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The Solubilities of Selected Elements in Liquid Plutonium

XVI. Yttrium

by

David F. Bowersox

THE SOLUBILITIES OF SELECTED ELEMENTS IN LIQUID PLUTONIUM

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ABSTRACT

The solubility of yttrium in liquid plutonium increases with temperature from 0.44 wt % Y at 700°C to 2.55 wt % Y at 990°C. The data fit the equation

$$\log N_Y = 1.12 - 2.97 \times 10^3 T^{-1} ,$$

where N_Y is the mole fraction of yttrium in a saturated solution at absolute temperature, T.

I. INTRODUCTION

The solubilities of carbon, tantalum, tungsten, rhenium, niobium, molybdenum, vanadium, thalium, zirconium, chromium, titanium, manganese, and lanthanum in liquid plutonium have been reported.[1-3] The solubilities of these elements increased with temperature from 700 to 1000°C. Empirical equations of the form

$$\log N_i = A - B \times 10^3 T^{-1}, \quad (1)$$

where N_i is the mole fraction of i in solution, A and B are empirical constants, and T is the absolute temperature, were constructed from the solubility data by least-squares calculations. In most cases, these solutes were of limited solubility (less than 10 at.% in this temperature range). However, both titanium and manganese are more soluble.

The phase diagram in the plutonium-rich area of the Y-Pu system indicates a simple eutectic-type binary with essentially no yttrium solubility in the solid plutonium.[4] In the yttrium-rich area, the plutonium solubility is 15 at.% in α-Y at 820°C;[4] this increases to 20 at.% at 640°C.[5] This study was restricted to mixtures containing less than 20 at.% Y and to the temperature range 700 to 1000°C.

II. EXPERIMENTAL

Electrorefined plutonium[6] and high-purity yttrium were used for this study. The analyses of these elements are summarized in Table I. The yttrium was analyzed for all the rare earth elements; in most cases the concentration was less than the limit of detection (3 to 100 ppm). The highest concentrations were tantalum, gadolinium, and dysprosium at 50 ppm. The equipment and procedures were similar to those described earlier.[6] There was no evidence of interaction between the CaF_2 crucibles and either yttrium or plutonium. The samples, which contained plutonium and yttrium, were dissolved, and aliquots were analyzed for yttrium. The estimated relative standard deviation of the analytical method is 2.4% in the concentration range of interest.[7]

Table I

ANALYSES OF PLUTONIUM AND YTTRIUM

Element	ppm in Pu[a]	ppm in Y	Element	ppm in Pu	ppm in Y
Li	0.005	< 3	Co	< 0.5	< 30
Bi	0.05	< 3	Zn	< 5	<300
Na	2	< 10	Am	75	...
Mg	1	4	O	10	...
Ca	3	10	Mo	< 0.5	< 10
Al	5	150	W	63	...
La	1	50	Th	3	<300
Si	7	4	Ta	< 5	...
Pb	< 0.5	< 10	Zr	0.7	...
Cu	< 0.3	8	H	5	...
Ni	0.5	30	C	< 10	...
Cr	0.5	< 3	F	< 2	...
B	< 0.3	< 10	V	< 0.5	< 10
Mn	< 0.1	< 5	Fe	2.5	40
Sn	< 0.5	< 10	Pu	99.99%	...

[a]Parts per million parts Pu, by weight.

III. RESULTS

Samples were withdrawn from Pu-Y mixtures at timed intervals to determine the time required to reach saturation. Results at 850°C, which are typical of these measurements, are given in Table II. Saturation was reached in less than 7 h throughout the entire temperature range. Additional measurements demonstrated that solubilities at a given temperature were also independent of the direction of approach to saturation, which indicates that this system is reversible.

A series of measurements of the solubility of yttrium in plutonium as a function of temperature from 700 to 1000°C were made under equilibrium conditions. A minimum of four measurements was made at 50° intervals. The results are summarized in Table III.

