The Cd-Sn (Cadmium-Tin) System

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Equilibrium Diagram

The Cd-Sn system consists of: the liquid, L; two solid solution phases, (Cd) and (Sn); the Sn-rich intermediate phase β; and three invariant reactions—a eutectic, a eutectoid, and a peritectic. The assessed phase diagram is presented in Fig. 1. The invariant temperatures and compositions are listed in Table 1, and the solubilities of Cd in (Sn) and Sn in (Cd) estimated by various researchers are listed in Table 2.

Liquidus

The liquidus curves established early by the cooling curve method [01Kap, 12Sch, 13Lor, 13Maz, 35Han] show good correspondence and fit with differential thermal analysis (DTA) results [1890Hey, 1892Hey, 38Han, 82Eva]. As shown in Fig. 1, the curve fitted through experimental points based on thermal measurements runs very close to that calculated from the thermodynamic data. The liquidus proposed in [68Nis], which was extrapolated from the transformation energy, is not included in the present assessment, because it strongly differs from the average.

Invariant Reactions

The eutectic temperature was established by various authors as in the range 176 to 182 °C, and the composition was placed within 66.5 to 70.4 at.% Sn (see Table 1). The composition 66.55 at.% Sn proposed in [30Sto]—based on cooling curve analysis of eight alloys of composition close to the eutectic—is accepted for the present assessment, and the temperature 176 °C established in [13Maz], [64Kul], [35Han], and [38Han], is also accepted. ([38Han] was based on careful thermal analysis of a large number of alloys.)

The data concerning the peritectic reaction temperature (223 °C) are in very good agreement (see Table 1), but they show significant differences regarding the composition of β. From the available data, the composition 99 at.% Sn is accepted, based on DTA and tensile test results on quenched liquid alloys. [82Eva] pointed out that conventional slow cooling of alloys in the peritectic range can generate persistent nonequilibrium structures, leading to misinterpretation of cooling curve results. From [82Eva], the upper branch of the range of the existence of β (which is very close to the fracture test

Fig. 1 Assessed Cd-Sn Phase Diagram

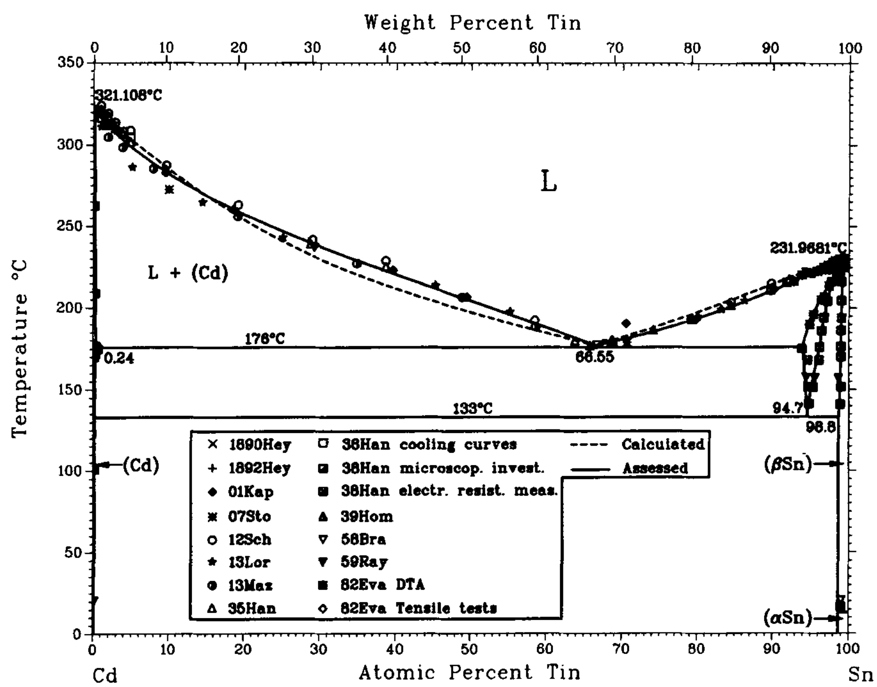

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Table 1 Reported Cd-Sn Invariant Compositions and Temperatures

