ANL-5719

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois

TID-14623

SOLUBILITY OF 3-d TRANSITION METALS IN LIQUID CADMIUM*

by

M. G. Chasanov, P. D. Hunt, I. Johnson and H. M. Feder

Chemical Engineering Division

September, 1961

To be Presented for Publication in
Transactions of The Metallurgical
Society of AIME

Operated by The University of Chicago
under
Contract No. W-31-109-eng-38

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

Abstract

The solubilities of the metals from scandium to nickel, inclusive, in liquid cadmium were determined by sampling saturated solutions. At 400°C these solubilities (in ppm) are: Sc, 8200; Ti, 150; V, < .2; Cr, 2; Mn, 2500; Fe, 1; Co, 22; Ni, 12000. Relative partial molal enthalpies and excess partial molal entropies at infinite dilution were determined for the solutes Cr, Mn, Fe, and Co. Cr, Fe, and Co are nearly insoluble in cadmium because both energetic and entropic factors are unfavorable.

Three new intermetallic phases, $ScCd_3$, TiCd, and Ti_2Cd, encountered in the course of this work, are reported.

M. G. CHASANOV, P. D. HUNT, I. JOHNSON and H. M. FEDER are associated with the Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois.

Measurements of the solubility of the 3-d transition metals in liquid cadmium have been reported[1] only for iron. The present measurements for the entire series were made as an aid to the study of the systematics of alloy formation.

EXPERIMENTAL

The apparatus and sampling techniques used for the solubility determinations were similar to those described by Martin et al.[2] Temperatures were measured with a Pt/Pt-10% Rh thermocouple sheathed in recrystallized alumina and immersed in the solution. The thermocouple was recalibrated periodically during the course of the investigation. Thermocouple voltages were measured to the nearest 0.01 millivolt with a Rubicon model 2732 potentiometer. A scaled-down version of the apparatus, in which the total metal charge was about 90 grams, was employed to measure the solubility of scandium. Two-mm I.D. Vycor filter pipets were used to sample the scandium-cadmium solutions; the samples weighed about two grams.

Cadmium with a minimum purity of 99.95% was used; the only impurities detected spectrochemically were Cu and Mg, both less than ten ppm. The purities of the other metals were: scandium, 99.9%; titanium, 99.92%; vanadium, 99.9%; chromium, 99.99%; manganese, 99.9+%; iron, 99.90%; cobalt, 99.95%; and nickel, 99.96%. Solidified melts were routinely analyzed spectrographically. No significant contamination by the crucible, sampling pipets, or other materials of construction was observed.

The entire specimen obtained by sampling was dissolved to preclude analytical errors due to segregation on cooling. Colorimetric methods[3] were used for the analyses of cobalt (2-nitroso-1-napthol), manganese (permanganate), nickel (dimethylglyoxime), titanium (peroxide), and vanadium (thiocyanate).[4] Chromium, iron, and scandium were neutron-irradiated to produce 27.8 d Cr^{51}, 45.1 d Fe^{59} and 85 d Sc^{46}. The dissolved samples were gamma-counted to determine solute concentrations.

For the separation of intermediate phases from cadmium-rich alloys selective leaching by saturated ammonium nitrate solutions was employed. The concentration of cadmium in the successive leaches was followed polarographically and the process was terminated when the rate of cadmium dissolution decreased markedly.

For the further investigation of intermediate phases 1/4 in. diam. powder compacts were pressed at 80000 psi and annealed in argon at 315-330°C for ten days. Larger quantities of alloys were prepared in sealed tantalum capsules heated in a rocking furnace.

RESULTS

The solubility data are given in Table I and are expressed as atom fraction N in solution in Fig. 1. Each binary system is discussed separately in the following sections.

