

The Co-Si (Cobalt-Silicon) System

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Equilibrium Diagram

The equilibrium phases in the Co-Si system are: (1) the liquid, L; (2) the Co-rich, fcc terminal solid solution, (α Co); (3) the Co-rich,

cph terminal solid solution, (ϵ Co); (4) the tetragonal phase α Co₃Si, stable between 1193 and 1214 °C; (5) Co₂Si, with two modifications—low-temperature, orthorhombic α Co₂Si, stable below ~1320 °C, and high-temperature β Co₂Si, with an unknown

Table 1 Special Points of the Assessed Co-Si Phase Diagram

Reaction	Composition of the respective phases, at. % Si			Temperature, °C	Reaction type
L \leftrightarrow CoSi	50			1460	Congruent
L \leftrightarrow β Co ₂ Si	33.3			1334	Congruent
L \leftrightarrow CoSi ₂	66.7			1326	Congruent
L + β Co ₂ Si \leftrightarrow α Co ₂ Si	-31	-32.6	-33	~1320	Peritectic
L \leftrightarrow CoSi + CoSi ₂	61.8	-52	66.7	1310	Eutectic
L \leftrightarrow β Co ₂ Si + CoSi	39.7	35.8	-49	1286	Eutectic
L \leftrightarrow CoSi ₂ + (Si)	77.5	66.7	-100	1259	Eutectic
(α Co) + L \leftrightarrow (ϵ Co)	16.5	21.4	17.6	1250	Peritectic
β Co ₂ Si \leftrightarrow α Co ₂ Si + CoSi	35.1	-34	49	1238	Eutectoid
L + α Co ₂ Si \leftrightarrow α Co ₃ Si	24.4	-32.6	25.0	1214	Peritectic
L \leftrightarrow (ϵ Co) + α Co ₃ Si	23.1	18.4	25.0	1204	Eutectic
α Co ₃ Si \leftrightarrow (ϵ Co) + α Co ₂ Si	25.0	18.1	-32.6	1193	Eutectoid

Table 2 Experimental Data on Co-Si Invariant Reactions

Reference	Reaction	Composition of the respective phases, at. % Si			Temperature, °C	Reaction type	
[34Vog](a)	L \leftrightarrow (α Co) + α Co ₃ Si	23.1	14.6	25.0	1200	Eutectic	
	L + α Co ₂ Si \leftrightarrow α Co ₃ Si	24.8	33.3	25.0	1210	Peritectic	
	α Co ₃ Si \leftrightarrow (α Co) + α Co ₂ Si	25.0	13.7	33.3	1160	Eutectoid	
	β Co ₂ Si \leftrightarrow L		33.3		1332	Congruent	
	L \leftrightarrow β Co ₂ Si + CoSi	39.6	36.0	50.0	1270	Eutectic	
	β Co ₂ Si \leftrightarrow α Co ₂ Si + CoSi	35.7	34.0	50.0	1208	Eutectoid	
	[37Has]	L \leftrightarrow (α Co) + α Co ₃ Si	23.1	14.0	25.0	1195	Eutectic
		L + α Co ₂ Si \leftrightarrow α Co ₃ Si	23.9	32.3	25.0	1212	Peritectic
		α Co ₃ Si \leftrightarrow (α Co) + α Co ₂ Si	25.0	13.3	32.3	1170	Eutectoid
		β Co ₂ Si \leftrightarrow L		33.3		1332	Congruent
L \leftrightarrow β Co ₂ Si + CoSi		39.7	35.8	49.1	1286	Eutectic	
β Co ₂ Si \leftrightarrow α Co ₂ Si + CoSi		35.1	34.1	49.1	1238	Eutectoid	
CoSi \leftrightarrow L			50.0		1460	Congruent	
L \leftrightarrow CoSi + CoSi ₂		61.8	52.1	66.7	1310	Eutectic	
CoSi ₂ \leftrightarrow L			66.7		1326	Congruent	
L \leftrightarrow CoSi ₂ + (Si)		77.5	66.7	97.9	1259	Eutectic	
[64Kal]	CoSi \leftrightarrow L		50.0		1465	Congruent	
[68Kal1]	CoSi ₂ \leftrightarrow L		66.7		1322	Congruent	
[72Boo]	L \leftrightarrow (α Co) + α Co ₃ Si	25.0	1200	Eutectic	
	α Co ₃ Si \leftrightarrow (α Co) + α Co ₂ Si	25.0	...	33.3	1170	Eutectoid	
	L + α Co ₂ Si \leftrightarrow α Co ₃ Si	...	33.3	25.0	1210	Eutectic	
	(α Co) + L \leftrightarrow (ϵ Co)	16.5	21.4	17.5	1250	Peritectic	
	L \leftrightarrow (ϵ Co) + α Co ₃ Si	23.1	18.4	25.0	1204	Eutectic	
[73Kos](a)	α Co ₃ Si \leftrightarrow (ϵ Co) + α Co ₂ Si	25.0	18.1	...	1193	Eutectoid	
	L + α Co ₂ Si \leftrightarrow α Co ₃ Si	24.4	...	25.0	1214	Peritectic	

