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X-Ray Diffraction Studies of Binary Plutonium - Uranium Alloys An Interim Report

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ABSTRACT

This report describes x-ray diffraction studies of Pu-U alloys carried on at LLNL in 1972. These studies were part of a larger project to understand the 2-phase, "banded" microstructures observed in Pu-15 wt% U alloys by Riefenberg¹ and Ellinger.² Our work has produced relatively high-quality diffraction patterns for both components of the "banded" structures, but computer indexing of these patterns did not produce acceptable solutions for either the zeta-phase (previously called pseudocubic²) or the second component of the "banded" structures.

In this work we have determined the effect of uranium on α -Pu's lattice parameters and have extended the data for the effect of uranium on β -Pu's lattice parameters.

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I. INTRODUCTION

This report describes work carried out at LLNL about 1972. We report it here to pique new interest in Pu-U alloy research. The work was an extension of experimentation started at Dow Chemical's Rocky Flats Plant by D. H. Riefenberg et al.¹ Riefenberg's work aimed at explaining the "banded" zeta Pu-U microstructures observed by several investigators.^{1,2}

Our X-ray diffraction studies had two goals. First, we wanted to precisely define the diffraction pattern of each component of the "banded" zeta-phase. And, second, we planned to try indexing these unknown powder patterns using LLL computer programs. A cubic indexing had been proposed² earlier for the zeta phase. But, the authors observed anisotropic thermal expansion of the phase, and speculated that it might be tetragonal with $c/a = 1$. The low-uranium constituent of the "banded" zeta has never been conclusively identified, although Riefenberg¹ speculated it was β -Pu.

II. EXPERIMENTAL PROCEDURES

A. Alloy Preparation

Five alloys with nominal compositions of 5, 15, 32, 40, and 50 wt% uranium were vacuum-induction-cast utilizing electro-refined plutonium containing less than 200ppm impurities and uranium containing less than 600 ppm impurities. Chemical analyses were taken from the tops and bottoms of the castings and no significant compositional differences were found.

B. Metallography

Samples were ground through 600 grit SiC paper using standard techniques. They were then mechanically polished using 0.25 μ m diamond paste with kerosene as a lubricant. The samples were electropolished with a solution of 2 parts tetra-phosphoric acid, 3 parts water and 5 parts ethoxy ethanol at 10V and 0.5a for one minute. Then they were etched in a mixture of 133 ml of acetic acid and 7 ml of water with 25 g of CrO_3 in solution.

C. X-Ray Diffraction

X-ray diffractometer patterns were routinely taken of each alloy (or alloy heat treatment). Prior to analysis, each sample was metallographically prepared, with the last step being a light electropolish to remove any residual surface damage. (No etching was done for these samples.)

They were then wrapped in a commercial plastic wrap and scanned. Ni-filtered copper radiation and specimen rotation in the sample plane were generally used.

When higher precision scans were desired, a number of procedural changes were made. The scanning range started at $7^\circ 2\theta$, instead of the normal $24^\circ 2\theta$. All mounting plastic was eliminated from the x-ray beam by removing the sample from the metallographic mount. The sample was then bonded to a special sample mount, and the entire mount/sample assembly was coated lightly with machine oil. The oil served to pin down any loose contamination on the mount. After oiling, all parts of the mount except the sample surface were covered with a commercial plastic wrap. This facilitated handling and still left the sample as the only mass in the beam capable of contributing to the diffraction pattern or its background.

The specially prepared sample mount was then placed in the diffractometer sample holder where runs taking 2 hours or more could be safely made.

The observed 2θ values were corrected for scan rate by comparison with an external, silicon standard. A sample holder blank correction was made to eliminate any lines not part of the sample pattern.

Computational analysis of the x-ray data was performed in a variety of ways. The first indexing attempts (for high-symmetry systems) were done using the INDEX program of Goebel.³ When these efforts failed, the QUEST program of Smith⁴ was used to look for low-symmetry solutions. Unit cell refinements were done using an LLL-modified revision of Mueller's^{5,6} NET-124 code.