Scandium - The charge contained 3 weight percent scandium. The measured solubilities are represented by Eq. (1a) and (1b) to within* 0.4% and 0.8%, respectively.

$$\log N_{Sc} = 1.935 - 2.434 \times 10^3 T^{-1}; \quad 349^\circ \text{ to } 421.5^\circ C \qquad (1a)$$

$$\log N_{Sc} = 2.933 - 5.335 \times 10^3 T^{-1} + 1.534 \times 10^6 T^{-2}; \quad 421.5^\circ \text{ to } 606^\circ C \qquad (1b)$$

* The indicated uncertainties are relative standard deviations between the experimental data and the equations fitted to them by the method of least squares.

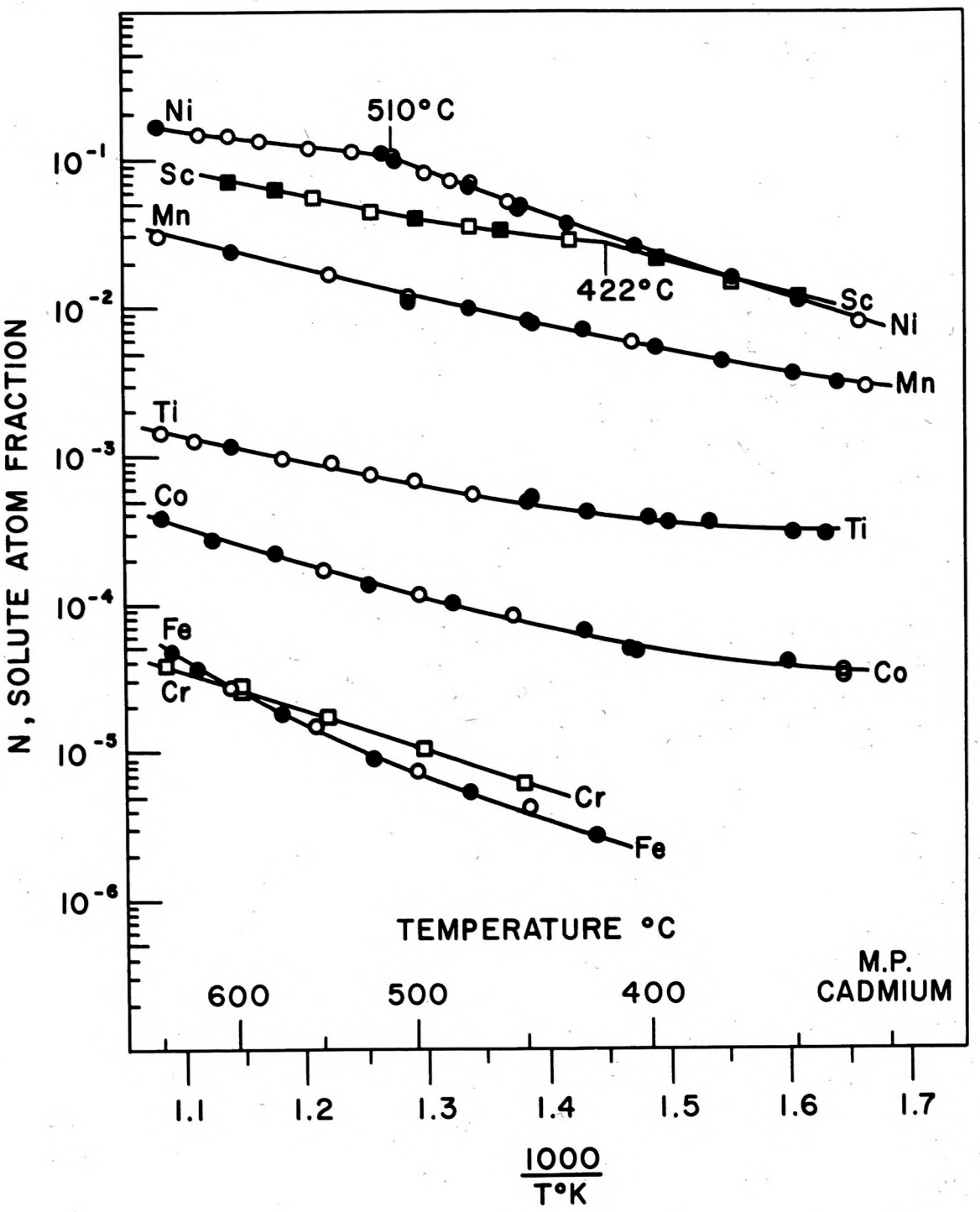
Table I. Solubilities of the 3-d Transition Metals in Liquid Cadmium