(a) Data read from the figure.

structure, stable between 1238 °C and the congruent melting temperature of 1334 °C; (6) the cubic intermediate phase CoSi , stable up to its congruent melting at 1460 °C; (7) the cubic phase CoSi_2 , stable up to its congruent melting at 1326 °C; and (8) the cubic solid solution, (Si), with negligible solid solubility of Co. The assessed phase diagram of the Co-Si system is shown in Fig. 1, and a detail of the high-temperature equilibria between 14 and

42 at.% Si is shown in Fig. 2. The special points of the assessed diagram and reported experimental data are listed in Tables 1 and 2, respectively.

Terminal Solid Solubilities

The $(\alpha\text{Co})/(\epsilon\text{Co})$ phase equilibria illustrated in Fig. 1 and 2 were determined by differential thermal analysis (DTA) [73Kos] and

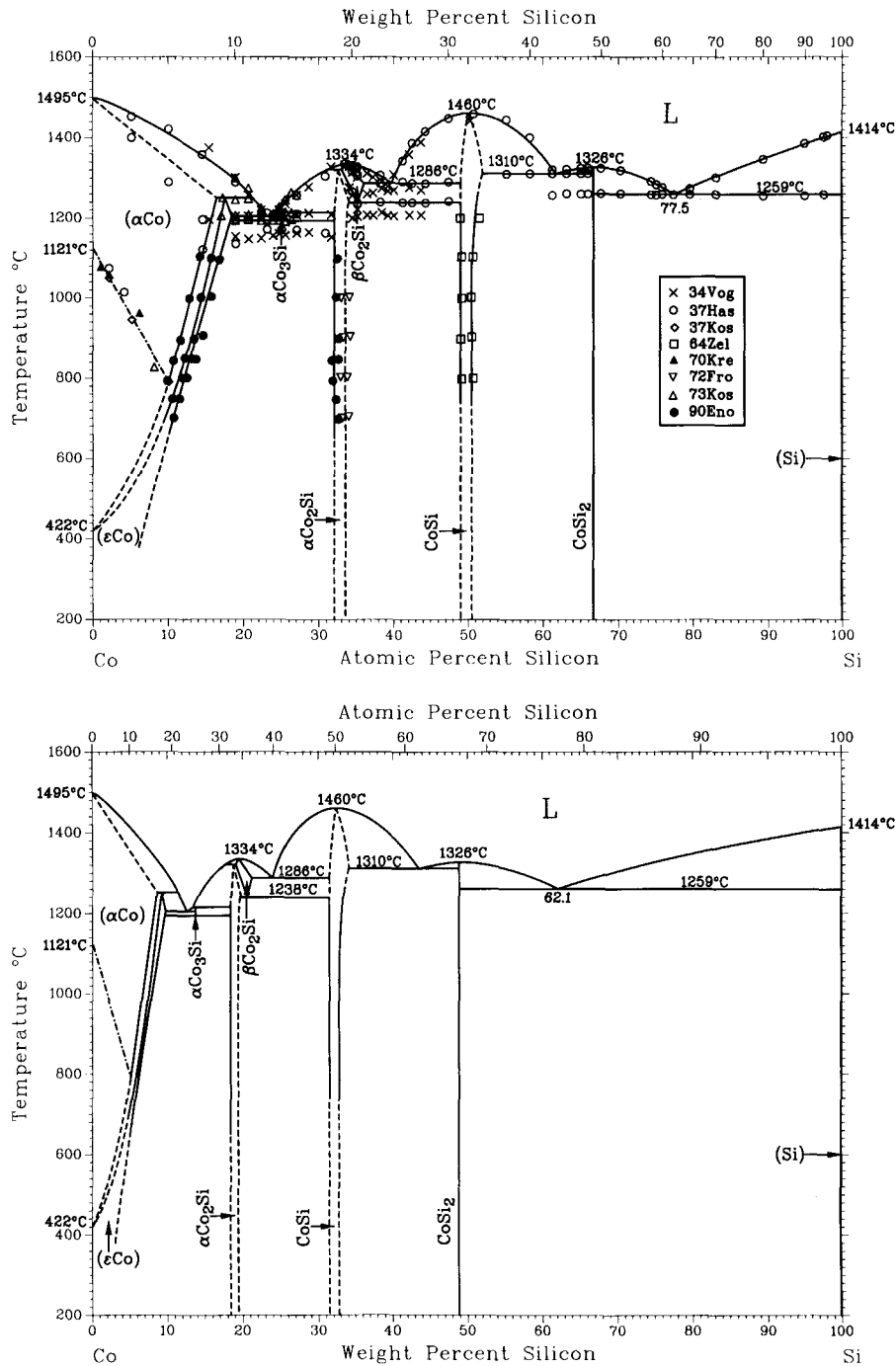


Fig. 1 Assessed Co-Si phase diagram.

Section II: Phase Diagram Evaluations

electron probe microanalysis (EPMA) [90Eno], with both sets of data in good agreement at high temperatures. These studies of phase equilibria show that (ϵ Co) is stable up to the peritectic temperature of 1250 °C, and that the maximum Si solubility in (ϵ Co) is 18.4 at.% Si at the Co-Co₂Si eutectic temperature of 1204 °C [73Kos]. The high-temperature terminal solid solubilities

