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The Co-Si-V (Cobalt-Silicon-Vanadium) System

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Introduction

Only limited information is available for the Co-Si-V system. One partial isothermal section close to the Co-V system has been reported. This reports solid solibility of AB_3 phases in each other and the existence of several ternary intermediate phases.

Binary Systems

The Co-Si system [Massalski2] (Fig. 1) has five intermediate phases, $Co_3Si(\iota)$, $\alpha Co_2Si(\rho_1)$, $\beta Co_2Si(\rho_2)$, $CoSi(\zeta)$, and $CoSi_2(\pi)$ of which the βCo_2Si, CoSi, and $CoSi_2$ phases melt congruently at 1334, 1460, and 1326 °C, respectively. The $Co_3Si(\iota)$ and $\alpha Co_2Si(\rho)$ phases form through peritectic reactions, $L + \rho_1 \leftrightarrow \iota$ at 1214 °C and $L + \rho_2 \leftrightarrow \rho_1$ at ~1320 °C. With the addition of Si to Co, the close packed hexagonal (cph) (ϵCo) phase is stabilized to high temperatures, and at 1250 °C a peritectic reaction, L + (φCo) ↔ (ϵCo), occurs. The $Co_3Si(\iota)$ and $\beta Co_2Si(\rho)$ phases exist only at high temperatures and decompose through eutectoid reactions i ↔ (ϵCo) + ρ_1 at 1193 °C and $\rho_2 \leftrightarrow \rho_1 + \zeta$ at 1286 °C. The four eutectic reactions L ↔ (ϵCo) + ι, $L \leftrightarrow \rho_2 + \zeta$, $L \leftrightarrow \zeta + \pi$, and L ↔ π + (Si) occur at 1204, 1286, 1310, and 1259 °C, respectively.

The Co-V system [Massalski2] (Fig. 2) has three intermediate phases, Co_3V (γ), σ, and CoV_3 (β). The σ phase forms through the peritectic reaction L + (V) σ at 1422 °C. The (φ_pCo) phase transforms congruently to cubic Co_3V (γ') phase at 1070 °C, and then the γ' phase transforms to hexagonal Co_3V (γ) at ~1025 °C. The CoV_3 (β) phase forms through the peritectoid reaction σ + (V) ↔ β at 1025 °C. At the Co end, the transformation (φ_fCo) ↔ (ϵCo) occurs at 422 °C. At above ~5 at.% V, the (φCo) phase has been suggested to transform from the paramagnetic φ_p state to ferromagnetic φ_f state through a eutectoid type reaction. Only one eutectic reaction L ↔ (φ_pCo) + σ occurs at 1248 °C.

The Si-V system [Massalski2] (Fig. 3) has four intermediate phases, $SiV_3(\beta)$, $Si_3V_5(\xi)$, Si_5V_6 (θ), and Si_2V (δ), of which the β, ξ, and δ phases melt congruently at 1925, 2010, and 1697 °C, respectively. Except for the β phase, the other intermediate phases are single-composition stoichiometric phases. The Si_5V_6 phase occurs through the peritectic reaction $L + \xi \leftrightarrow \theta$ at 1670 °C, and it undergoes the eutectoid transformation $\theta \leftrightarrow \xi + \delta$ at ~1160 °C. The four eutectic reactions L ↔ (V) + β, $L \leftrightarrow \beta + \xi$, $L \leftrightarrow \theta + \delta$, and L ↔ δ + (Si) occur at 1870, 1895, 1640, and 1400 °C, respectively.

Binary and Ternary Phases

In the three binary systems of the Co-Si-V system, 12 intermediate phases form. In the investigated region of the Co-Si-V system, the existence of a large number of ternary intermediate phases have been reported. The structure data for the binary and ternary phases are given in Table 1.

Ternary System

To study the effect of Si on the stabilization of the σ phase in transition metal systems, the V-Co-Si system was studied by [1960Gup] only very close to the σ phase region. Electrolytic grade component elements were arc-melted under a He atmosphere. The alloys were sealed in evacuated fused silica capsules, and were annealed at 1175 °C for 72 h and quenched in water. The annealed alloys were characterized by metallography and x-ray diffraction methods. Fig. 4 shows that the σ phase in the Co-V system dissolves a maximum of ~5 at.% Si. The face-centered cubic (fcc) (φ_pCo) phase at ~34 at.% V was found in equilibrium with the σ phase along a line extending from ~45 at.% Co at 0 at.% Si to ~38 at.% Co at ~3 at.% Si.

