

- Systems," *Thermochim. Acta*, 30, 201-215 (1979) in German. (Thermo; Experimental)
- *80Day: A. Dayer and P. Feschotte, "Binary Systems Co-Ge and Ni-Ge Comparison Study," *J. Less-Common Met.*, 72, 51-70 (1980) in French. (Equi Diagram, Crys Structure; Experimental; #)
- 82Lar: V.I. Larchev and S.V. Popova, "The Polymorphism of Transition Metal Monogermanides at High Pressures and Temperatures," *J. Less-Common Met.*, 87, 53-57 (1982). (Crys Structure; Experimental)
- 82Tom: J. Tomiska, L. Erdelyi, H. Nowotny, and A. Neckel, "Determination of the Thermodynamic Excess Properties of Liquid Co-Ge Alloys by Mass Spectrometry," *High Temp. Sci.*, 15, 41-54 (1982). (Thermo; Experimental)

- 83Nis: T. Nishizawa and K. Ishida, "The Co (Cobalt) System," *Bull. Alloy Phase Diagrams*, 4(4), 387-390 (1983). (Crys Structure, Magnetism; Review)
- 85Fro: M.G. Froberg and S. Anik, "Thermodynamic Relations Between Component Activities and Gas Solubilities in Binary Metallic Systems," *Ber. Bunsenges. Phys. Chem.*, 89, 130-134 (1985). (Thermo; Experimental)
- *90Eno: H. Enoki, K. Ishida, and T. Nishizawa, "Phase Equilibria in Co-rich Portions of the Co-Si and Co-Ge Systems," *J. Less-Common Met.*, 160, 153-160 (1990). (Equi Diagram, Crys Structure; Experimental; #)
- *Indicates key paper.
#Indicates presence of a phase diagram.

Co-Ge evaluation contributed by K. Ishida and T. Nishizawa, Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan. This work was supported by the Japanese Committee for Alloy Phase Diagrams. Part of the literature search was provided by ASM International. Literature searched through 1987. Professor Nishizawa is the Alloy Phase Diagram Program Category Editor for binary cobalt alloys.

The Co-Pd (Cobalt-Palladium) System

By K. Ishida and T. Nishizawa
Tohoku University

Equilibrium Diagram

The equilibrium phases of the Co-Pd system are: (1) the liquid, L; (2) the fcc solid solution with complete solubility at all compositions, (α Co,Pd); and (3) the Co-rich cph solid solution, (ϵ Co). The assessed Co-Pd phase diagram (Fig. 1) is based on the experimental liquidus and solidus data listed in Table 1 [36Gru]. The magnetic transformation temperature changes continuously from 1121 °C for pure Co to -266 °C for a 99.9 at.% Pd alloy [35Gru, 36Gru, 61Boz, 67Bag, 68Bag] (see "Magnetism"). The equilibrium between (α Co) and (ϵ Co) is unknown, but it is estimated from the data on the (α Co) \leftrightarrow (ϵ Co) transformation temperatures that the allotropic phase boundary is lowered by the addition of Pd (see "Metastable Phases").

Metastable Phases

The martensitic transformation temperatures of (α Co) \leftrightarrow (ϵ Co) on heating and cooling were measured by [35Gru] and [70Kra] and are listed in Table 2. The M_s point is lowered, but the reverse temperature A_s is raised by the addition of Pd. The allotropic

Table 1 Co-Pd Liquidus and Solidus Data from Thermal Analysis

Composition, at.% Pd	Temperature, °C	
	Liquidus	Solidus
5.....	1432	1408
10.....	1372	1331
15.....	1318	1270
20.....	1279	1244
25.....	1255	1238
30.....	1239	1218
35.....	1229	1220
40.....	1224	1216
45.....	1220	1216
50.....	1217	1214
55.....	1231	1225
60.....	1258	1245
65.....	1285	1272
70.....	1311	1300
75.....	1340	1329
80.....	1371	1357
85.....	1407	1390
90.....	1452	1437
95.....	1505	1499

From [36Gru].

Table 2 (α Co) \leftrightarrow (ϵ Co) Transformation Temperatures

Reference	Method	Composition, at.% Pd	Temperature, °C		
			Heating, A_s	Cooling, M_s	$T_0 = (A_s + M_s)/2$
[35Gru].....	Magnetic	0	442	408	425
		5	456	277	367
		5	480	275	378
		10	<473	180	<327
[70Kra].....	Dilatometric	0.29	451	390	421
		1.62	464	338	401

Section II: Phase Diagram Evaluations

phase boundary, $T_0 = (M_s + A_s)/2$, is lowered. This fact suggests that Pd stabilizes (α Co), rather than (ϵ Co).