shown in Fig. 1 are comparable to those reported by [63Luo], [67Pan], and [88Lik], but the exact lower-temperature solubility is less certain. Experimental data on the solid solubilities of (α Co) and (ϵ Co) are presented in Table 3. The solid solubility of Co in (Si) is very small; data reported by [57Col] and [77Kit] are given in Table 4.

Table 3 Co-Si Solid Solubility Data

Reference	Temperature, °C	Composition, at. % Si										
		(α Co)	(ϵ Co)		α Co ₂ Si		β Co ₂ Si		CoSi		Comment	
		Si-poor	Si-rich	Si-poor	Si-rich	Si-poor	Si-rich	Si-poor	Si-rich	Si-poor		Si-rich
[34Vog].....	1275	34.0	(a, b)
	1255	34.4	
	1221	35.1	
[64Zel].....	1200	48.5	50.9	(c)
	800 to 1100	49.0	50.6	
[72Fro].....	700 to 1000	33.0	33.6	(d)
[73Kos].....	1221	...	17.2	(a, b)
[90Eno].....	1100	14.4	15.2	(e)
		16.9	(f)
	1000	12.7	13.8	(e)
		15.6	(f)
	900	11.6	13.3	14.4	...	32.2	(e)
		14.5	...	32.6	(f)
	850	10.6	12.1	12.9	...	31.7	(e)
		13.6	...	32.7	(f)
	800	10.0	11.4	12.1	...	31.8	(e)
	750	...	10.2	11.2	...	32.1	(e)
	700	10.5	...	32.6	(e)

(a) Data read from the figure. (b) Thermal analysis. (c) X-ray data. (d) Metallography. (e) EPMA (diffusion couple). (f) EPMA (two-phase specimen).

