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The Solubilities of Selected Elements
in Liquid Plutonium
XI. Zirconium

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The Solubilities of Selected Elements
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XI. Zirconium

by

D. F. Bowersox

J. A. Leary

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THE SOLUBILITIES OF SELECTED ELEMENTS
IN LIQUID PLUTONIUM
XI. ZIRCONIUM

by
D. F. Bowersox and J. A. Leary

ABSTRACT

The solubility of Zr in liquid Pu has been measured from 700° to 950°C under reversible conditions. The solubility increases from 0.81% (by weight) Zr at 700°C to 7.6% Zr at 950°C. The data fit the empirical equation

$$\log N_{\text{Zr}} = 2.86 - 4.42 \times 10^3 T^{-1},$$

where N_{Zr} is the mole fraction of Zr in solution and T is the temperature in degrees Kelvin.

INTRODUCTION

This study extends a program designed to study the solubilities of selected elements in liquid Pu in a systematic manner. The solubilities of C, Ta, W, and Re;⁽¹⁾ Nb;⁽²⁾ Mo;⁽³⁾ V;⁽⁴⁾ and Tm⁽⁵⁾ from 700 to 1000°C have been reported. This paper summarizes the investigation of the solubility of Zr.

Zirconium is quite soluble in solid Pu; in fact, a continuous series of solid solutions between epsilon Pu and beta Zr are formed.⁽⁶⁾ From the estimated liquidus line of the phase diagram,⁽⁷⁾ the solubility appears to increase rapidly from about 2 at. % Zr at 700°C to about 20 at. % Zr at 950°C. There is no compound formation in the Pu-Zr binary system in the temperature range of these solubility experiments.

These studies should be of interest in such practical areas as liquid metal containment, the behavior of impurity elements during melting and casting, and the behavior of impurity elements in liquid metal fuel. Such

studies also furnish data that may contribute to a better understanding of liquid metals in general.

EXPERIMENTAL

The analyses of the electrorefined Pu⁽⁸⁾ and the high purity Zr which were used are summarized in Table I. The apparatus, the procedures, and the techniques employed have been described in earlier reports.⁽¹⁾ The precision of the results is controlled by at least three factors: temperature control and measurement, sampling errors, and precision in analyses. The temperature was measured and controlled to at most $\pm 2^\circ\text{C}$ and errors in sampling are believed to be minimal. Segregation occurred during the freezing of samples, probably because of the rapid decrease in solubility upon cooling. Therefore, in order to avoid errors due to segregation, each sample was weighed and completely dissolved prior to analysis for Zr. Zirconium was determined according to the procedure of Bricker and Waterbury,⁽⁹⁾ to ± 3 relative percent by spectrophotometric analyses.

Table I

Analyses of Pu and Zr

Element	ppm in Pu ^a	ppm in Zr ^b	Element	ppm in Pu ^a	ppm in Zr ^b
Li	< 0.005	< 10	Co	< 1	< 100
Be	< 0.001	< 10	Zn	< 10	< 300
Na	1	< 100	Am	72	----
Mg	2	< 10	O	10	105
Ca	< 2	< 100	Mo	< 1	< 100
Al	1	< 35	W	48±1	----
La	< 1	----	Th	< 15	----
Si	6	< 100	Ta	< 25	----
Pb	< 1	< 100	Zr	< 10	100
Cu	2	< 10	H	10±5	----
Ni	1	< 100	C	10±10	33
Cr	< 1	< 10	F	< 2	----
B	< 0.5	< 10	V	< 30	----
Mn	< 0.5	< 10	Fe	20	27
Sn	< 1	< 100	Pu	100.00	----

^aParts per million parts Pu, by wt.

^bParts per million parts Zr, by wt.

RESULTS AND CONCLUSIONS

Solute concentrations were measured at 750, 850, and 950°C at timed intervals to determine the rate of approach to saturation regardless of the direction of approach. The results of the experiments at 850°C are summarized in Table II. Results at 750 and 950°C were similar. Within the precision of measurements, saturation was reached within 6 h in every case, and the concentrations were independent of the direction of approach. It appears that equilibrium criteria for the system have been met.

Table II

The Solubility of Zr in Liquid Pu
as a Function of Time at 850°C

Undersaturation Approach		Oversaturation Approach	
Total time, h	Wt% Zr	Total time, h	Wt% Zr
4.0	2.49	5.0	3.18
6.0	3.12	17.0	3.19
24.0	3.25	30.0	3.15
30.0	3.19	50.0	3.18
48.0	3.22	65.0	3.20

Table III

The Solubility of Zr in Liquid Pu

Temperature, °C	No. of Measurements	Average Solubility	
		Wt%	At. %
700	6	0.81 ± 0.02	2.09
750	6	1.34 ± 0.04	3.44
800	5	2.14 ± 0.06	5.42
850	8	3.24 ± 0.04	8.06
900	6	5.20 ± 0.20	12.60
950	5	7.60 ± 0.10	17.70

The solubility was then measured under equilibrium conditions from 700 to 950°C at temperatures selected in a random order. The solubility values, which are given in Table III, increased from 2.09 at. % Zr at 700°C to 17.70 at. % Zr at 950°C. These values are in agreement with estimates made from the phase diagram.⁽⁷⁾

DISCUSSION

In Fig. 1, the averages given in Table III are plotted on a logarithmic scale against the inverse of the absolute temperature. The linear relationship between these variables was calculated by least squares treatment of all the solubility measurements included in

Fig. 1. Zirconium solubility vs reciprocal temperature.

Table IV

Calculated vs Independent Measured Values
of the Solubility of Zr in Liquid Pu

Temperature, °C	Solubility, Wt %	
	Experimental	Calculated ^a
725	1.10 ± 0.02	1.04
775	1.74 ± 0.04	1.68
825	2.64 ± 0.05	2.62

^aCalculated by Eq. (1).

Table III. The resulting equation is

$$\log N_{\text{Zr}} = 2.86 - 4.42 \times 10^3 T^{-1}, \quad (1)$$

where N_{Zr} is the mole fraction of Zr in solution, and T is the temperature in degrees Kelvin.

Several independent measurements of the solubility were made at 725, 775, and 825°C under equilibrium conditions. In Table IV these measurements are compared with values calculated by Eq. (1). The agreement is within the precision of the experimental design.

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