The other phases in equilibrium with the σ phase were not identified, but the presence of a three phase equilibrium at the top of the σ phase field was indicated by [1960Gup].

In subsequent related explorations of the stabilization of R and $MgZn_2$-type Laves phases by Si [1961Bar1, 1961Bar2], an R phase was found to be present in the V-Co-Si system at the $Co_{40}Si_{15}V_{45}$ composition at 1100 °C [1961Bar1], and a $MgZn_2$-type Laves phase Γ_1 was found to exist at the $Co_5Si_3V_4$ composition [1961Bar2] at 1100 °C. These compositions are shown in Fig. 4. The existence of a Γ_1 phase in V-Co-Si system was also reported by [1961Gla] at the $Co_{37}Si_{29}V_{34}$ composition (point 2 in Fig. 4). The lattice parameters of the R and the Γ_1 phases were reported to be $a = 1.078$ nm, $c = 1.914$ nm [1961Bar1] for the R phase, and $a = 0.47$ nm and $c = 0.747$ nm [1961Bar2] and $a = 0.471$ and $c = 0.724$ nm [1961Gla] for the Γ_1 phase. The R phase was found to be in equilibrium with the σ phase [1961Bar1]. One other phase found in equilibrium with the σ phase [1961Bar1] was the χ phase, which was discovered by [1961Gla] at the $Co_{52}Si_{20}V_{28}$ composition. The probable phase equilibria involving the σ, φ, χ, and R phases are given schematically in Fig. 4. Because no equilibrium between the Γ_1 phase and the σ phase was reported and because the φ_1 phase composition was found to be close to the χ and R phases, it is possible that the Γ_1 phase is in equilibrium with the χ and R phases.

In a search for electron phases in transition metal-Si ternary systems, a more complete investigation of the Co-Si-V system in the region 0 to ~50 at.% Si was made by [1966Bar]. Co and V, each of 99.9+ mass% purity, and Si of 99.98 mass% purity were used to prepare the alloys by arc melting under a He atmosphere. The alloys were sealed in an evacuated fused silica capsules and were annealed at 1100 °C (time of annealling was not mentioned) and

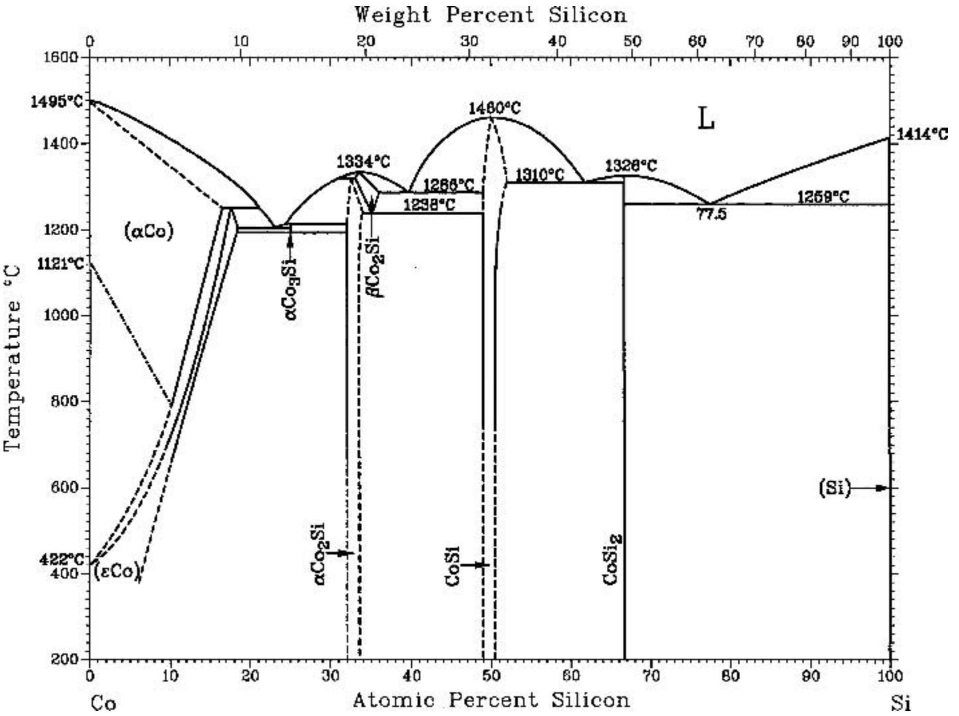

Fig. 1 Co-Si phase diagram [Massalski2]