Sc		Ti		V		Cr		Mn		Fe		Co		Ni	
Temp., °C	Wt Pct	Temp., °C	ppm	Temp., °C	ppm	Temp., °C	ppm	Temp., °C	Wt Pct	Temp., °C	ppm	Temp., °C	ppm	Temp., °C	Wt Pct
348.8	0.423	339.2	119	650	<0.2	451.0	2.78	327.5	0.129	420.8	1.29	333.5	16.7	330.3	0.388
372.0	0.584	349.6	120			499.6	4.95	336.4	0.142	449.7	2.27	334.6	16.4	347.4	0.538
397.7	0.820	378.6	133			548.4	8.33	349.6	0.159	475.2	2.61	353.5	20.6	369.5	0.760
430.8	1.15	394.2	143			599.4	11.4	374.4	0.198	500.7	3.79	404.3	22.0	400.4	1.19
460.7	1.32	399.6	149			599.9	12.3	396.4	0.248	523.9	4.47	405.4	22.1	425.4	1.77
474.7	1.42	424.4	162			650.6	16.7	405.1	0.268	554.6	6.52	426.4	32.9	449.5	2.46
501.7	1.62	447.4	204					426.4	0.316	575.1	8.79	454.5	43.8	453.4	2.55
522.7	1.86	449.6	199					446.4	0.372	609.0	13.4	483.4	51.4	457.4	2.77
557.7	2.24	474.4	236					449.0	0.394	630.5	17.3	501.5	59.2	474.4	3.48
577.6	2.51	502.5	290					475.5	0.454	647.0	22.2	523.4	62.8	474.4	3.53
606.4	2.94	523.4	298					503.4	0.566			548.4	85.6	483.4	3.92
		547.8	392					504.4	0.620			579.4	111	494.4	4.60
		573.4	390					546.5	0.770			617.4	138	503.4	5.18
		603.9	510					603.4	1.19			653.4	180	503.4	5.38
		628.9	550					652.4	1.48					518.4	5.83
		651.4	640											532.4	6.07
														555.4	6.31
														582.4	6.62
														606.3	7.21
														631.4	7.50
														652.4	8.10

Fig. 1 - Solubility of 3-d transition metals in liquid cadmium. Shaded symbols, rising temperatures; open symbols, falling temperatures. Vanadium not detected ($N_V < 4 \times 10^{-7}$) at 650°C.

SOLUBILITY OF 3-d TRANSITION METALS IN LIQUID CADMIUM

Shaded Symbols - Rising Temperatures
Open Symbols - Falling Temperatures



The break in the solubility curve (Fig. 1) at about 422°C indicates[2] a peritectic transformation at that temperature. Thermal analysis of a furnace-cooled 3 wt pct scandium alloy showed a reproducible arrest at 414°C on heating. Fig. 2 shows the peritectic rimming in this alloy.

From a 5 wt pct alloy which had been ice-quenched from 500°C hexagonal needles were isolated. This material was found to contain 11.5 pct Sc and 88.3 pct Cd; $ScCd_3$ would have 11.8 pct Sc. For this new phase the hexagonal lattice parameters (preliminary[5]) are a_o = 6.33 Å and c_o = 4.85 Å. The X-ray density for eight atoms per unit cell is 7.55 g per cm^3; the pycnometric density was 7.7 g per cm^3. The same phase was also identified in an ingot from the solubility experiment; it is presumably the solid phase in equilibrium with the saturated liquid above 422°C. The equilibrium solid phase below the peritectic temperature has not yet been characterized.