Electron diffraction studies on vapor deposited thin films of Co-Pd alloys revealed two types of ordered phases; one is an $L1_2$, AuCu₃-type structure (α') found in the composition range between 60 and 90 at.% Pd, with an order-disorder transition tem-

perature estimated to be about 830 °C for the 80 at.% Pd alloy; the other has the $L1_0$, AuCu-type structure (α''), with a narrow region of composition around 50 at.% Pd [72Mat]. These phases are indicated to be metastable, because bulk samples with the compositions Co₃Pd, CoPd, and CoPd₃ did not show any trace of the corresponding superlattice reflections. The metastable phase diagram for thin films proposed by [72Mat] is shown in Fig. 2.

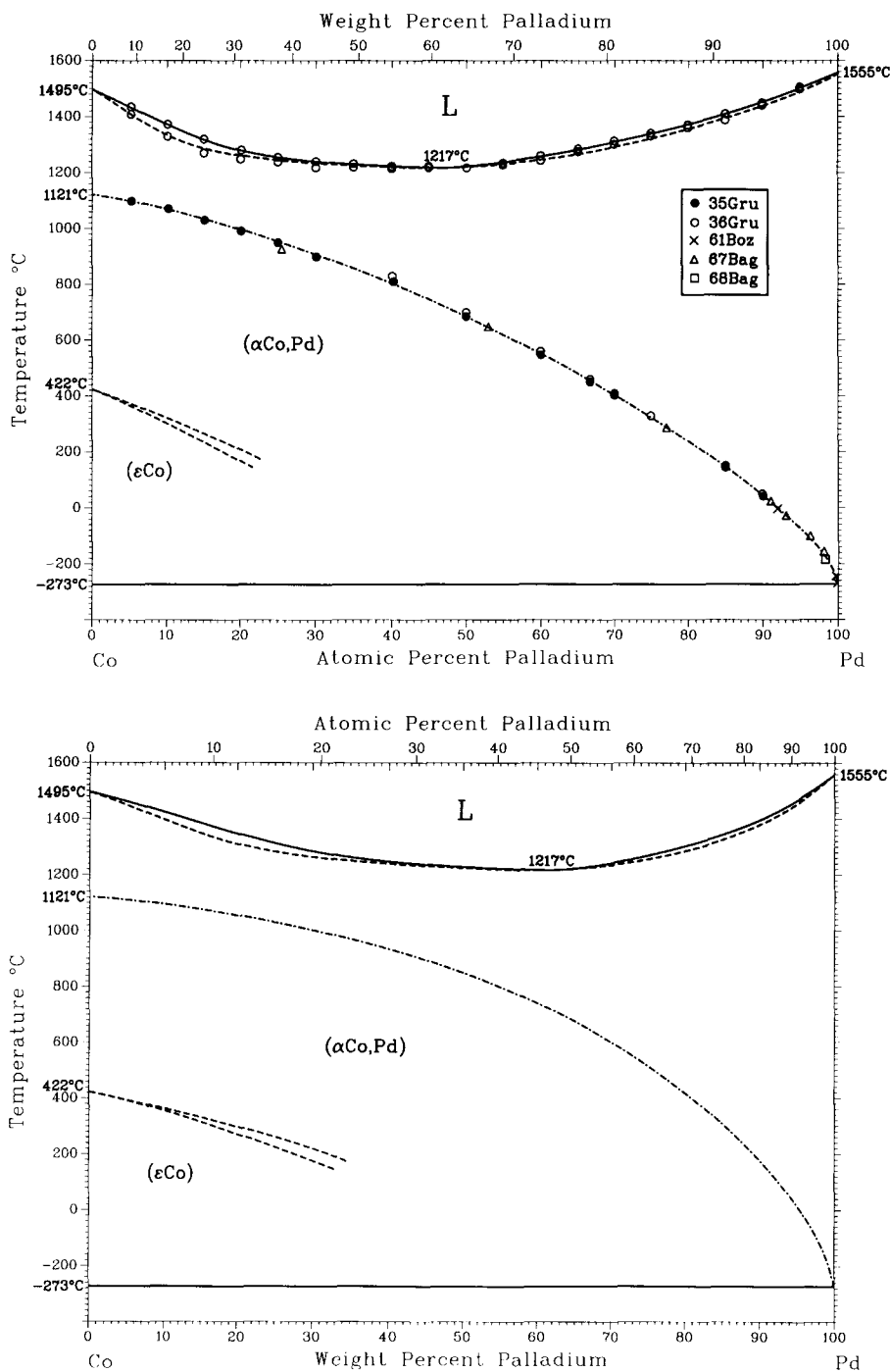


Fig. 1 Assessed Co-Pd phase diagram.