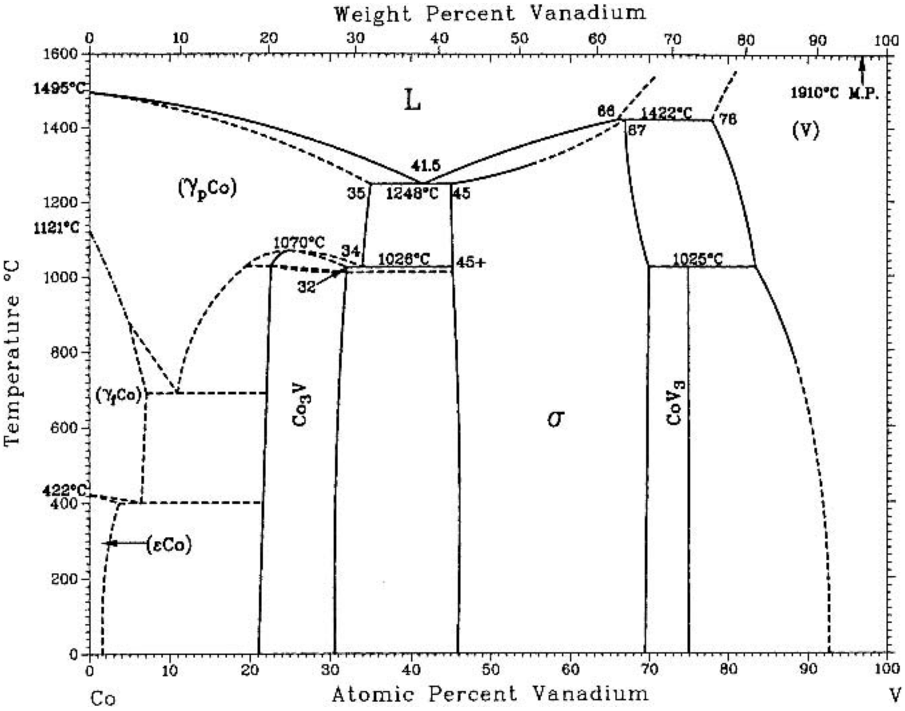

Fig. 2 Co-V phase diagram [Massalski2]

quenched in water. X-ray diffraction and metallography were used for phase identification and phase boundary determination. A few alloys that were close to the phase boundaries were chemically analyzed to accurately locate the phase boundaries.

The 1100 °C isothermal section established by [1966Bar] is given in Fig. 5. At 1100 °C, the σ, χ, and R phases, and two regions of $MgZn_2$ type Laves phase, Γ_1 and Γ_1', exist. A comparison of the isothermal section at 1175 °C in Fig. 4 with the isothermal section at 1100 °C in Fig. 5 shows a

