The Co-Sn (Cobalt-Tin) System

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Equilibrium Diagram

The equilibrium phases of the Co-Sn system are: (1) the liquid, L; (2) the Co-rich, fcc terminal solid solution, (αCo); (3) the Co-rich, cph terminal solid solution, with a small solid solubility of Sn, (εCo); (4) Co_3Sn_2, with two modifications—high-temperature, hexagonal βCo_3Sn_2, stable up to its congruent melting at 1170 °C, and low-temperature, orthorhombic αCo_3Sn_2, stable below ~500 °C; (5) the hexagonal phase CoSn, stable up to the peritectic temperature of 936 °C; (6) the tetragonal intermediate phase $CoSn_2$, stable up to the peritectic temperature of 525 °C; and (7) the tetragonal solid solution, (βSn), with negligible solid solubility of Co.

The assessed Co-Sn phase diagram is shown in Fig. 1, and the invariant reactions are listed in Table 1.

Terminal Solid Solubilities

[38Has] estimated that the solid solubility of Sn in (αCo) is about 2 at.% Sn at 1033 °C from Curie temperature measurements. However, [85Com] showed with Sn activity measurements that the solubility is less than 1.25, 0.91, and 0.42 at.% Sn at 1000, 800, and 500 °C, respectively. The solid solubility of Sn in (εCo) was reported as 1.67 at.% Sn at 536 °C by [38Has], but this seems too high in comparison with the data of [85Com]. No data on the terminal solid solubility of Co in (βSn) are available, but this solubil-

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

Reaction	Composition of the respective phases, at.% Sn			Temperature, °C	Reaction type
$L \leftrightarrow \beta Co_3Sn_2$		~36.5		1170	Congruent
$L \leftrightarrow (\alpha Co) + \beta Co_3Sn_2$	20.5	~1.0	~35	1112	Eutectic
$\beta Co_3Sn_2 + L \leftrightarrow CoSn$	~78	41.5	50	936	Peritectic
$CoSn + L \leftrightarrow CoSn_2$	50	97	66.7	525	Peritectic
$\alpha Co_3Sn_2 \leftrightarrow \beta Co_3Sn_2$		~41.5		~500	Allotropic
$(\alpha Co) \leftrightarrow (\varepsilon Co) + \alpha Co_3Sn_2$	<99.5	<99.5	~41	~420	Eutectoid
$L \leftrightarrow CoSn_2 + (\beta Sn)$	~99.5	66.7	<99.5	229	Eutectic

Table 2 Co-Sn Liquidus Data

Reference	Comment	Composition, at.% Sn	Temperature, °C: Liquidus	Invariant		
[08Lew]	Thermal analysis	0	1440	...	...	...
		1.04	1434	...	...	...
		2.32	1397	1096	...	...
		4.90	1374	1096	...	...
		7.74	1333	1095	...	...
		10.78	1292	1098	...	...
		17.73	1160	1098	...	...
		18.99	1102	1093	...	...
		20.78	1099	1091	...	...
		22.63	1104	1095	...	...
		24.54	1111	1096	...	...
		26.50	1130	1095	...	...
		32.46	1151	...	...	...
		35.04	1146	...	523	...
		42.25	1137	944	532	...
		47.50	1133	940	535	...
		53.50	1101	945	536	231
		56.16	1097	950	536	228
		59.28	1079	946	536	225
		65.92	1036	932	525	230
		73.13	974	945	536	229
		80.54	906	...	515	231
		89.64	790	...	506	228
		94.27	567	...	505	229
		100	232	...	...	...

(continued)

ity is estimated to be less than 0.5 at.% Co, because the solubilities of transition metals in (βSn) are very small [Massalski].

Liquidus and Solidus

The Co-Sn liquidus temperatures were determined by thermal analysis in the Co-rich region by [38Has] and over the whole range of composition by [08Lew] and [08Zem]. [69Dar] determined the solubility of Co in liquid Sn by analyzing the composition of the liquid in equilibrium with Co after heating at each temperature. These data are summarized in Table 2, together with the invariant temperatures. The invariant reactions are: (1) L ↔ (αCo) + βCo_3Sn_2 at 1112 °C, with the eutectic composition of 20.5 at.% Sn; (2) βCo_3Sn_2 + L ↔ CoSn at 936 °C; (3) CoSn + L ↔ $CoSn_2$ at 525 °C; and (4) L ↔ $CoSn_2$ + (βSn) at 229 °C.