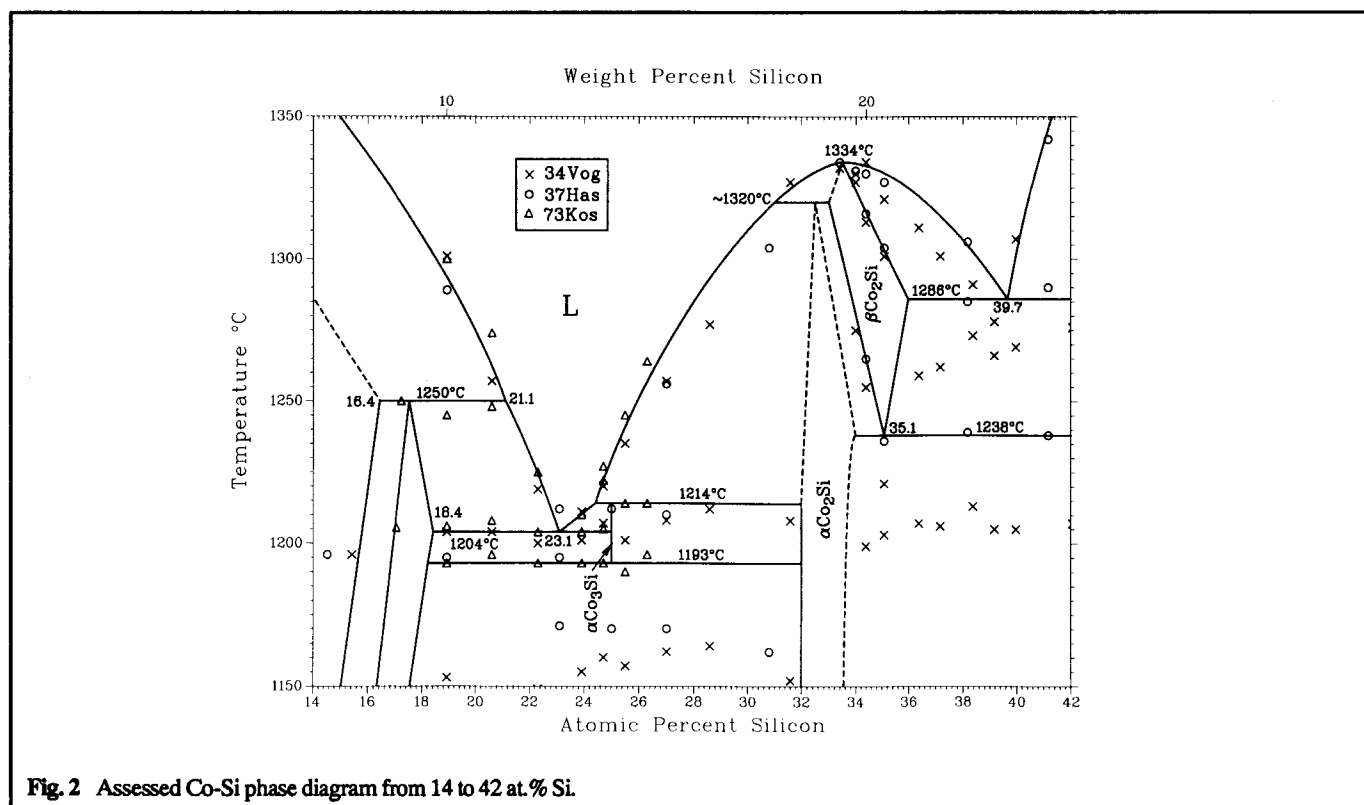


Fig. 2 Assessed Co-Si phase diagram from 14 to 42 at.% Si.

Liquidus and Solidus

Co-Si liquidus and solidus temperatures were measured by DTA in the composition ranges 15 to 50 at.% Si [34Vog], 0 to 100 at.%

Table 4 Solid Solubility of Co in (Si)

Reference	Temperature, °C	Solubility (N _{Co}), cm ⁻³
[57Col].....	1200	10 ¹⁶
[77Kit].....	1270	1.3 × 10 ¹⁶
	1250	1.1 × 10 ¹⁶
	1200	6.3 × 10 ¹⁵
	1200	4.7 × 10 ¹⁵
	1150	3.0 × 10 ¹⁵
	1100	9.9 × 10 ¹⁴
	1100	1.0 × 10 ¹⁵
	1000	1.3 × 10 ¹⁴

Note: As measured by radiotracer method.

Si [37Has], and 17 to 26 at.% Si [73Kos]. These data are shown in Table 5.

Intermediate Phases

αCo₃Si. The stable αCo₃Si illustrated in Fig. 1 is the subject of considerable controversy, and was not yet conclusively identified in quenched samples. The evidence for its existence relies almost solely on thermal analysis results and microstructural observation of its presumed eutectoid decomposition [34Vog, 37Has, 72Boo, 73Joh, 73Kos], which [37Kos], [63Kuz], and [67Pan] could not detect. According to the metallographic and DTA studies of [72Boo], αCo₃Si is stable between 1170 and 1210 °C, and [73Kos] ascertained the existence of αCo₃Si by DTA between 1193 and 1214 °C. One possible cause for the disagreement may lie in the purities of the material used in the particular investigation; [76Liv] showed that adding small quantities of Al, Ta, or W to a stoichiometric αCo₃Si alloy suppressed the formation of a eutectoid structure. [73Joh] examined the crystal structure of αCo₃Si quenched to room temperature by X-ray diffraction