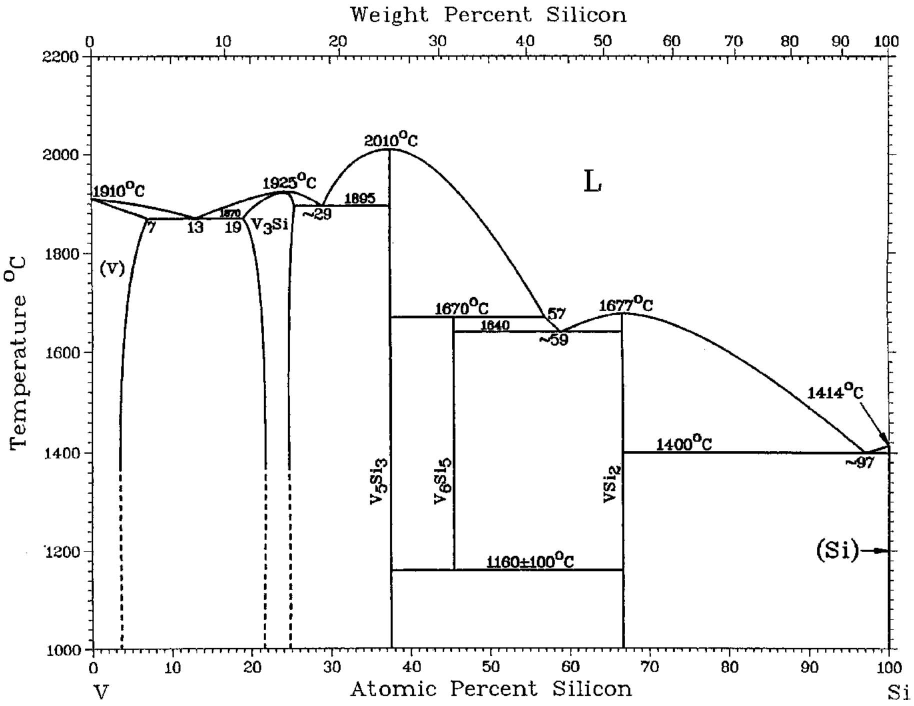

Fig. 3 Si-V phase diagram [Massalski2]

Table 1 Binary and ternary phases in the Co-Si-V system

Phase designation	Composition(a)	Pearson symbol	Space group	Type	Lattice parameter, nm *a*	*b*	*c*
φ	(φCo)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
α	(V)	*cI*2	$Im\bar{3}m$	W	…	…	…
ϵ	(ϵCo)	*hP*2	$P6_3/mmc$	Mg	…	…	…
Si	(Si)	*cF*8	$Fd\bar{3}mc$	c(Diamond)	…	…	…
ι	(Co_3Si)	…	…	…	…	…	…
ρ_1	αCo_2Si(32 to 34 Si)	*oP*12	*Pnma*	Co_2Si	0.7109	0.4918	0.3738
ρ_2	βCo_2Si(~32 to 35.8 Si)	…	…	…	…	…	…
ζ	CoSi	*cP*8	$P2_13$	FeSi	0.4447	…	…
π	$CoSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5376	…	…
γ′	Co_3V	*cP*4	$Pm\bar{3}m$	$AuCu_3$	…	…	…
γ	Co_3V	*hP*24	$P\bar{6}m2$	Co_3V	0.5032	…	1.227
σ	~44 to ~72 V	*tP*30	$P4_2/mnm$	σ(Cr,Fe)	0.8843	…	0.4586
β	CoV_3	*cP*8	$Pm\bar{3}n$	Cr_3Si	0.4676	…	…
β	SiV_3	…	…	…	0.4721	…	…
ξ	Si_3V_5	*tI*32	*I4/mcm*	Si_3W_5	0.943	…	0.476
θ	Si_5V_6	*oI*44	*Immm*	Nb_6Sn_5	…	…	…
δ	Si_2V	*hP*9	$P6_222$	$CrSi_2$	0.4571	…	0.6372
χ	$Co_{56}Si_{15}V_{30}$	*cI*58	$I\bar{4}3m$	αMn	0.8766	…	…
R	$Co_{35}Si_{19}V_{46}$	*hR*53	$R\bar{3}$	R(Co,Cr,Mo)	1.078	…	1.914
B	$Co_{27}Si_{27}V_{46}$(a)	…	…	…	…	…	…
C	$Co_{34}Si_{27}V_{39}$(a)	…	…	…	…	…	…
α′	$Co_{59}Si_{26}V_{15}$(a)	*cF*16	$Fm\bar{3}m$	$AlFe_3$(c)	…	…	…
Γ_1	$Co_5Si_3V_4$	*hP*12	$P6_3/mmc$	$MgZn_2$	0.47	…	0.747
Γ_1'	$Co_{26.7}Si_{40}V_{33.3}$(a)	*hP*12	$P6_3/mmc$	$MgZn_2$	…	…	…
E	CoSiV	*oP*12	*Pnma*	$PbCl_2$	0.5954	0.3584	0.6852(b)
J	$Co_{45}Si_{40}V_{15}$(a)	…	…	…	…	…	…

(a) Compositions in at.%.