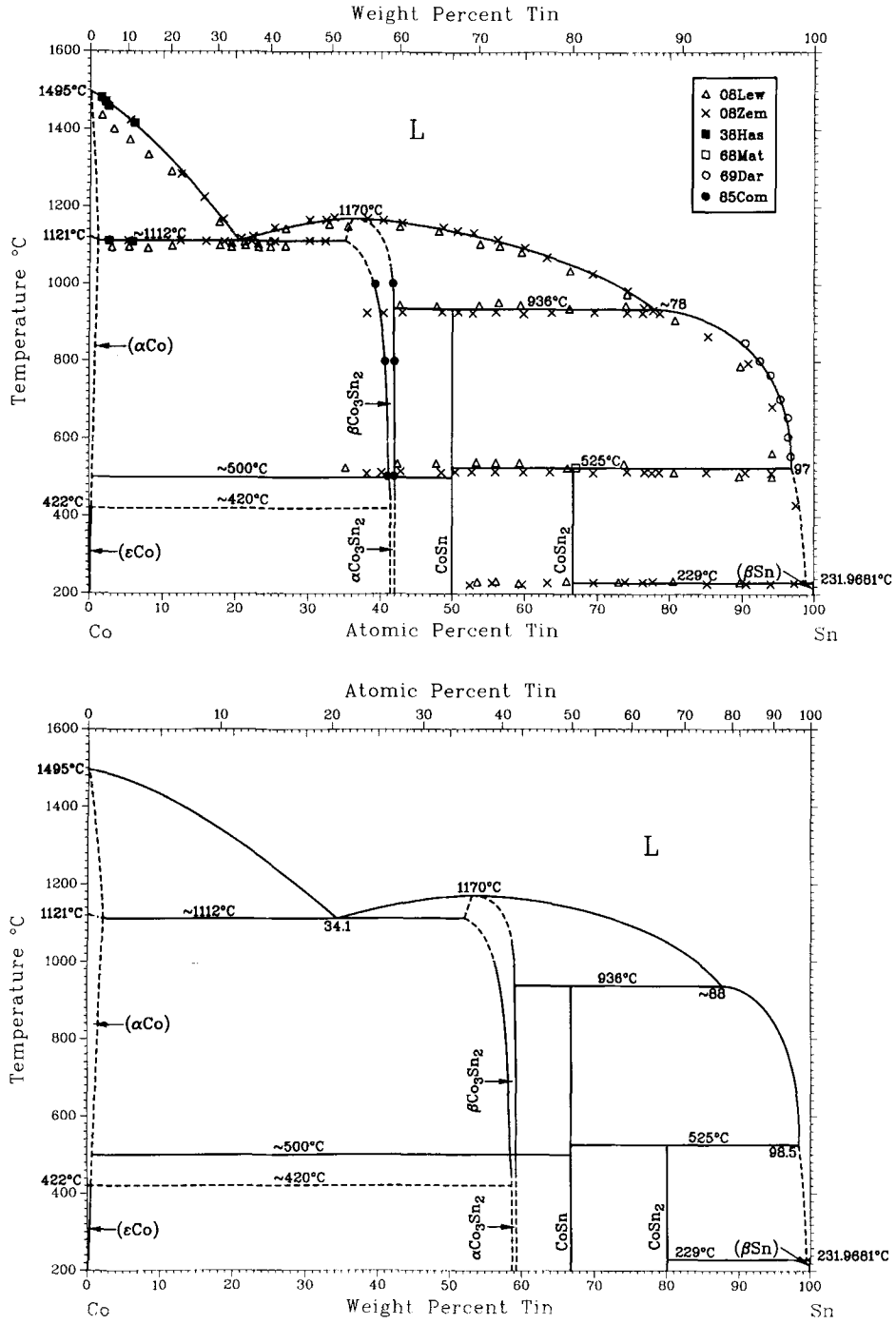

Fig. 1 Assessed Co-Sn phase diagram.