Table 3 Co-Pd Crystal Structure Data

Phase	Composition, at. % Pd	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(α Co,Pd).....	0 to 100	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	A1	Cu	[83Nis]
(ϵ Co).....	0 to ~20	<i>hP2</i>	<i>P6$_3$/mmc</i>	A3	Mg	[83Nis]
Metastable phases(a)						
α''	~48 to ~52	<i>tP2</i>	<i>P4/mmm</i>	L1 ₀	AuCu	[72Mat]
α'	60 to 90	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	L1 ₂	AuCu ₃	[72Mat]

(a) Evaporated films.

Table 4 Co-Pd Lattice Parameter Data

Phase	Composition, at. % Pd	Lattice parameters, nm		Comment	Reference
		<i>a</i>	<i>c</i>		
(α Co,Pd).....	0	0.35446	[83Nis]
	20	0.3633	...	Read from figure	[61Boz]
	40	0.3708	...	Read from figure	[61Boz]
	60	0.3778	...	Read from figure	[61Boz]
	80	0.3839	...	Read from figure	[61Boz]
	87	0.3854	...	Read from figure	[61Boz]
	92	0.3864	...	Read from figure	[61Boz]
	95	0.3871	...	Read from figure	[61Boz]
	99	0.3877	...	Read from figure	[61Boz]
	100	0.389	...	Read from figure	[61Boz]
	25	0.366	...	Read from figure	[72Mat]
	50	0.375	...	Read from figure	[72Mat]
	75	0.383	...	Read from figure	[72Mat]
	100	0.38901	[King1]
(ϵ Co).....	0	0.25071	0.40695	...	[83Nis]
Metastable phases					
α''	<50	0.4106	0.3888	Quenched from 700 °C	[72Mat]
		0.4118	0.3912	Quenched from 800 °C	[72Mat]
	>50	0.4048	0.3928	Quenched from 700 °C	[72Mat]
		0.4071	0.3952	Quenched from 800 °C	[72Mat]
α'	~62	0.3800	...	Quenched from 700 °C	[72Mat]
	~69	0.3820	...	Quenched from 800 °C	[72Mat]

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data on the stable and metastable phases in the Co-Pd system are summarized in Tables 3 and 4, respectively. The lattice parameters of the (α Co,Pd) fcc solid solution are shown in Fig. 3 [61Boz, 72Mat, 83Nis, King1]. The form of the lattice parameter vs composition curve is convex upwards.

Thermodynamics

Low-temperature specific heats were studied in Co-rich alloys [67Tak, 69Boe], as well as over the whole range of composition [69Whe].

The enthalpy of mixing in the liquid phase at 1600 °C was determined by calorimetry; results show a small positive deviation from ideal solution behavior [77Vat]. [77Vat] also calculated the activities and compared them with the experimental values by

Sryvalin quoted in [77Vat]. A model calculation of the surface energy of the Co-Pd melt was presented by [70Bog]. The activities in the fcc solid solution were determined from solid electrolyte emf measurements by [65Sch] and [70Bid]. These data show that the activity of Co in Pd exhibits a positive departure from ideal solution behavior in Co-rich alloys and a negative departure in Pd-rich alloys, whereas the activities of Pd indicate a negative departure from ideality at all compositions. These complexities were discussed in connection with the magnetic contribution by [70Bid].

Magnetism

The magnetic properties of the Co-Pd system were studied extensively [35Gru, 36Gru, 61Boz, 67Bag, 67Tak, 68Bag, 69Boe, 69Whe] and are summarized in Table 5. Ferromagnetism exists in solution up to 99.9 at. % Pd, where the Curie temperature is -266 °C [61Boz].