Reaction	Composition, at.% Sn			Temperature, °C	Reaction type	Reference
L ↔ β + (Cd)		70.4		176	Eutectic	[01Kap]
		70.59		177	Eutectic	[07Sto]
		67.6		177	Eutectic	[12Sch]
		68.8		176	Eutectic	[13Maz]
		68.8		177	Eutectic	[26Fed]
		66.55		...	Eutectic	[30Sto]
		...		182	Eutectic	[31Mat]
		65.8		176	Eutectic	[35Han]
		66.55		176	Eutectic	[35Han, 58Bra]
		66.5		176	Eutectic	[64Kul]
		68.2		...	Eutectic	[68Nis]
		...		177	Eutectic	[82Eva]
	66.55	~94	0.24	176	Eutectic	Assessed
β ↔ (Sn) + (Cd)		...		130	Eutectoid	[01Kap, 82Eva]
		90.0		122 to 135	Eutectoid	[07Sto]
		...		127	Eutectoid	[12Sch]
		95.3		130	Eutectoid	[13Maz]
		...		120	Eutectoid	[26Fed]
		95.4		129	Eutectoid	[31Mat]
		94.7		128	Eutectoid	[35Han]
		94.7		133	Eutectoid	[38Han]
		88.45		133	Eutectoid	[68Nis]
		...		133	Eutectoid	[82Eva]
	94.79	8.8	~0.2	133	Eutectoid	Assessed
L + (Sn) ↔ β		97.9		223	Peritectic	[38Han, 64Kul]
		98.5		223	Peritectic	[39Hom]
		99.0		223	Peritectic	[82Eva]
	96.0	99.4	99.0	223	Peritectic	Assessed

Table 2 Maximum Cd-Sn Mutual Solubilities

Reference	Solubility of Cd in (Sn), at.% Cd	Temperature, °C	Solubility of Sn in (Cd), at.% Sn	Temperature, °C
[1898Her]	...		25	...
[07Sto]	5 to 10	...	...	...
[16Buc]	3	...	3	...
[26Fed]	10	...	0	...
[35Han]	5.8	176	2.8	176
[35Sto]	...	...	0.24	...
[38Han, 58Bra]	1.16	176	0.24	176
[39Hom]	0.63	223	...	...
[55Gla]	...	...	4.5	176
[59Ray]	1.13	156	...	...

results of [39Hom]) is accepted in the present evaluation.

Various interpretations have been offered in the early works for the nature of the solid-state reaction at 133 °C—as a peritectoidal formation of the intermediate phase $CdSn_4$ [07Sto], as a polymorphic transformation of Sn, decomposing eutectoidally at lower temperatures [12Sch, 12Gue, 13Maz, 26Fed], or as a monotectoidal decomposition of two solid solution phases [31Mat, 35Han]. The eutectoid reaction at 133 °C β ↔ (Sn) + (Cd) reported in [38Han] and based on cooling curve, microscopic and electrical resistivity measurements at composition 94.7 at.% Sn was confirmed in [64Kul], [68Nis], and [82Eva]. The β region was accepted for the assessed phase diagram after [38Han], [39Hom], [58Bra], and [82Eva], as indicated in Fig. 2, which shows the Sn-rich portion of the Cd-Sn phase diagram.

Mutual Solid Solubilities

Solid solubilities of Sn in (Cd) ranging from 0.24 to 4.5 at.% Sn were reported in [16Buc], [30Sch], [35Sto], [38Han], [55Gla], [58Bra], and [64Kul]. From the existing data, the maximum solubility of 0.24 at.% Sn at 176

Table 3 Cd-Sn Crystal Structure Data

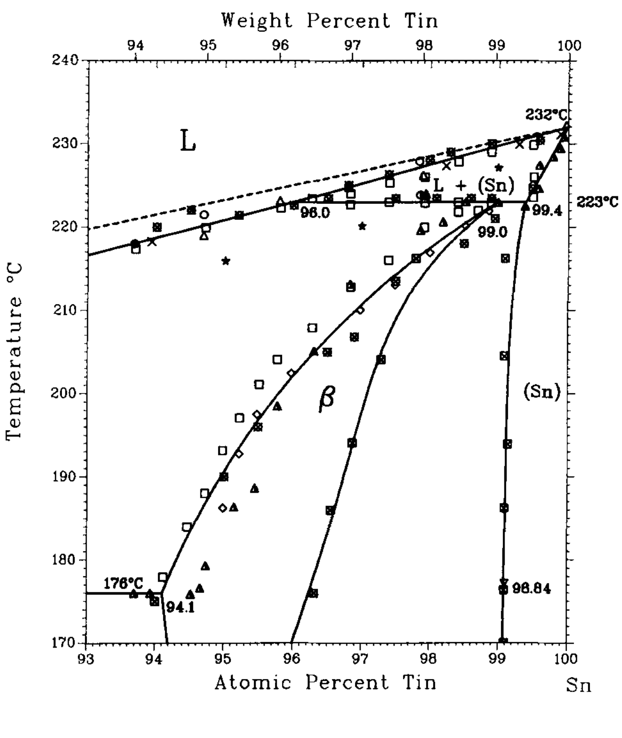
Phase	Composition, at.% Sn	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Cd)	0 to 0.24	*hP2*	*P6$_3$/mmc*	*A3*	Mg	[King1]
β	94.0 to 99.0	*hP2*	*P6$_3$/mmc*	*A3*	Mg	[54Ray]
(Sn)	98.84 to 100	*tI4*	*I4$_1$/amd*	*A5*	βSn	[King1]