Table 5 Co-Si Liquidus and Solidus Data from Thermal Analysis

Composition, at.% Si	Liquidus	Solidus	Invariant	Composition, at.% Si	Liquidus	Solidus	Invariant
From [34Vog](a)				From [37Has](cont.)			
15.4.....	1375	...	1196	38.2.....	1307	...	1285 1239
18.9.....	1301	...	1204 1153	41.2.....	1342	...	1290 1238
20.6.....	1257	...	1204 1147	42.5.....	1386	...	1286 1238
22.3.....	1219	...	1200 1149	44.3.....	1415	...	1285 1237
23.9.....	1211	...	1201 1155	47.4.....	1447	...	1289 1241
24.7.....	1220	...	1207 1160	50.8.....	1458
25.5.....	1235	...	1201 1157	55.2.....	1444	...	1309
27.0.....	1257	...	1208 1162	58.3.....	1400	...	1310
28.6.....	1277	...	1212 1164	61.3.....	1320	...	1310 1256
31.6.....	1327	...	1208 1152	63.2.....	1321	...	1310 1260
33.4.....	1332	65.1.....	1323	...	1310 1259
34.0.....	1330	1327	1275	66.0.....	1324	...	1310 1259
34.4.....	1334	1313	1255 1199	67.7.....	1323	...	1260
35.1.....	1321	1301	1221 1203	70.3.....	1318	...	1260
36.4.....	1311	...	1259 1207	74.4.....	1291	...	1258
37.2.....	1301	...	1262 1206	75.1.....	1283	...	1257
38.4.....	1291	...	1273 1213	75.9.....	1276	...	1259
39.2.....	1278	...	1266 1205	77.4.....	1258
40.0.....	1307	...	1269 1205	79.6.....	1273	...	1259
42.1.....	1358	...	1276 1207	83.1.....	1300	...	1258
43.7.....	1388	...	1269 1207	89.4.....	1346	...	1255
50.3.....	1441	95.0.....	1385	...	1255
				97.6.....	1401	...	1258
				98.1.....	1405
From [37Has]				From [73Kos](a)			
5.1.....	1452	1400	...	17.2.....	1250
10.0.....	1421	1289	...	18.9.....	1300	...	1245 1206 1193
14.5.....	1358	...	1196 1121	20.6.....	1274	...	1248 1208 1196
18.9.....	1289	...	1195 1135	22.3.....	1225	...	1204 1193
23.1.....	1195 1212 1171	23.9.....	1210	...	1204 1193
25.0.....	1212 1170	24.7.....	1227	...	1222 1205 1193
27.0.....	1256	...	1210 1170	25.5.....	1245	...	1214 1190
30.8.....	1304	...	1162	26.3.....	1264	...	1214 1196
33.4.....	1334				
34.0.....	1331				
34.4.....	1330	1316	1265				
35.1.....	1327	1304	1236				

(a) Data read from the figure.

Section II: Phase Diagram Evaluations

(XRD), and tentatively assigned an unspecified tetragonal structure.

Co₂Si. [34Vog] and [37Has] studied the transformation behavior of Co₂Si by thermal analysis; both data sets on the stability range of high-temperature βCo₂Si are in good agreement. However, neither investigation was able to produce retained βCo₂Si, and the calorimetric experiments of [72Fro] could not reproduce the transformation. More explicit confirmation of this phase is desirable. Low-temperature αCo₂Si melts peritectically at 1320

°C (L + βCo₂Si ↔ αCo₂Si) and also participates in eutectoid reactions at 1193 and 1238 °C and the peritectoid reaction at 1214 °C. The homogeneity range of αCo₂Si was reported to be 33.0 to 33.6 at.% Si between 700 and 1000 °C from metallographic observations [72Fro].

CoSi. Cubic CoSi is stable below its congruent melting temperature of 1460 °C. The homogeneity range determined by X-ray measurements is from 49.0 to 50.6 at.% Si in the temperature range 800 to 1000 °C and from 48.5 to 50.9 at.% Si at 1200 °C [64Zel].

CoSi₂. Cubic CoSi₂, with an almost stoichiometric composition, is stable below its congruent melting temperature of 1326 °C.

Table 6 Co-Si Transformation Temperatures

Reference	Composition, at.% Si	Temperature, °C		Method
		Heating	Cooling	
[37Has].....	2.1	537	469	Dilatometric
		536	468	Magnetic
	4.1	597	524	Dilatometric
		596	525	Magnetic
	8.1	687	594	Dilatometric
688		595	Magnetic	
11.4	738	635	Dilatometric	
	[37Kos](a).....	2.1	482	384
5.1		658	458	Dilatometric
		654	468	Magnetic
10.0		795	550	Dilatometric
		795	555	Magnetic
14.5	1025	982	Magnetic	
[70Kra].....	1.77	526	459	Dilatometric
	8.15	454	402	Dilatometric
	9.86	449	400	Dilatometric
[73Kos](a).....	2.1	533	463	Dilatometric
		526	470	Thermal
	4.1	602	513	Thermal
	6.1	684	558	Dilatometric
		672	565	Thermal
	8.1	728	580	Dilatometric
		739	590	Thermal
	10.0	782	596	Dilatometric
		778	596	Thermal

(a) Data read from the figure.