D. Electron Microanalysis

Electron microanalysis was carried out on various alloys with a M.A.C. 400S microprobe. The operating parameters for quantitative analysis were an accelerating potential of 20kV, a specimen current of 40 μ A and a count time of 60 s. Uranium M α and Pu-M α radiations were diffracted by PET crystals. Conversion of the x-ray intensities was accomplished using Steel's⁷ MICROANALYSIS Program. Verification of the program's accuracy was made by comparing results on homogeneous alloys with chemical results.

III. RESULTS

A. Zeta Phase Studies

Because of the uncertainty about the zeta structure, we decided to obtain high precision experimental patterns for the phase. This data would

then be subtracted from "banded" zeta patterns to produce a pattern for the low-uranium component of the structure.

Long-term heat treatment in the high temperature zeta-phase field produced pure zeta-phase alloys at 32, 40 and 50 wt% U. In each case, the bulk alloy analysis (Table I), microprobe analysis (Table II) and metallography confirmed the single phase nature of the alloys. There was no "banding" in these alloys. These alloys were scanned with the modified x-ray diffractometer procedure mentioned above to produce high-precision zeta-phase diffraction patterns. Computer indexing of these patterns failed for the high-symmetry crystal systems.

A possible structure solution was obtained for these patterns in the monoclinic system. However, the calculated de Wolff criterion⁸ is only 3.2. To have a valid indexing, this number should exceed 10, and hence the solution is suspect. The number of unindexed lines for this solution is zero (Table III). The lattice parameters for the proposed cell are shown in Table IV along with the calculated densities. The density calculation assumed 68 atoms per unit cell. A bulk density measurement could only be obtained for the 32 wt% U alloy, since the other alloys were microcracked. The bulk density of the 32 wt% U alloy was 18.44_5 Mg/m^3 , in good agreement with the calculated value of 18.5_0 Mg/m^3 .

At this point we cannot say whether the previous structure² or this monoclinic solution is best. Against the cubic (or tetragonal) solution are the large number of impurity lines (10 of the first 35) and the inclusion of two-composition structures (e.g. the 32.5 at. % U alloy) in the solution. Arguing against the monoclinic solution is the low de Wolff criterion value.

B. Studies of the low-uranium composition phase

Coupons with large volume fractions of this phase were produced in a 15 wt% U alloy by (1) solution treating in the ϵ -Pu field (3 to 5 days), (2) slow cooling (~ 7 to 8°C/h) into the eta-plus-zeta field (~ 310 to 325°C), (3) holding these 5 to 6 days, and (4) water quenching. This procedure was carried out on 5 coupons. Four of the coupons were examined on two different sides to provide additional data sets, since we had preferred orientation might be a problem. This gave a total of nine diffractometer traces which were summed to provide a more accurate diffraction pattern of the composite structure (Table V).

Unfortunately, the net pattern (after zeta removal) bears some resemblance to β -Pu, to α -Pu, and to eta-phase Pu-U. However, even the combination of all three of these phases does not account for all important lines in the pattern. Attempts to index the pattern using computer techniques failed, too. We just cannot identify this phase (or phases) now.

C. The effect of uranium on the lattice parameters of α -Pu and β -Pu

Table VI shows the effects of uranium data shown for α -Pu with 5 wt% U dissolved and β -Pu with 9 wt% U dissolved are for metastable alloys. However, it is interesting that uranium expands the α -Pu lattice and contracts that of β -Pu. The β -Pu results confirm and extend earlier work.⁹ The α -Pu in the 5 wt% U alloy is quite stable, and was produced by all heat treatments we tried, though we did not try the very-long equilibration treatments used by Ellinger.² We do not dispute his data about the equilibrium solubility of uranium in plutonium, and are only commenting about the stability of non-equilibrium α -Pu.