Section II: Phase Diagram Evaluations

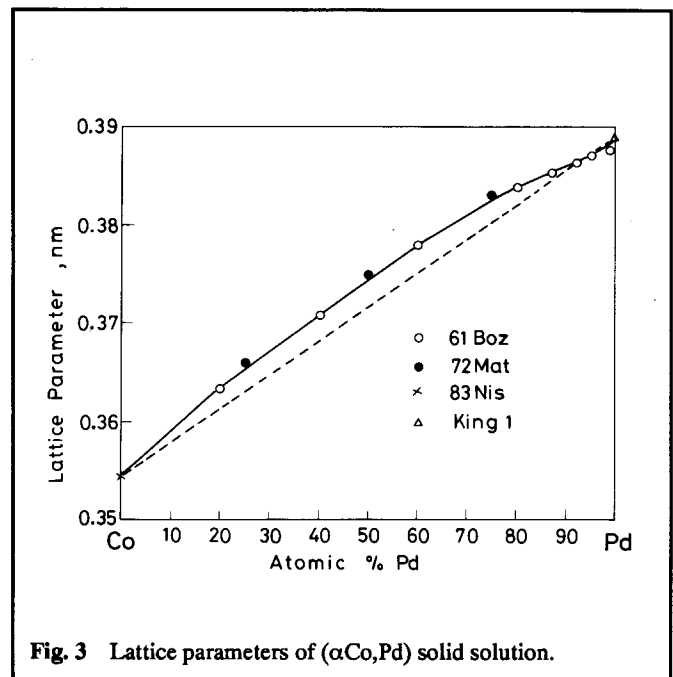
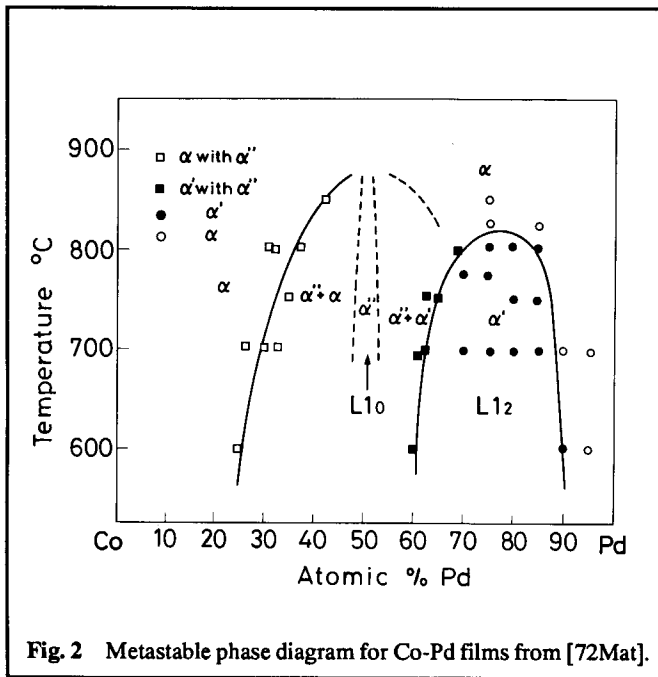
Table 5 Magnetic Properties of the Co-Pd System

Reference	Method	Composition, at. % Pd	Curie temperature, °C	Magnetic moment, μ_B	Saturation magnetization, G
[35Gru]	Magnetic	0	1119
		5	1094
		5	1097
		10	1068
		15	1030
		20	990
		25	948
		30	900
		40	808
		50	686
		60	546
		66.7	448
		70	400
		85	145
90	43		
[36Gru]	Electrical resistivity	40	830
		50	700
		60	557
		66.7	458
		70	405
		75	325
		85	147
		90	48
[61Boz]	Magnetic	20	...	1.55(a)	...
		40	...	1.30	...
		60	...	1.05	...
		80	...	0.74	...
		87	...	0.60	...
		92	-3	0.38	...
		95	...	0.30	...
		99.5	-247	0.10	...
[67Bag]	Magnetic	99.9	-266	0.05	...
		25.3	927	...	1130
		52.7	647	...	850
		77.0	287	...	510
		91.1	22	...	310
		93.1	-23	...	280
		96.5	-103	...	190
		98.2	-153	...	130
		99.5	-248	...	20
		98.5	-188	...	69
[68Bag]	...	98.5	-188	...	69

(a) Data read from the figure.