Metastable Phases

[63Luo] reported that an (αCo) solid solution up to 15 at.% Si was obtained by rapid quenching from the melt, which is within the solubility limit of equilibrium (αCo). It was recognized that the formation and transformation behaviors of αCo₃Si and αCo₂Si are complex and are quite different on heating from those on cooling [72Boo, 73Joh, 73Kos, and 74Boo]. This is mainly due to suppression of the formation of αCo₃Si on cooling. The metastable eutectic reaction L ↔ (αCo) + αCo₂Si at ~1192 °C was found by [72Boo] and was supported by [74Boo] and [75Liv], whereas [73Kos] did not detect this reaction. According to [73Joh], αCo₃Si transforms ultimately to a eutectoid structure of αCo₂Si and the Co-rich solid solution, but the reaction only was observed to proceed *via* a transition phase with an orthorhombic structure not distinguished from that of αCo₂Si. This phase appears to form by a massive transformation. [73Kos] found a metastable ordered phase of βCo₃Si with D0₁₉ structure, with a composition of ~8 at.% Si at temperatures below about 570 °C.

The tetragonal phase Co₂Si₃, formed at pressures >4 GPa and temperatures of 500 to 750 °C, is metastable under ordinary conditions. After annealing at 700 °C, it decomposes into αCoSi₂ and CoSi [82Lar].

Table 7 Co-Si Crystal Structure Data

Phase	Composition, at.% Si	Pearson symbol	Space group	Strukturbericht designation	Prototype	Comment	Reference
(αCo).....	0 to 16.4	cF4	Fm $\bar{3}$ m	A1	Cu	422 < T < 1495 °C	[83Nis]
(εCo).....	0 to 18.4	hP2	P6 ₃ /mmc	A3	Mg	T < 1245 °C	[83Nis]
αCo ₃ Si.....	25	t**	1193 < T < 1214 °C	[73Joh]
αCo ₂ Si.....	-32 to -34	oP12	Pnma	C23	Co ₂ Si	T < -1320 °C	[Pearson1]
βCo ₂ Si.....	-32 to 35.8	?	?	?	?	1238 < T < 1334 °C	...
CoSi.....	49 to -52	cP8	P2 ₁ 3	B20	FeSi	T < 1460 °C	[Pearson1]
CoSi ₂	66.7	cF12	Fm $\bar{3}$ m	C1	CaF ₂	T < 1326 °C	[Pearson1]
(Si).....	-100	cF8	Fd $\bar{3}$ m	A4	C(diamond)	T < 1414 °C	[King1]
Metastable phases							
βCo ₃ Si.....	-8 to 25	hP8	P6 ₃ /mmc	D0 ₁₉	Ni ₃ Sn	T < 570 °C	[73Kos]
Co ₄ Si.....	-20	?	?	?	?	Thin film	[86Apr]
γCo ₂ Si.....	-25	o**	(a)	[73Joh]
Co ₂ Si ₃	60	tP20	P4c2m	...	Ru ₂ Sn ₃	P > 4.0 GPa 500 < T < 700 °C	[82Lar]

(a) Formed by massive transformation.

