions; the N-phase extended from ~20 to 37 at.% Cr, the R phase extended from 27 to 35 at.% Cr, and the χ-phase extended from ~21 to 33 at.% Cr. As at 800 and 1000 °C, at 1150 °C also the CoSi and CrSi phases formed a continuous solid-solution region, ζ, which was found in equilibrium with the ρ_1, N, λ, π, and δ phases. The phase equilibrium above 50 at.% Si for 800, 1000, and 1150 °C were found to be similar. The shape of the σ-phase region determined by [1996Kun] even after making an adjustment of the phase boundary (schematic, dashed lines) to conform to the binary data, does not agree with those given by [1960Gup] at 1175 °C and [1965Bor] at 1000 °C. The shapes of σ-phase region determined by

[1960Gup] and [1965Bor] are about the same. Since there is very little change in the shape of the σ-phase region over a wide temperature range of 1000 and 1175 °C, it is improbable that at a slightly lower temperature than 1175 °C there will be a drastic change in the shape of the σ-phase region. This difference could be due to the fact that [1996Kun] used only a few alloys and used only EPMA of the alloys to draw the approximate phase boundary of the σ-phase region. Possibly this is also true of the phase boundaries of the other intermediate phases. Further work is possibly needed to determine the phase boundaries of the intermediate phases at 1150 °C using metallography.

The three isothermal sections of the Co-Cr-Si system between 800 and 1150 °C show continuous solid solution region ζ between the CoSi and CrSi phases. This suggests the possible existence of a pseudobinary system between the CoSi and CrSi phases. The existence of the pseudobinary will divide the Co-Cr-Si system into two parts, one with Si content <50 at.% and the other with Si content >50 at.%. Above 50 at.% Si all three isothermal sections between 800 and 1150 °C show similar phase equilibria; that is, the ζ phase is in equilibrium with the π and δ phases and the π and δ phases are in equilibrium with Si. With this information, it is possible to suggest a probable liquidus projection for the Co-Cr-Si system above 50 at.% Si. Above 50 at.% Si both the Co-Si and Cr-Si system have two eutectic reactions each, namely e_5 and e_8 in the Co-Si system and e_4 and e_6 in the Cr-Si system (see Fig. 9). A peritectic reaction ρ_1, however, occurs in the Cr-Si system very close to the CrSi phase. Above 50 at.% Si region of the Co-Cr-Si system, all the three isothermal sections between 800 and 1150 °C do not show any phase equilibrium involving the λ phase, which occurs in the peritectic reaction ρ_1. This suggests that the liquid composition line from the peritectic reaction ρ_1 crosses over the CoSi-CrSi pseudobinary line into the region of <50 at.% Si (Fig. 9). On the basis of this assumption the probable liquidus projection for the Co-Cr-Si system above 50 at.% Si has been worked out and is given schematically in Fig. 9. The liquidus projection will involve two peritectic-type reactions U_1 and U_2 and last liquid will solidify at the Co-Si binary at e_8. The corresponding partial reaction scheme is given in Fig. 10. The CoSi-CrSi pseudobinary cannot be a simple isomorphous type system because the CrSi phase forms through a peritectic reaction. On the basis of the suggested liquidus projection (Fig. 9) of the Co-Cr-Si system, a probable pseudobinary section of the CoSi-CrSi system is given schematically in Fig. 11. The pseudobinary should be established experimentally.

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# indicates presence of phase diagram.

Co-Cr-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.