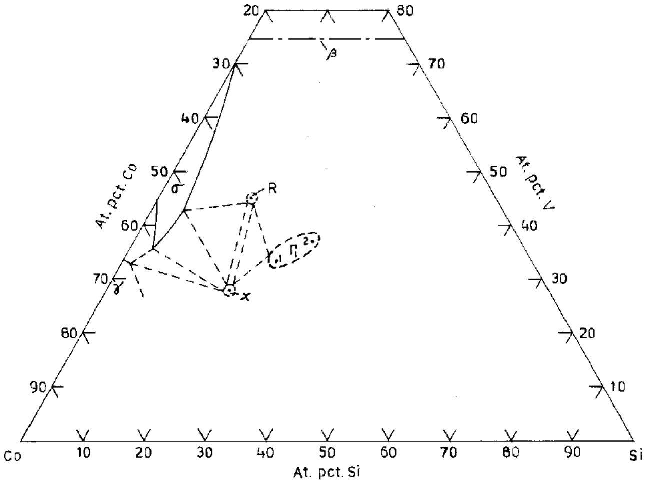

Fig. 4 The extension of the σ phase in the Co-Si-V system at 1175 °C [1960Gup]. Also shown are the compositions at which the R, X, and Γ_1 phases were reported at 1100 °C. The probable pseudobinary line CoV_3-SiV_3 is shown by dash-dot line.

significant shift in the compositional range of stability of the σ phase. Both are in accord with the range of homogeneity of σ in the binary Co-V system at 0 at.% Si, and the σ phase boundaries of the two sections closely agree in the V-poor composition region 34 to 42 at.% V but show strongly divergent behavior at compositions >42 at.% V. In the 1175 °C section of Fig. 4, a maximum Si content in the σ phase is indicated as ~5 at.% at a V content of ~42 at.% and with a Si content decreasing monotonically at V compositions greater than ~42 at.%. In contrast, the 1100 °C section of Fig. 5 shows that the σ phase boundary at V compositions >42 at.% V exhibits a continuous increase in Si content with increasing V content to reach a maximum Si composition of ~12 at.% Si at a V composition of ~76 at.%. Figure 5 shows that the compositional coordinates, ~5 at.% Si and ~42 at.% V correspond to the point of contact of σ with the $\sigma + \chi +$ R three-phase field, while the Si composition maximum at ~12 at.% Si and ~76 at.% V corresponds to the point of contact of σ with the $\sigma + \beta +$ R three-phase field. In Fig. 4 at 1175 °C, the contour of the σ phase boundary shows a smooth monotonic curvature at V compositions >42 at.% with no indication of a contact between the σ and β phases. The implication is that Gibbs energy balances among the σ, β, and R phases change significantly over a 75 °C interval.

The χ phase region was found to be reasonably wide, extended from ~21 to 32 at.% V and ~8 to 20 at.% Si. The R phase region was found to extend from 41 to 51 at.% V and 13 to 22 at.% Si, and extended parallel to the σ phase region. Unlike what was reported earlier (Fig. 4), the $MgZn_2$-type Laves phase regions Γ_1 and Γ_1' were found to exist along a line of 33.3 at.% V separated by a small E phase region (~1 at.% wide) existing at the CoSiV composition. Both the Γ_1 and Γ_1' phase regions were found to be ~2 at.% V wide, the Γ_1 phase region extended from ~26 to 31 at.% Si, and the Γ_1' phase region extended from ~38 to 44 at.% Si. It appears possible that the $MgZn_2$-type Laves phase exists at some temperature other than 1100 °C as an elongated region covering the entire composition regions of the Γ_1 E, and Γ_1' phases. The phase equilibria of the Co-Si-V system should be studied at temperatures lower and higher than 1100 °C to find whether a single extended Γ_1 phase exists in the ternary system.