Table 8 Co-Si Lattice Parameter Data

Phase	Composition, at. % Si	Lattice parameters, nm			Comment	Reference
		a	b	c		
(αCo).....	0	0.35446	Pure αCo	[83Nis]
	4	0.35420	(a, b)	[63Luo]
	8	0.35395	(a, b)	[63Luo]
	11.5	0.35365	(a, b)	[63Luo]
	13	0.35355	(a, b)	[63Luo]
	15	0.35350	(a, b)	[63Luo]
(εCo).....	0	0.25071	...	0.40695	Pure εCo	[83Nis]
	5.1	0.24925	...	0.4050	...	[37Has]
	10.0	0.2486	...	0.4015	...	[37Has]
	14.5	0.2474	...	0.3970	(εCo) + αCo ₂ Si	[37Has]
	18.9	0.2475	...	0.3970	(εCo) + αCo ₂ Si	[37Has]
	4	0.2500 to 0.2503	...	0.4050 to 0.4084	800 to 1200 °C	[88Lik]
αCo ₃ Si.....	25	0.842	0.3738	0.581	...	[73Job]
αCo ₂ Si.....	33	0.4918	0.3730	0.7109	...	[Pearson1]
		0.4908	0.3725	0.7095	...	[Pearson2]
		0.4919	...	0.7104	...	[72Fro]
CoSi.....	50	0.4447	[Pearson1]
	49.1	0.44477	[64Zel]
	49.4	0.44467	[64Zel]
	49.6	0.44464	[64Zel]
	49.8	0.44446	[64Zel]
	49.9	0.44445	[64Zel]
	50.1	0.44444	[64Zel]
	50.4	0.44426	[64Zel]
	50	0.4448	[71Wal]
	50.7	0.4444	[64Zel]
CoSi ₂	66.7	0.5365	[Pearson1]
		0.53526	[87Wei]
Si.....	100	0.54306	[King1]
Metastable phases						
βCo ₃ Si.....	25	0.4976	...	0.4069	...	[73Kos]
Co ₂ Si ₃	60	0.5234	...	0.8543	...	[82Lar]

(a) Data read from the figure. (b) Splat quenched from the melt.

Table 9 Enthalpy Coefficients and Heats of Fusion for Cobalt Silicides

Phase	a	Coefficients, J/mol			Heat of fusion
		b	c × 10 ³	d × 10 ⁻⁵	
αCo ₂ Si(s).....	-24906	70.785	4.532	2.443	54 300
Co ₂ Si(L).....	-30708	136.74			
CoSi(s).....	-15400	47.1	5.95	5.67	69 200
CoSi(L).....	2920	87.4			
CoSi ₂ (s).....	-25200	71.64	7.569	9.501	100 200

Laser irradiation of thin Co films on single-crystalline Si was studied by [79Gur]. In the 0.1-μm Co film, Co₂Si, CoSi, and CoSi₂ were formed. CoSi₂ films on (111) Si substrates were obtained by solid phase epitaxy [80Sai] and by evaporation of Co onto Si [82Sor]. CoSi₂, CoSi, Co₂Si, and Co₄Si were obtained by solid-state reaction at 800 °C within thin bilayers of amorphous Si and Co evaporated onto SiO₂ substrates. The crystal structure of Co₄Si could not be determined [86Apr].

As with many other silicides, the fabrication of amorphous Co-Si alloys is of interest; [88Kim] showed that a minimum of 13.5

Table 10 Fitted Thermodynamic Parameters for Co-Si Liquid Alloys

Regular solution

$$\Delta G^{ex} = -112.073X_{Co}X_{Si} \quad (R^2 = 0.958)$$

Subregular Solution

$$\Delta G^{ex} = X_{Co}X_{Si}(-92.481X_{Co} - 133.151X_{Si}) \quad (R^2 = 0.971)$$

Subsubregular solution

$$\Delta G^{ex} = X_{Co}X_{Si}(-34.179X_{Co} - 99.958X_{Si} - 193.065X_{Co}X_{Si}) \quad (R^2 = 0.990)$$

Quasiregular solution

$$\Delta G^{ex} = -275.995X_{Co}X_{Si}(1 - T/3075) \quad (R^2 = 0.971)$$

at.% Si was necessary to produce amorphous Co-Si films by sputtering. An estimate of the glass transition temperature for Co_{1-x}Si_x (x = 0.33, 0.397, 0.618, 0.775) was reported by [79Nie].

The martensitic transformation of (αCo) ↔ (εCo) was studied by [37Has], [37Kos], [70Kra], and [73Kos]; the transformation temperatures are given in Table 6.

Section II: Phase Diagram Evaluations

Table 11 Experimental and Estimated Heats of Formation of Cobalt Silicides

Reference	Heat of formation, kJ/mol		
	$\alpha\text{Co}_2\text{Si}$	CoSi	CoSi ₂
[37Oel].....	-115.4	-92.0	-102.9
[73Cha].....	-113.1	-95.0	-98.7
[79Kau].....	-176.7	-144.9	-201.1
[81Mac].....	...	-92.0	...
[84Pas].....	-99.2	-89.5	-104.2
[88Nie].....	-90	-62	-45

Table 12 Co-Si Curie Temperatures

Reference	Composition, at. % Si	Curie Temperature, °C	
		(αCo)	(ϵCo)
[37Has].....	2.1	1074	...
	4.1	1014	...
	8.1	882	...
	11.5	754	...
	2.1	1050	...
[37Kos](a).....	5.1	945	...
	10.0	790	...
	14.5	625	735
	1.0	1078	...
[70Kre](a).....	2.1	1058	...
	6.1	962	...
	8.1	827	...