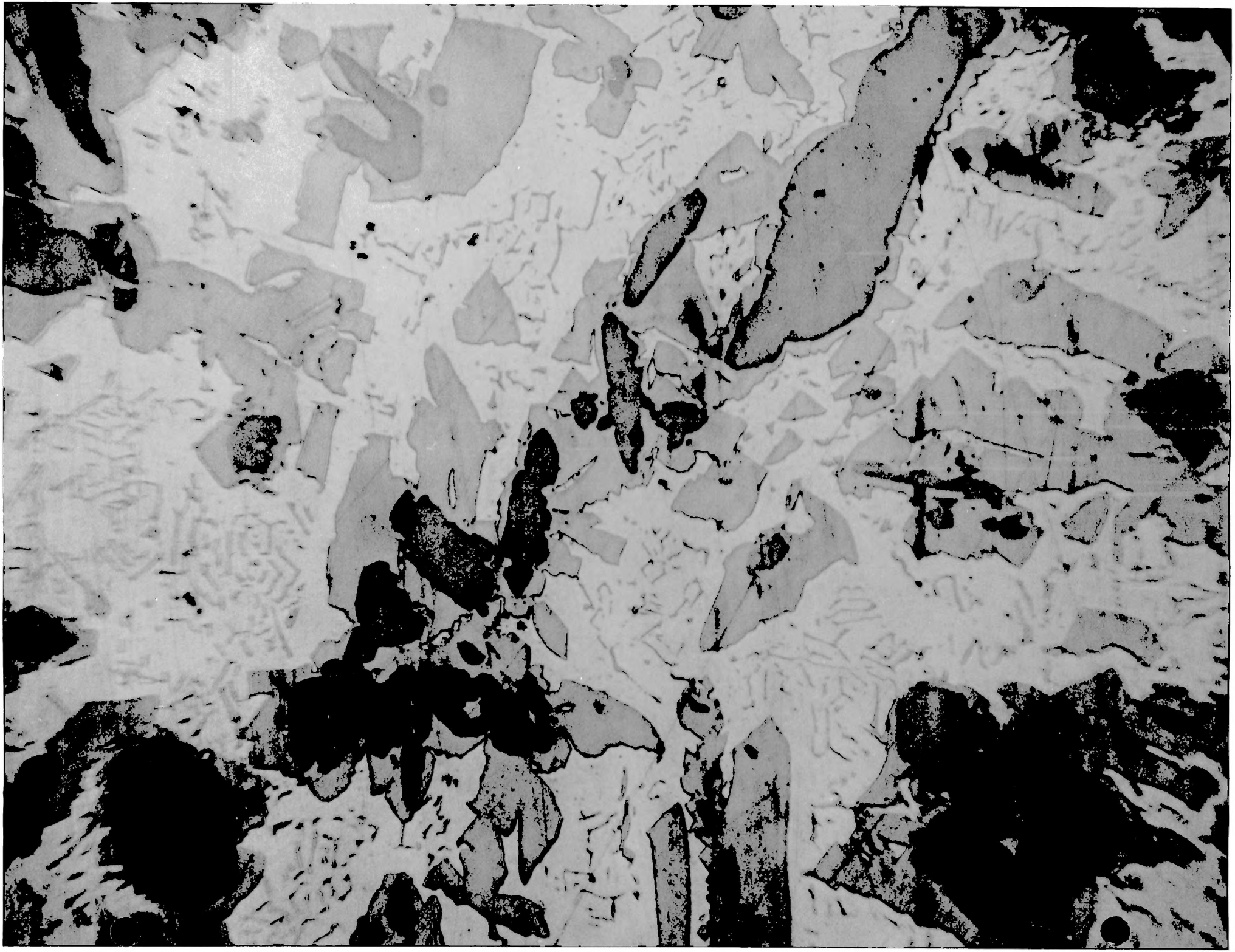
Titanium - The solubility data are represented by Eq. (2) to within 5 pct.

$$\log N_{Ti} = 1.690 - 5.960 \times 10^3 T^{-1} + 1.683 \times 10^6 T^{-2}; \ 339\text{-}620^\circ C \qquad (2)$$

The melts were charged with 0.03, 0.5, and 2 wt pct titanium.