The liquidus line proposed in the Pu-Y phase diagram indicates a much higher solubility of yttrium in this temperature range.[4] For example, at 850°C, the average measured solubility is 2.98 at.% Y, which is a

Table II

THE SOLUBILITY OF YTTRIUM IN LIQUID PLUTONIUM AS A FUNCTION OF TIME AT 850°C

(Approach from Undersaturation)

Total Time, hr	Solubility, wt % Y
7.0	1.12
24.0	1.12
48.0	1.14
72.0	1.14
96.0	1.10

Table III

THE SOLUBILITY OF YTTRIUM IN LIQUID PLUTONIUM

Temperature, °C	Average Solubility	
	Wt Percent	Atom Percent
700	0.44 ± 0.02	1.17 ± 0.05
750	0.64 ± 0.01	1.70 ± 0.03
800	0.88 ± 0.02	2.33 ± 0.10
850	1.13 ± 0.04	2.98 ± 0.08
900	1.51 ± 0.03	3.96 ± 0.08
950	1.82 ± 0.05	4.75 ± 0.13
990	2.55 ± 0.10	6.57 ± 0.26

little over half the value of 5.0 at.% Y estimated from the phase diagram. The liquidus line was estimated as a straight line connecting the melting points of plutonium and yttrium. Evidently, the liquidus rises very sharply from the melting point of plutonium with little or no lowering of the eutectic melting point, and then curves towards the melting point of yttrium. Similar differences between estimates of solubility based upon proposed liquidus lines and measurements were noted with V-Pu, Cr-Pu, Nb-Pu, and Mo-Pu.[2,8]

The solubility of yttrium in liquid plutonium can be represented by

$$Y(s) + Pu(\ell) = Pu(\ell, \text{sat'd with } Y) \quad (2)$$

The average solubilities, expressed as at.% Y, are plotted on a logarithmic scale against the inverse of the absolute temperature in Fig. 1. This plot shows an approximately linear relationship between the data and (1/T). A linear equation was constructed by least-squares computations on all the data used in Table III. The resulting equation is

$$\log N_Y = 1.12 - 2.96 \times 10^3\ T^{-1} \quad (3)$$

The line in Fig. 1 is the graphical representation of this equation.

The partial molar enthalpy $\Delta\bar{H}^*_Y$, was calculated by

$$\Delta\bar{H}^*_Y = T[\Delta S_f - R \ln N_Y] \,, \quad (4)$$

where ΔS_f is the total entropy from an ideal, supercooled liquid state of yttrium at temperature T to fusion, and the solution is assumed to be regular. The enthalpy of solution is 10.5 ± 0.2 kcal/mole, and, therefore, the excess enthalpy of solution, $\Delta\bar{H}^{xs}_Y$, is 7.8 kcal/mole.

The Hildebrand solubility parameter, δ_Y, was calcu-

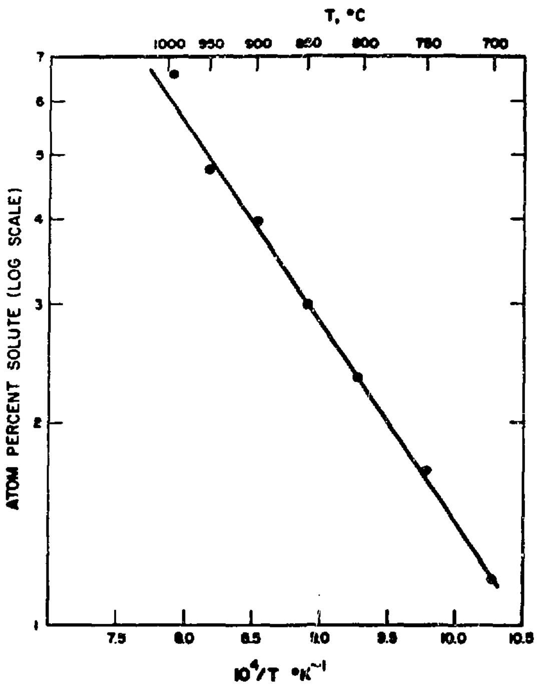

Fig. 1. Average solubilities vs inverse absolute temperature.

lated from the excess enthalpy by

$$\delta_Y = \left(\Delta \bar{H}^{xs}_Y / \bar{V}_Y\right)^{1/2} + \delta_{Pu}, \qquad (5)$$

where $\bar{V}_Y$ is the molar volume of Y and δ_{Pu} is 81.[9,10] This parameter is calculated as 60.9, which is 0.84 of theoretical (the square root of the energy of vaporization of yttrium divided by the molar volume). It has been found that the solubility parameters of tungsten, tantalum, niobium, vanadium, molybdenum, and chromium in liquid plutonium also average 0.84 of theoretical.[11] These elements do not form compounds with plutonium.

IV. ACKNOWLEDGMENTS

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