(a) Data read from the figure.

Crystal Structures and Lattice Parameters

The crystal structures of most of the phases in the Co-Si system are well-established; exceptions include $\alpha\text{Co}_3\text{Si}$ and $\beta\text{Co}_2\text{Si}$, neither of which was unambiguously identified as a stable phase. Crystal structure and lattice parameter data for the stable and metastable phases of the Co-Si system are summarized in Tables 7 and 8, respectively.

Thermodynamics

Several thermodynamic investigations of both liquid and solid alloys in the Co-Si system were reported, the first of these being the enthalpy of formation determinations made by [37Oel]. High-temperature heat capacity measurements were made for $\alpha\text{Co}_2\text{Si}$ [72Fro], CoSi [68Kal1], and CoSi₂ [64Kal]. The parameters for the standard $H_T - H_{298}$ equation ($a + bT + cT^2 + dT^{-1}$) are given in Table 9, along with the measured heats of fusion. For $\alpha\text{Co}_2\text{Si}$, the allotropic transformation had no apparent impact on the thermodynamic results. Subambient heat capacity measurements were made for CoSi [64Kal] and CoSi₂ [68Kal2].

Three experimental investigations of Gibbs energies of formation in molten Co-Si alloys were made. [68Mar] obtained activity coefficients of Si by equilibrating various Co-Si alloys with Ag-Si melts; their results are in substantial agreement with those of [64Sch], performed by determining the equilibria between these alloys and a calcium silicate melt. As might be expected, a strong negative deviation from ideal behavior was demonstrated, show-

ing some asymmetry with respect to composition; this was also shown by the two activity measurements of [64Bow], obtained by equilibrating liquid alloys with an SiO₂-H₂-H₂O environment. [80Kha1] and [80Kha2] analyzed the cause of the large negative value of the entropy of mixing in the liquid state determined by [64Sch] and concluded that it is due to an electronic contribution. Regression analysis was performed against the combined results of [64Sch] and [68Mar] to determine the coefficients of some common thermodynamic model equations; these are listed in Table 10. Heats of formation of molten alloys in this system were measured by [60Gel] as well as [37Oel]; the terminal heat of solution of Co in liquid Si was more negative in the former results. The enthalpy of mixing in the liquid state was calculated by [71Pet], [83Pas], [84Pas], and [85Fro]. The work of [37Oel] also yielded ΔH_{298}^0 values for the solid silicides, which are compared in Table 11 to the modeling results of [73Cha], [79Kau], [84Pas], and [88Nie].

The specific heat of CoSi was measured in the temperature range 0.5 to 9 K, and the electronic specific heat coefficient was determined to be 1.1 mJ/mol · K² [74Mar].

The order-disorder transition temperatures for $A2 \leftrightarrow B2$ and $B2 \leftrightarrow D0_3$ reactions in the bcc phase were evaluated by analyzing the experimental data on Fe-Co-Si alloys [79Ind]. [79Kau] presented an analytical description of the thermodynamic properties of the liquid, (αCo), (ϵCo), (Si), and the compound phases, and from these, he computed a phase diagram.

Thermal diffusivity and conductivity of Co alloys with 0 to 6 at. % Si were measured, and deep troughs at the Curie temperature were observed by [70Kre].

Magnetism

The Curie temperature of (αCo) phase was determined by [37Has], [37Kos], [70Kre], and [73Kos]; values are listed in Table 12.

Several studies of magnetic susceptibility of cobalt silicide alloys and compounds were made, including [55Ben1], [55Ben2], [66Shi], [72Ama], and [75Dov]; the results showed that CoSi is diamagnetic, and CoSi₂ paramagnetic. Debye temperatures were derived by a variety of experimental techniques [64Kal, 65And, 72Ama, 74Mar, 84Hen, 86Apr, 87Nav]. For CoSi₂, a single value of 220 K is reported [86Apr], whereas for CoSi, reported values range between 487 and 600 K, and for CoSi₂ between 450 and 500 K. Saturation magnetization and intrinsic coercivity measurements were made for high-Co eutectic/eutectoid compositions by [73Joh] and [75Liv], and studies of the thermoelectric properties of CoSi were made by [64Asa] and [81Zai].

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Section II: Phase Diagram Evaluations

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- *Indicates key paper.
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