Chemical and X-ray analysis of crystals isolated from a furnace-cooled melt revealed a previously unreported intermetallic phase TiCd. Ti, found 29.9 wt pct; theor. 29.9 wt pct. The symmetry of TiCd is primitive tetragonal[5], a_o = 2.904 Å and c_o = 8.954 Å. The X-ray density is 7.05 g per cm^3; the pycnometric density was 7.07 g per cm^3. Equimolar Ti-Cd compositions, annealed below 620°C for a week or more, showed these same characteristics.

Fig. 2 - Photomicrograph of cadmium-3 wt pct scandium alloy. Dark phase contained in lighter envelopes is $ScCd_3$. Etched with nital. X530.



Thermal arrests at 620°C were obtained on heating alloys containing 10, 20, and 30 wt pct titanium. Crystals of TiCd were observed to decompose above 620°C to yield cadmium and an additional phase. Therefore, the thermal arrest at 620°C has been ascribed to the peritectic decomposition of TiCd. The higher temperature phase was identified as Ti_2Cd by synthesis. Ti, found 46.4 wt pct; theor. 46.0 wt pct. The pycnometric density of Ti_2Cd was 6.28 g per cm^3. This phase is body-centered tetragonal[5] with lattice parameters: a_o = 2.865 Å and c_o = 13.42 Å. The existence of a phase with the composition Ti_2Cd has been previously reported.[6]

Vanadium - Charges containing one wt pct of vanadium in the form of 2 mm. chips were heated at 650°C for at least a week. The solubility of vanadium in liquid cadmium was extremely small. A value of <0.2 ppm at 650°C was found by chemical analysis; a determination by neutron activation analysis did not further refine this limit. To preclude the possibility that an oxide coating on the vanadium was hindering solution another solubility experiment was performed with 0.1 weight percent magnesium added to the melt. After 68 hours vanadium was still below the detectable limit. Examination of the alloys showed no evidence of reaction.

Chromium - Hindricks[7] reported that chromium did not dissolve in liquid cadmium heated to 650°C. In our studies a small solubility was found; however, the rate of solution was extremely slow and 180 hours of equilibration at 650°C were required for the melt to become saturated. The small solubility coupled with the slow attainment of saturation resulted in consistent data being obtained only above 450°C. The data reported here are for an experiment in which 200 ppm of neutron-irradiated chromium flowers were charged. The data are represented by Eq. (3) to within 6 pct.

$$\log N_{Cr} = -1.606 - 2.605 \times 10^3 T^{-1}; \quad 450\text{-}650^\circ C \qquad (3)$$

Examination of the solubility ingots showed no reaction. A number of powder compacts having Cd/Cr atom ratios from 10 to 0.2 were prepared. No indication of intermetallic phases was revealed by X-ray examination.

Manganese - The charges contained 0.59 and 2 wt pct of electrolytic manganese. The solubility data are represented by Eq. (4) to within 3 pct.

$$\log N_{Mn} = 1.263 - 3.054 \times 10^3 T^{-1} + 0.4476 \times 10^6 T^{-2}; \ 328\text{-}652^\circ C \qquad (4)$$

Zwicker[8] found no intermetallic phases in 20 and 30 wt pct manganese alloys heated to 1200°C; he observed a slight solid solubility of α-manganese in cadmium. In our studies various powder compacts prepared from α-manganese and cadmium gave only the diffraction patterns of the constituents after annealing for as long as two weeks at 450°C. Thermal analysis of 10, 20, and 30 wt pct manganese alloys showed only eutectic arrests at 320.1°C and inflections at about 730°C due to the α-β transition of manganese.