Table 4 Cd-Sn Lattice Parameter Data at 25 °C

Phase	Composition, at.% Sn	Lattice parameters, nm *a*	*c*	Reference
(Cd)	0	0.29788	0.56167	[King1]
β (a)	95.11	0.32328	0.30023	[54Ray]
(Sn)	99.0	0.58284	0.31804	[63Rid]
	99.3	0.58293	0.31806	[63Rid]
	99.6	0.58302	0.31809	[63Rid]
	99.8	0.58306	0.31811	[63Rid]
	100	0.58316	0.31815	[King1]

(a) At 176 °C.

Fig. 2 Enlargement of the Sn-Rich Region of the Cd-Sn Phase Diagram



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°C is accepted, based on the microscopic observations and thermal analysis results of [38Han], [58Bra], and [35Sto]. These data were used for construction of the (Cd) solid solubility curve (Fig. 3) because they show very good agreement. Results obtained using hardness measurements [30Sch, 55Gla] or thermoelectric force measurements [16Buc] gave too high values of solid solubility, probably due to a metastable phase formation.

Similarly, too high values of solubility of Cd in (Sn) —reaching 10% Cd [07Sto, 12Gue, 26Fed, 35Han]— resulted from erroneous interpretation of metastable conditions that can occur in the Sn-rich region. The solid solubility of 0.63 at.% Cd in (Sn) at 223 °C (accepted from [39Hom] and [82Eva]) increases with decreasing temperature to 1.16 at.% Cd at 176 °C (from [38Han], [58Bra], and [59Ray]) and does not change with further lowering of temperature [38Han, 58Bra], as shown in Fig. 2.

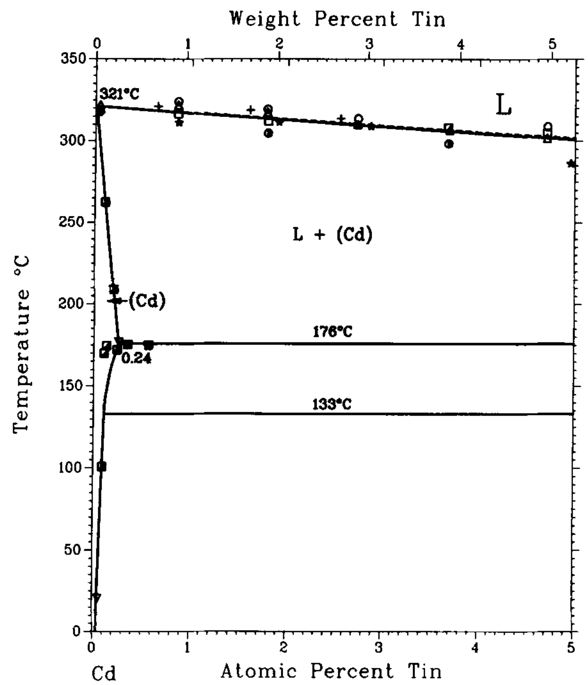
Metastable Phases

Splat quenching experiments with Cd-Sn alloys reported in [66Kan] and [68Sri] indicated formation of two kinds of metastable phases: (1) an AlCu-type fcc structure in the range 10 to 25 at.% Sn, with parameters $a = 0.4443$ nm (10 at.% Sn) and $a = 0.4507$ nm (25 at.% Sn); and (2) a hexagonal ω phase in the range 55 to 85 at.% Sn, with lattice parameters $a = 0.3171$ nm and $c = 0.2973$ nm (55 at.% Sn) and $a = 0.3192$ nm and $c = 0.2993$ nm (85 at.% Sn). All metastable phases obtained at −190 °C disappeared on heating to 20 °C.