Cited References

- 35Gru:** G. Grube and O. Winkler, "Magnetic Investigation in the Cobalt-Palladium System," *Z. Elektrochem.*, **41**, 52-60 (1935) in German. (Equi Diagram, Meta Phases, Magnetism; Experimental; #)
- *36Gru:** G. Grube and H. Kastner, "Electric Conductivity and Phase Diagram in Binary Alloys, Report 18, Palladium-Cobalt System," *Z. Elektrochem.*, **42**, 156-160 (1936) in German. (Equi Diagram, Magnetism; Experimental; #)
- 61Boz:** R.M. Bozorth, P.A. Wolff, D.D. Davis, V.B. Compton, and J.H. Wernick, "Ferromagnetism in Dilute Solutions of Cobalt in Palladium," *Phys. Rev.*, **122**, 1157-1160 (1961). (Equi Diagram, Crystal Structure, Magnetism; Experimental; #)
- 65Sch:** K. Schwerdtfeger and A. Muan, "Activity Measurements in Pt-Ni, Pd-Ni and Pd-Co Alloys at 1000 and 1200 °C," *Acta Metall.*, **13**, 509-515 (1965). (Thermo; Experimental)
- 67Bag:** D.M.S. Bagguley, W.A. Crossley, and J. Liesegang, "Ferromagnetic Resonance in a Series of Alloys II. Binary Alloys of Cobalt with Platinum and Palladium, and One Iron-Palladium Alloy," *Proc. Phys. Soc.*, **90**, 1047-1058 (1967). (Equi Diagram, Magnetism; Experimental)
- 67Tak:** T. Takahashi and M. Shimizu, "Magnetic Specific Heats of Dilute Pd-Fe and Pd-Co Alloys," *J. Phys. Soc. Jpn.*, **23**, 945-948 (1967). (Thermo, Magnetism; Experimental)
- 68Bag:** D.M.S. Bagguley and J.A. Robertson, "Ferromagnetic Resonance in Dilute Binary Alloys of Pd and Pt with Fe and Co," *Phys. Lett. A*, **27**, 516-517 (1968). (Equi Diagram, Magnetism; Experimental)
- 69Boe:** B.M. Boerstoel, G.J. Nieuwenhuys, and G.J. van Den Berg, "The Magnetic Field Dependence of the Specific Heat of Dilute Pd-Co Alloys," *Phys. Lett. A*, **29**, 526-527 (1969). (Thermo, Magnetism; Experimental)
- 69Whe:** J.C.G. Wheeler, "The Low-Temperature Specific Heats of a Number of Ferromagnetic Pd-Co and Pt-Co Alloys," *J. Phys. C*, **2**, 135-146 (1969). (Thermo, Magnetism; Experimental)



70Bid: L.R. Bidwell, F.E. Rizzo, and J.V. Smith, "The Thermodynamic Properties of Cobalt-Palladium Solid Solutions," *Acta Metall.*, 18, 1013-1019 (1970). (Thermo; Experimental)

70Bog: M.P. Bogdanovich, Y.P. Vorobyev, A.N. Men, and G.I. Chufarov, "Complex Structure and Surface Energy of Binary Metal Melts," *Fiz. Met. Metalloved.*, 29(2), 445-448 (1970) in Russian; TR: *Phys. Met. Metallogr.*, 29(2), 237-240 (1970). (Thermo; Theory)

70Kra: W. Krajewski, J. Kruger, and H. Winterhager, "Allotropic Transformation and Thermal Expansion of Cobalt Binary Alloys Between 100 and 800 °C," *Cobalt*, 48, 120-128 (1970) in German. (Meta Phases; Experimental)

72Mat: Y. Matsuo, "Ordered Alloys in the Cobalt-Palladium System," *J. Phys. Soc. Jpn.*, 32, 972-978 (1972). (Meta Phases, Crys Structure; Experimental)

77Vat: N.A. Vatolin and Yu.S. Kozlov, "Enthalpy of Formation of Liquid Alloys of Palladium with Nickel, Cobalt or Chromium," *Izv. Akad. Nauk SSSR, Met.*, (1), 76-79 (1977) in Russian; TR: *Russ. Metall.*, (1), 67-71 (1977). (Thermo; Experimental)

83Nis: T. Nishizawa and K. Ishida, "The Co (Cobalt) System," *Bull. Alloy Phase Diagrams*, 4(4), 387-390 (1983). (Crys Structure; Compilation)

*Indicates key paper.

#Indicates presence of a phase diagram.

Co-Pd evaluation contributed by K. Ishida and T. Nishizawa, Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan. This work was supported by the Japanese Committee for Alloy Phase Diagrams. Part of the literature search was provided by ASM International. Literature searched through 1987. Professor Nishizawa is the Alloy Phase Diagram Program Category Editor for binary cobalt alloys.