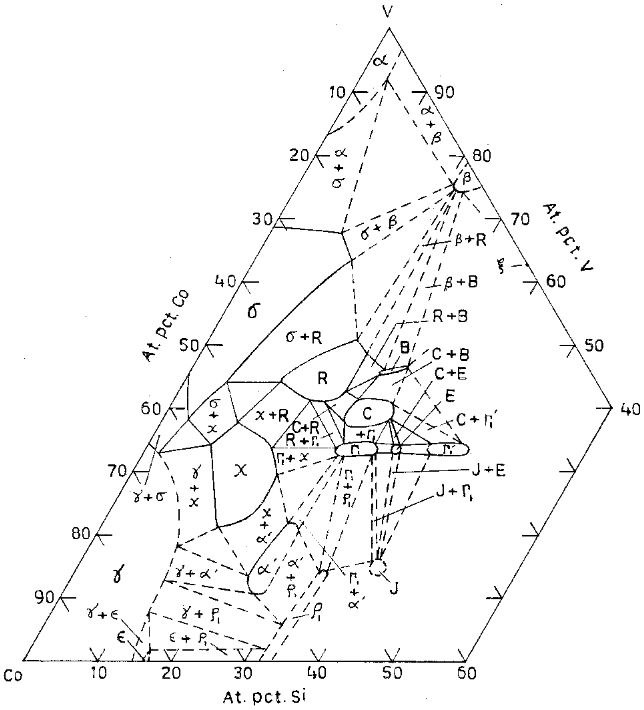

Fig. 5 1100 °C partial isothermal section of the Co-Si-V System [1966Bar].

Several other intermediate-phase regions were established in the Co-Si-V system at 1100 °C. A small lens-shaped β phase region, ~1 at.% V wide and 3 at.% Si long, was found at approximately the $Co_{27}Si_{27}V_{46}$ composition. A C phase region, ~27 to 42 at.% V and ~24 to 30 at.% Si wide, was found at approximately the composition $Co_{34}Si_{27}V_{39}$, and a body-centered cubic (bcc) α' phase (elongated along the 26 at.% Si line, about ~11 to 22 at.% V long and ~3 at.% Si wide) was found around the composition $Co_{59}Co_{26}V_{15}$. A J phase was also found to exist at around the $Co_{45}Si_{40}V_{15}$ composition. The phase boundary of the J phase region was not determined accurately. The σ phase was found to be in equilibrium with the α, φ, R, and χ phases, and the Γ_1 phase was found to be in equilibrium with the χ, R, C, E, J, ρ_1, and α' phases. The α Co_2Si (ρ_1) phase boundary was not determined, but it was found to extend to ~14 at.% V along the 33 at.% Si line. The C phase was found to be in equilbrium with the R, B, Γ_1, Γ_1' and E phase regions. The B, R, and σ phases were also found to be in equilibrium with the β phase of the Si-V binary. [1966Bar] also showed the σ phase to be in equilibrium with the β phase of the Co-V binary. Because the CoV_3 phase is not stable above 1025 °C, the three-phase equilibrium $\sigma + \beta$ (CoV_3) + α is not possible and, hence, is not shown in Fig. 5. Because at the Co-end of the Co-V system both fcc φ and cph ϵ phases exist at 1100 °C, one should expect the presence of a cph ϵ phase region in the ternary, and a φ + ϵ + ζ three-phase equilibrium is to be expected. This was not shown by [1966Bar] and is shown schematically in Fig. 5.

The CoV_3 and SiV_3 phases are isostructural. In an investigation aimed at finding a split structure in ternary Cr_3Si-type phases (due to a third element occupying preferentially the bcc position of the Cr_3Si-type structure), [1969Jei] studied several ternary systems, one of which was the Co-Si-V system. The alloys were arc-melted under an argon atmosphere using 99.8 mass% V and 99.9 mass% Co and Si, were sealed in evacuated quartz capsules, and were annealed at 550 °C for 45 days, 850 °C for 4 days, and 1050 °C for 20 days. Up to 850 °C, the alloys were single-phase β, but at 1050 °C some alloys were found to be two-phase, β and another phase that was not identified. In the Co-Si-V system, no split structure was found. The observation of the β phase in alloys at 1050 °C is possible because SiV_3 exists as high as 1925 °C. These results suggest the existence of a pseudobinary between the CoV_3 and SiV_3 phases, which is indicated in Fig. 4.

The Co-Si-V system should be studied above 50 at.% Si to establish the complete phase equilibria in the ternary system.

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Co-Si-V 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 Program Co-Category Editor for ternary nickel alloys.