Crystal Structures and Lattice Parameters

The (Cd) solid solution has hexagonal *A*3 structure, and (Sn) has tetragonal *A*5 structure. High-temperature X-ray studies of [54Ray] and [54Sch] indicated the β has simple hexagonal *A*3 structure. Crystal structures and lattice parameters are described in Tables 3 and 4. Table 4 includes *a* and *c* lattice parameters of (Sn) at 25 °C vs

Fig. 3 Enlargement of the Cd-Rich Region of the Cd-Sn Phase Diagram



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Cd contents [63Rid]. The earlier study of [54Lee], performed in the same composition range, showed anomalous changes of (Sn) parameters with increasing Cd content that most probably do not correspond to the equilibrium features of the structure. The X-ray study of [38Str] indicated the following crystallographic relationship between eutectic components:

[001]Sn || [11$\bar{2}$0]Cd and (100)Sn || (0001)Cd

Studies of the structure of molten Cd-Sn alloys using X-ray diffraction [59Ale] and magnetic susceptibility measurements [73Kuz] did not detect a tendency to liquid separation, contrary to the emf measurements of [78Oka], where at high Cd content, a possibility of cluster formation was suggested. This question needs further experimental study with other than X-ray methods, because as mentioned in [59Ale], similar scattering factors of Sn and Cd make it difficult to recognize structures formed within the liquid.

Thermodynamics

Electromotive force measurements of liquid Cd-Sn alloys were made by [23Tay] from 430 to 585 °C in the range 18.4 to 91.65 at.% Sn; by [51Ell] from 375 to 600 °C in the range 5.13 to 89.6 at.% Sn; by [64Kul] from 400 to 600 °C in the range 17.79 to 90.12 at.% Sn; by [74Zab] from 412 to 582 °C in the range 10 to 90 at.% Sn; by [78Oka] from 310 to 450 °C in the range 5 to 89.9 at.% Sn; and by [78Zab] from 402 to 547 °C in the range 90 to 97 at.% Sn.

Table 5 Cd-Sn Liquidus Calculated from Thermodynamic Data

Composition, at.% Sn	Temperature, °C	Composition, at.% Sn	Temperature, °C
Cd branch		51.89	197
0.93	317	58.60	187
3.17	307	64.46	177
5.58	297	64.99	176
8.19	287	66.55	173
11.04	277	**Sn branch**	
14.18	267	94.78	223
17.70	257	91.99	217
21.69	247	86.96	207
26.28	237	81.28	197
31.61	227	74.63	187
37.80	217	66.42	177
44.73	207		

Calorimetric measurements were made by [27Kaw] at 350 °C in the range 18.2 to 84.2 at.% Sn and by [55Kle] at 350 and 450 °C in the range 5.6 to 97 at.% Sn. [74Boo] determined the partial heat of solution of Cd in its infinite dilution in liquid Sn at 325 °C. Vapor pressure measurements over the liquid alloys were made by [60Ale] from 294 to 327 °C in the range 10 to 90 at.% Sn and by [79Les] from 577 to 757 °C in the same concentration range. The only thermodynamic study of the solid alloys was made calorimetrically by [65Pre], who determined the Gibbs energy of formation of β at 94.8 at.% Sn and 133 °C.

All the data available were transformed into excess Gibbs energies of Cd and were plotted against Sn concentration at two arbitrarily chosen temperatures—407 and 577 °C. Five sets of data [23Tay, 51Ell, 60Ale, 64Kul, 74Zab] were chosen for further compilation. Based on the chosen results, values of the excess Gibbs energy of Cd were fitted by a two-coefficient polynomial:

$$G^{ex}{}_{Cd} = \sum_{2}^{3} A_i X^i{}_{Sn} \quad \text{J/mol} \qquad \text{(Eq 1)}$$

with:

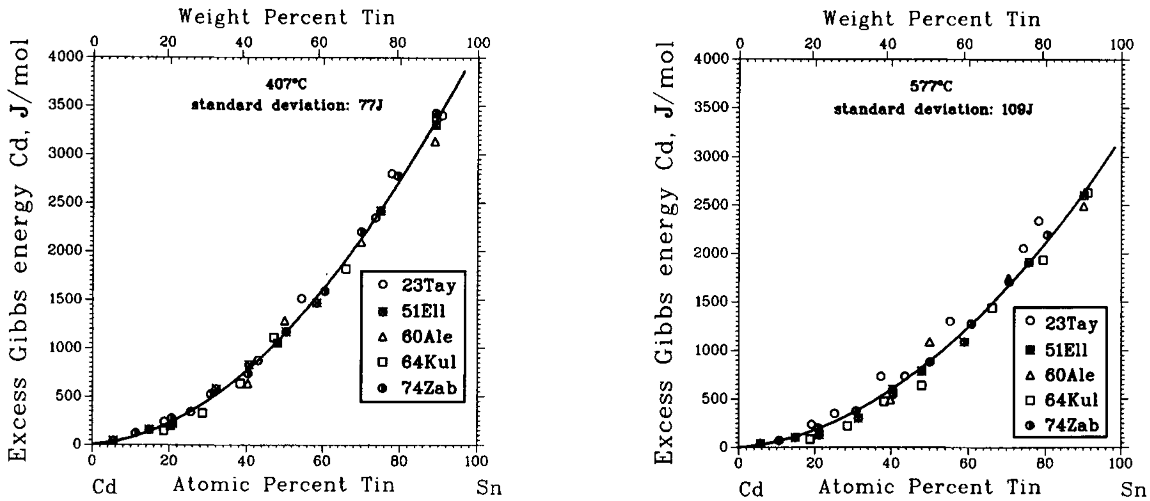
$A_2 = 10\,045 - 6.984\,T$

$A_3 = -2834 + 2.259\,T$

where X_{Sn} is the molar fraction of Sn and T is in K.

In Fig. 4, calculated values of G^{ex}(Cd) were compared with experimental results of the five papers taken for compilation at 407 and 577 °C.

Fig. 4 Excess Gibbs Energy of Cadmium Calculated from Eq 1 vs Selected Experimental Data at 407 and 577 °C



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The corresponding relationship for the excess Gibbs energy of Sn was obtained through the Gibbs-Duhem equation:

$$G^{ex}{}_{Sn} = \sum_{0}^{3} B_i X^i{}_{Sn} \quad \text{J/mol} \qquad \text{(Eq 2)}$$

with:

$B_0 = 8629 - 5.853\,T$

$B_1 = -20\,091 + 13.965\,T$

$B_2 = 14\,296 - 10.371\,T$

$B_3 = -2834 + 2.259\,T$

Phase diagram calculations were performed using the thermodynamic description of the liquid alloys derived above, melting data from [Hultgren,E], and the heat capacity contribution from [79Kub]:

$$\Delta_{fus}G(\text{Cd}) = 3914 + 37.6\,T + 6.15 \times 10^{-3}\,T^2 - 7.49\,T \ln T \quad \text{J/mol} \qquad \text{(Eq 3)}$$

$$\Delta_{fus}G(\text{Sn}) = 3905 + 66.9\,T + 13.68 \times 10^{-3}\,T^2 - 13.1\,T \ln T \quad \text{J/mol} \qquad \text{(Eq 4)}$$

The Cd branch of the liquidus was calculated assuming no solid solubility of Sn in (Cd) and ideal behavior was assumed for β to calculate Sn branch of the liquidus. The results are listed in Table 5. The eutectic composition of 64.46 at.% Sn derived along the Cd branch at 177 °C differs slightly from the value calculated on the Sn branch (66.42 at.% Sn). The single calculation of the eutectic composition assuming ideal solid solution of 0.25 at.% Sn in (Cd) resulted in 64.70 at.% Sn at 177 °C or 66.50 at.% Sn at 174 °C.

The composition of the liquid in the peritectic reaction at 223 °C was calculated as 96.10 at.% Sn, assuming ideal solid solution of 0.78 at.% Cd in Sn, whereas calculation along the Sn branch yielded 94.78 at.% Sn. Liquidus compositions calculated along the Sn branch and using data of [65Pre] for β were 3.65 at.% Sn lower at the peritectic temperature and 4.29 at.% Sn higher at the eutectic temperature than those derived above.

Effects of Pressure

[79Cla] studied the Cd-Sn system under pressures up to 4 GPa using DTA. It was shown that the eutectoid temperature rises smoothly with increasing pressure up to 200 °C at 3 GPa. The eutectic temperature rises with an initial slope of 40.5 °C GPa^{-1} and reaches 290.9 °C at 3.8 GPa, where a triple point is encountered. With increasing pressure, the difference between the peritectic temperature and the liquidus increases from 4 to 10 °C. Schematic phase diagrams at 3.0 GPa and 4.0 GPa (presented in [79Cla]) become more complex with increasing pressure, due to the formation of new phases—the high-pressure modification, Sn′ (described earlier in [76Pis]), and at 4 GPa, the high-pressure modification, β′.

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* Indicates key paper.

# Indicates presence of a phase diagram.

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