Iron - Tammann and Oelsen[1] determined the solubility of iron in cadmium by a magnetic method. They reported solubilities of 2 or 3 ppm at 400 and 700°C. Our data were obtained by a radiochemical method using neutron-irradiated fine iron wire, and are represented by Eq. (5) to within 8 pct.

$$\log N_{Fe} = 3.973 - 10.96 \times 10^3 T^{-1} + 3.023 \times 10^6 T^{-2}; \ 421\text{-}647^\circ C \qquad (5)$$

In agreement with previous investigators[9,10] no intermediate phases were observed by metallographic examination.

Cobalt - A melt containing 0.5 wt pct cobalt powder was used to obtain the solubility data, which are represented by Eq. (6) to within 11 pct.

$$\log N_{Co} = 1.594 - 6.515 \times 10^3 T^{-1} + 1.705 \times 10^6 T^{-2}; \ 334\text{-}653^\circ C \qquad (6)$$

In agreement with previous investigators[10,11] no intermediate phases were observed by metallographic examination.

Nickel - Liquidus data from thermal analyses of the nickel-cadmium system at a few cadmium-rich compositions have been reported by Voss[12] and Swartz and Phillips.[13] The results of Swartz and Phillips are in substantial agreement with the values given in Table I. The solubility data, obtained with charges containing 6 and 10 wt pct nickel, are represented by Eq. (7a) and (7b) to within 2 and 1 pct, respectively.

$$\log N_{Ni} = 5.037 - 6.050 \times 10^3 T^{-1} + 1.045 \times 10^6 T^{-2}; \quad 330\text{-}510^\circ C. \qquad (7a)$$

$$\log N_{Ni} = 1.683 - 3.729 \times 10^3 T^{-1} + 1.287 \times 10^6 T^{-2}; \quad 510\text{-}652^\circ C. \qquad (7b)$$

The break in the solubility curve (Fig. 1) indicates a peritectic transformation at 510°C, previously reported at 502°C.[12] and 490°C.[13] The phase undergoing peritectic decomposition is presumed[14] to be of the γ-brass type. Swartz and Phillips[13] report the eutectic temperature and composition as 318°C. and 0.25 wt pct Ni. By use of the present solubility data and the heat of fusion of cadmium the predicted eutectic temperature and composition are 317.9°C and 0.3_3 wt pct Ni.