Table 2 Co-Sn Liquidus Data (continued)

Reference	Comment	Composition, at.% Sn	Temperature, °C			
			Liquidus	Invariant		
[08Zem]	Thermal analysis	0	1502	...	...	...
		5.00	1415	1110	...	...
		12.00	1280	1112	...	...
		15.40	1223	1112	...	...
		18.00	1165	1112	...	...
		20.50	1112	1112	...	...
		21.95	1122	1112	...	...
		25.00	1140	1112	...	...
		29.79	1164	1110	...	...
		32.00	1166	1109	...	...
		33.30	1171	...	...	...
		37.77	1167	923	510	...
		40.00	1163	924	512	...
		42.65	1160	926	515	...
		48.10	1147	927	515	...
		50.25	1138	927	515	...
		52.50	1132	927	515	221
		55.80	1115	927	515	225
		59.68	1097	927	515	227
		63.19	1070	927	515	229
		69.40	1028	927	515	229
		73.80	980	927	515	229
		76.39	940	927	515	229
		77.50	927	927	515	229
		78.48	922	...	515	229
		85.00	865	...	515	229
		90.49	798	...	513	229
		94.00	681	...	513	229
		97.50	430	...	...	229
		100	231.5	...	...	...
[38Has]	Thermal analysis	0	1492	...	...	...
		0.50	...	...	...	...
		1.00	1479	...	...	...
		1.67	1467	...	...	...
		2.18	1460	1109	...	...
		5.23	1412	1108	...	...
[68Mat](a)	Thermal analysis	66.7	...	...	525	...
[69Dar]	Equilibration, chemical analysis	90.39	848	...	...	...
		92.24	800	...	...	...
		94.01	766	...	...	...
		95.47	705	...	...	...
		96.40	656	...	...	...
		96.42	603	...	...	...
		96.62	554	...	...	...

(a) Data read from the figure.

Intermediate Phases

βCo_3Sn_2 is formed congruently at 1170 °C and has a range of homogeneity. From the activity data of [85Com], the homogeneous compositions are estimated to be 39.2 to 41.2, 40.2 to 41.6, and 40.7 to 41.3 at.% Sn at 1000, 800, and 500 °C, respectively. The stoichiometric compounds CoSn and $CoSn_2$ are formed by peritectic reaction with liquid compositions of ~78 and 97 at.% Sn, respectively.

Metastable Phases

Martensitic transformations of (αCo) ↔ (εCo) were studied by thermal dilatation [38Has, 70Kra], magnetic analysis [38Has] and X-ray diffraction [84Nik]. The transformation temperature on heating is raised, and the M_s temperature is lowered at the rate of about 50 to 60 °C/at.% Sn [38Has, 70Kra]. The crystal structure of the martensite is cph below 1.5 at.% Sn, whereas a seven-layer structure that contains a large number of random stacking faults is found from 1.5 to 8.1 at.% Sn [84Nik]. However, the data for alloys with high Sn content are questionable, because the solubility of Sn is rather limited.

[63Luo] reported that (αCo) solid solutions were obtained up to 5 at.% Sn by rapid quenching from the melt.

A metastable stoichiometric Co_3Sn compound prepared by splat quenching from the melt, decomposed into (αCo) and βCo_3Sn_2 at about 577 °C [80Sch]. [82Sin] also confirmed the metastable Co_3Sn phase by rapid cooling from the melt.

Amorphous films were obtained by co-evaporation of Sn and Co on liquid nitrogen-cooled substrates, with compositions over the range 25 to 77 at.% Sn, and the crystallization temperatures were