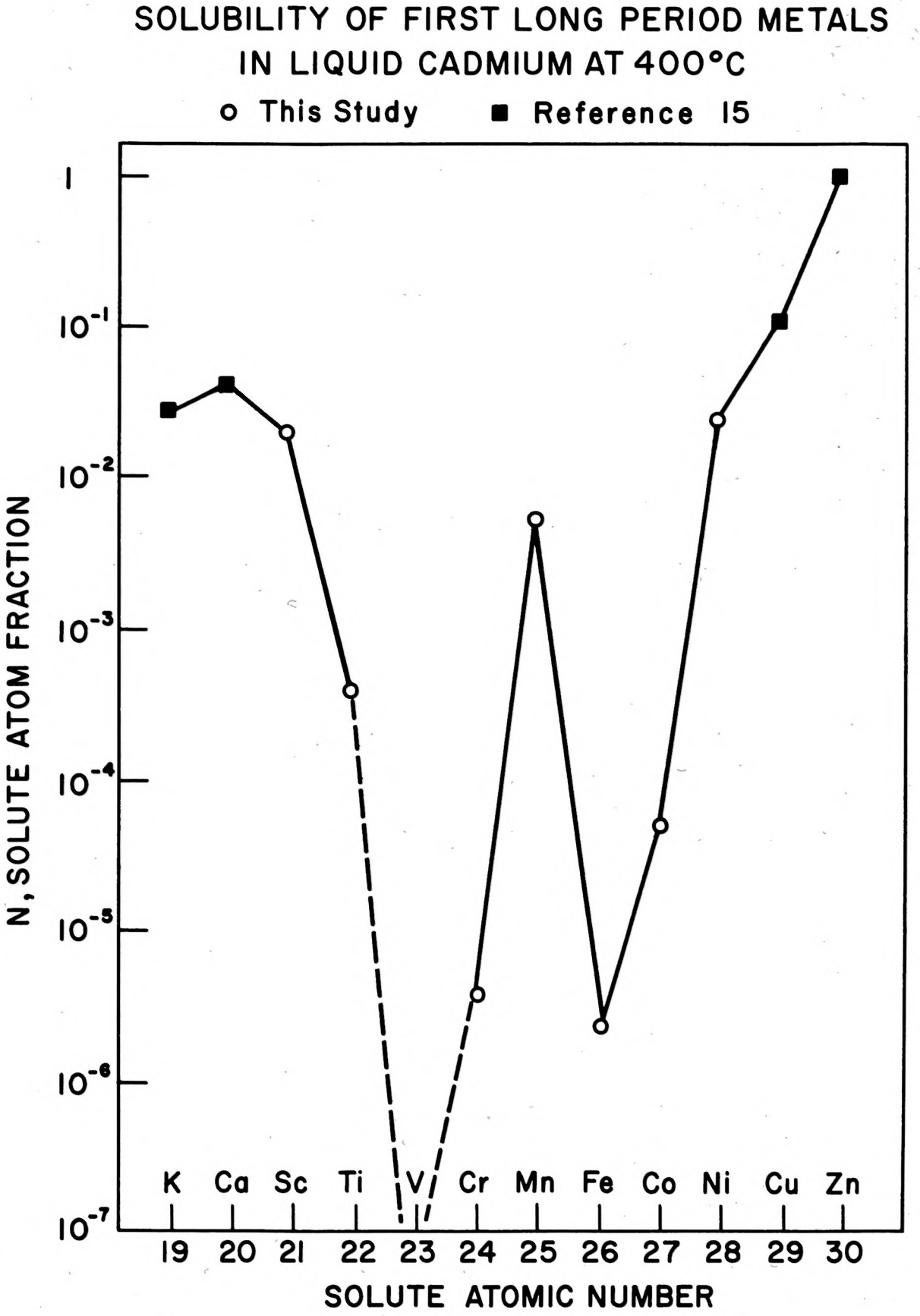
DISCUSSION

The variation of the solubility of the first long period metals in liquid cadmium is conveniently summarized in Fig. 3. Similar plots for other solvent metals have been presented and discussed by Kerridge.[15] A quantitative discussion of the features of Fig. 3 is not feasible because the necessary thermodynamic data are unavailable. For some of the systems considered, however, the equilibrium solid phase is the metal containing only negligible amounts[14] of cadmium in solid solution; for these systems thermodynamic data for the liquid solutions have been calculated from the solubility relations as follows. In sufficiently dilute solutions the

Fig. 3 - Solubility of first long period metals in liquid cadmium at 400°C.

○ This study

□ Reference 15.


SOLUBILITY OF FIRST LONG PERIOD METALS
IN LIQUID CADMIUM AT 400°C
o This Study
■ Reference 15
N, SOLUTE ATOM FRACTION
1
10-1
10-2
10-3
10-4
10-5
10-6
10-7
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
19 20 21 22 23 24 25 26 27 28 29 30
SOLUTE ATOMIC NUMBER

concentration dependence of the relative partial molal enthalpy, $\bar{L}_A$, and excess partial molal entropy, $\bar{S}_A^{xs}$, of the solute A may be expressed by Eq. (8) and (9), in which the superscript ^{o} refers to the infinitely dilute solution.