Table 3 Co-Sn Crystal Structure Data

Phase	Composition, at.% Sn	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(αCo)(a)	0 to ~2	*cF4*	$Fm\bar{3}m$	*A1*	Cu	[83Nis]
(εCo)(b)	0 to ~0.2	*hP2*	$P6_3/mmc$	*A3*	Mg	[83Nis]
βCo_3Sn_2(c)	~35 to ~42	*hP4*	$P6_3/mmc$	$B8_1$	NiAs	[76Ell]
αCo_3Sn_2(d)	~41 to ~42	*oP20*	*Pnma*	...	Ni_3Sn_2	[72Jai]
CoSn	50	*hP6*	*P6/mmm*	*B35*	CoSn	[Pearson1]
$CoSn_2$	66.7	*tI12*	*I4/mcm*	*C16*	Al_2Cu	[Pearson1]
(βSn)	~100	*tI4*	$I4_1/amd$	*A5*	βSn	[King1]
Metastable phases						
(εCo)(e)	0 to 1.5	*hP2*	$P6_3/mmc$	*A3*	Mg	[84Nik]
(ε'Co)(e)	1.5 to 8.1	...	$R\bar{3}m$	...	...	[84Nik]
Co_3Sn(f)	25	*cI2*	$Im\bar{3}m$	*A2*	W	[80Sch]
		cP2	$Pm\bar{3}m$	*B2*	CsCl	[82Sin]

(a) From 1495 to 422 °C at 0 at.% Sn. (b) Below 422 °C at 0 at.% Sn. (c) Stable above 500 °C. (d) Stable below 500 °C. (e) Martensite structure. (f) Splat cooled from the melt.

Table 4 Co-Sn Lattice Parameter Data

Phase	Composition, at.% Sn	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
αCo	0	0.35446	...	...	Pure αCo at >422 °C	[83Nis]
εCo	0	0.25071	...	0.40695	Pure εCo	[83Nis]
βCo_3Sn_2	41.7	0.4104	...	0.5171	...	[62Asa]
	38	0.4118	...	0.5187	...	[76Ell]
	39	0.4117	...	0.5186	...	[76Ell]
	40	0.4113	...	0.5185	...	[76Ell]
	41	0.4105	...	0.5176	...	[76Ell]
	42	0.4101	...	0.5173	...	[76Ell]
αCo_3Sn_2	39.5	0.820	0.709	0.522	(c)	[72Jai]
	40.0	0.8198	0.7089	0.5221	(c)	[72Jai]
CoSn	50	0.5279	...	0.4258	...	[Pearson1]
$CoSn_2$	66.7	0.6361	...	0.5452	...	[Pearson1]
		0.6363	...	0.5456	...	[72Hav]
βSn	100	0.58316	...	0.31815	...	[King1]
Metastable phases						
(αCo)	0.8	0.3551	...	...	(a,b)	[63Luo]
	1.54	0.3556	...	...	(a,b)	[63Luo]
	3.0	0.3566	...	...	(a,b)	[63Luo]
	5.0	0.3577	...	...	(a,b)	[63Luo]
Co_3Sn	25	0.29228	...	...	(b)	[80Sch]
		0.2939	...	...	(b)	[82Sin]

(a) Data read from the figure. (b) Phase obtained by splat cooling from the melt. (c) Probably containing a small amount of (εCo).

determined by electrical resistivity measurements and electron microscopy [82Gen]. The structural relaxation of these amorphous films was investigated by [86Aud]. [86Gaf] reported that an amorphous phase was obtained by solid state diffusion using an ultrafine powder of Co covered with a deposit of Sn.

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data on the stable and metastable phases of the Co-Sn system are summarized in Tables 3 and 4, respectively. The $\alpha Co_3Sn_2 \leftrightarrow \beta Co_3Sn_2$ transformation temperature was estimated by magnetic susceptibility measurements to be 547 [60Sch] or ~500 °C [62Asa].

Thermodynamics

The thermodynamic properties of liquid Co-Sn alloys were studied by [37Kor], [71Bow], and [71Ere]. The calorimetric data measured by [37Kor] at 1500 °C show exothermic enthalpies of formation in liquid alloys containing up to 60 at.% Sn, but endothermic values beyond this composition. [71Ere] also reported that the activity of Sn exhibits negative departures from ideal behavior in Co-rich liquids and positive deviations in Sn-rich liq-

Table 5 Thermodynamic Properties of Liquid Co–Sn Alloys at 1573 K

Composition, at.% Sn	ΔG_{Co}, J/mol	ΔG^{ex}_{Co}, J/mol	ΔG_{Sn}, J/mol	ΔG^{ex}_{Sn}, J/mol	$\Delta_f G$, J/mol	$\Delta_f H$, J/mol	$\Delta_f S$, J/mol·K
10	–1 390	0	–42 080	–11 980	–5 460	–1590	2.46
20	–3 590	–670	–29 830	–8 520	–8 840	–2260	4.18
30	–7 100	–2450	–18 660	–2 920	–10 580	–2300	5.26
40	–11 940	–5300	–9 600	+1 830	–11 000	–1800	5.85
50	–14 900	–5420	–6 250	+2 810	–10 580	–1050	6.06
60	–17 610	–5630	–3 940	+2 710	–9 410	–210	5.85
70	–19 790	–4060	–2 750	+1 940	–7 270	+540	4.96
80	–22 420	–1380	–1 670	+1 250	–5 820	+920	4.29
90	–26 670	+3430	–810	+510	–3 400	+840	2.69

From [71Ere].

Table 6 Partial and Integral Quantities of Formation for Solid Co-Sn Alloys

Composition, atomic fraction X_{Sn}	Phase	ΔH_{Co}, J/mol	ΔH_{Sn}, J/mol	$\Delta_f H$, J/mol	ΔS_{Co}, J/mol·K	ΔS_{Sn}, J/mol·K	$\Delta_f S$, J/mol·K
0.0091	(a)	20	–36 150	–310	0.09	–14.38	–0.04
0.405	βCo_3Sn_2	9 440	–49 060	–14 250	10.65	–30.01	–5.82
0.410	βCo_3Sn_2	8 790	–48 160	–14 560	11.73	–31.74	–6.08
0.415	βCo_3Sn_2	12 920	–54 040	–14 870	17.46	–39.84	–6.32
0.50	CoSn	...	...	–22 100	...	...	–12.80
0.667	$CoSn_2$	...	...	–14 730	...	...	–7.23

From [85Com].
Note: Reference states, Co(fcc) and Sn(L).
(a) $(\alpha Co)/(\alpha Co) + \beta Co_3Sn_2$ phase boundary.

Table 7 Co-Sn Magnetic Properties

Phase	Composition, at.% Sn	Curie temperature, °C	Comment	Reference
(αCo)	0	1121	...	[83Nis]
	1.00	1092	...	[38Has]
	1.67	1041	...	[38Has]
	2.18	1033	Two phase	[38Has]
	5.23	1034	Two phase	[38Has]
Co_3Sn	25	–227	Metastable phase	[80Sch]
βCo_3Sn_2	41.2	...	Paramagnetic	[60Sch]
	41.7	...	Paramagnetic	[62Asa]
αCo_3Sn_2	41.2	...	Paramagnetic	[60Sch]
	41.7	...	Asymptotic Curie temperature (≈ 407 °C)	[62Asa]
$CoSn_2$	66.7	...	Weak paramagnetic	[60Kan]

uids at 1300 °C, which is in good agreement with the data of [37Kor]. [71Bow] calculated the partial molar enthalpies and entropies of the liquid phase from the solubility data by [69Dar]. The thermodynamic properties of liquid Co-Sn alloys given by [71Ere] are shown in Table 5.

The enthalpies of formation of solid alloys were determined by a calorimetric method [37Kor, 79Pre] and by a solid-electrolyte galvanic-cell technique [85Com]. These data show large exothermic enthalpies of formation. [85Com] also measured the activity of Sn between 600 and 1050 °C. The partial and integral enthalpies and entropies obtained by [85Com] are shown in Table 6.

Magnetism

The effect of Sn on the Curie temperature of (αCo) was studied by [38Has]. The metastable compound Co_3Sn formed by splat quenching from the melt is ferromagnetic, and the Curie temperature was estimated to be about 227 °C [80Sch]. Other intermetallic compounds are paramagnetic [60Kan, 60Sch, 62Asa]. The hyperfine field at ^{119}Sn in (αCo) and (εCo) was studied as a function of temperature, and an anomalous temperature dependence was observed [67Jai, 69Cra]. The saturation magnetization of Co alloys with 0 to 50 at.% Sn was measured by [78Mal]. The magnetic properties of the Co-Sn system are summarized in Table 7.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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