$$\bar{L}_A = \bar{L}_A^o (1 - N_A)^2 \tag{8}$$

$$\bar{S}_A^{xs} = \bar{S}_A^{xs,o} (1 - N_A)^2 \tag{9}$$

If the pure liquid solute is chosen as the reference state and ΔF_A^m is the free energy of fusion of the solute at the temperature in question, Eq. (10)[16] follows.

$$\Sigma' = \frac{RlnN_A + \Delta F_A^m/T}{(1 - N_A)^2} = - \frac{\bar{F}_A^{xs}}{(1 - N_A)^2} = - \frac{\bar{L}_A^o}{T} + \bar{S}_A^{xs,o} \tag{10}$$

The solubility data and the appropriate thermal data[17] for each solute were used to plot Σ' as a function of 1/T. The values given in Table II were derived from the slopes and intercepts of the resulting linear plots.

Table II. Relative Partial Molal Enthalpies and Partial Molal Excess Entropies in Liquid Cadmium.

Solute	$\bar{L}^o$, kcal. per g.-atom	$\bar{S}^{xs,o}$, cal. per g.-atom ^oK
Cr	8.0	-9.4
Mn	4.2	-1.1
Fe	12	-5.6
Co	5.4	-8.7

A comparison of the properties of dilute solutions of transition and post-transition metals in cadmium is informative. The values[18] of $\bar{L}^o$ for

Ag, Cu, Zn, Ga, In, Tl, Sn, Pb, Sb, and Bi range from -6 to +4 kcal. per g.-atom. The corresponding values for Cr, Fe and Co, but not Mn, are definitely more positive. The values[18] of $\bar{S}^{xs,o}$ for the same post-transition metals range from -3 to +5 cal. per g.-atom ^{o}K. The corresponding values for Cr, Fe and Co, but not Mn, are definitely more negative. Thus, Cr, Fe and Co are nearly insoluble in liquid cadmium because both energetic and entropic factors are unfavorable.

ACKNOWLEDGMENTS

Special thanks are due to G. Kesser and R. Meyer for the development and testing of analytical methods and to R. Schablaske and B. Tani for making their X-ray diffraction results available to us prior to publication.

REFERENCES

1. G. Tammann and W. Oelsen: Z. anorg. Chem., 1930, vol. 186, p. 277.

2. A. E. Martin, J. B. Knighton, and H. M. Feder: J. Chem. and Eng. Data, in press.

3. E. B. Sandell: Colorimetric Determination of Traces of Metals, Interscience, 3rd ed., 1959.

4. C. E. Crouthamel, B. E. Hjelte, and C. E. Johnson: Anal. Chem., 1955, vol. 27, p. 507.

5. R. Schablaske and B. Tani, private communication.

6. California Institute of Technology, Letter Report No. 10, on Contract No. DA-04-495-ORD 18, to Watertown Arsenal, Dec., 1952.

7. G. Hindricks: Z. anorg. Chem., 1908, vol. 59, p. 427.

8. U. Zwicker: Z. Metallkunde, 1950, vol. 41, p. 399.

9. E. Scheil: ibid., 1947, vol. 38, p. 320.

10. F. Lihl and E. Buhl: ibid., 1955, vol. 46, p. 787.

11. W. Koster and E. Horn: ibid., 1952, vol. 43, p. 333.

12. G. Voss: Z. anorg. Chem., 1908, vol. 57, p. 69.

13. C. E. Swartz and A. J. Phillips: Trans. AIME, 1934, vol. 111, p. 333.

14. M. Hansen and K. Anderko: Constitution of Binary Alloys, McGraw-Hill, 2nd ed., p. 430, 1958.

15. D. H. Kerridge: J. Nucl. Energy, Part B, Reactor Technology, 1961, vol. 1, p. 215.

16. J. L. White: NRL Report 5555, Dec. 1960.

17. K. K. Kelley: Bureau of Mines Bulletin 584, 1960.

18. R. Hultgren and associates: Selected Values for the Thermodynamic Properties of Metals and Alloys, Minerals Research Laboratory, University of California, commencing 1955.