CONCLUSIONS

There were both positive and negative results from this work. On the bright side were the following achievements.

- High quality diffraction patterns were obtained using our modified x-ray procedure.
- These patterns permitted us to determine the effect of uranium on alpha-plutonium's lattice parameters, and
- The patterns also permitted us to confirm and extend the data for the effect of uranium on beta-plutonium's lattice parameters.

On the negative side, we were unable to do that which we intended to do, viz., determine the structures of the two components of "banded" Pu-U alloys.

Future Work

The equilibrated zeta Pu-U alloys (see Table II) from this study still exist (albeit with substantial americium "grown in" by the decay process). We plan to use these alloys (and possibly newly cast ones) to make another attempt at solving the zeta structure, this time with LLNL's new, automated¹¹ diffractometers.

We also will report on the work carried on in parallel with the x-ray studies soon. This work includes microprobe data on the "banded" structure and a minor revision to the Pu-U equilibrium diagram.

TABLE I. Chemical Analysis¹⁰ of three alloys used for equilibrated zeta phase study.

Alloy and casting location	Intended Wt% U	Wt% U found (*)	Wt% Pu found (*)	Elemental Sum
32 U-Top	32	31.79	66.13	99.92
32 U Bottom	32	31.78	67.91	99.69
40 U Bottom	40	40.61	60.47	101.08
40 U Bottom	40	40.46	60.77	101.18
50 U Top	50	50.58	50.10	100.68
50 U Bottom	50	49.75	50.19	99.94

(*) The probable error in each determination is approximately 1% of the amount present. All values are mean of duplicates, and the technique used was a solution x-ray method.¹⁰

TABLE II. Summary of microprobe data on equilibrated zeta phase.

Intended composition	Heat treatment	No. of microprobe determinations	Prenormalization(2) sum of at. % U and at. % Pu	Normalized at % U	Normalized at. % Pu
32	A	10	$100.4 \pm 0.6(3)$	$32.83 \pm 0.15(3)$	$67.17 \pm 0.15(3)$
32	B	10	101.2 ± 0.6	32.56 ± 0.26	67.49 ± 0.26
40	A	10	98.6 ± 0.7	40.80 ± 0.58	59.20 ± 0.58
40	B	8	99.0 ± 0.05	40.70 ± 0.32	59.29 ± 0.32
50	A	9	98.1 ± 0.5	50.56 ± 0.37	49.43 ± 0.37
50	B	10	99.8 ± 0.8	50.93 ± 0.24	49.06 ± 0.24

Notes:

1. A: Equilibrated in high zeta field and slow cooled.
B: Equilibrated in high zeta field and quenched.
2. Per MICROANALYSIS⁷ Program
3. $\pm 1 \sigma$ in each case.

TABLE III. Proposed solution for the zeta-phase structure in the Pu-U alloy system. The calculated Q values are based on the monoclinic structure presented in Table III. While the monoclinic structure indexes all lines, the de Wolff criterion is too low to assure that the indexing is correct. This data is for a Pu-32 wt% U alloy which has been equilibrated as single-phase, zeta Pu-U.

d obs (Å)	1/l ₀	hkl	Q obs	Q calc.	Q calc. - Q obs
4.732	< 1	01 $\bar{2}$	0.04473	0.04471	-0.00001
3.768	< 1	020	0.07055	0.07053	-0.00002
3.548	< 1	212	0.07958	0.07918	-0.00041
3.357	< 1	220	0.08887	0.08887	0.00000
3.208	< 1	02 $\bar{2}$	0.09734	0.09761	0.00027
3.146	< 1	30 $\bar{4}$	0.10122	0.10126	0.00004
3.070	< 1	32 $\bar{1}$	0.10631	0.10649	0.00018
2.954	< 1	3 $\bar{2}$ 2	0.11475	0.11471	-0.00004
2.875	2	1 $\bar{2}$ 3	0.12365	0.12396	0.00031
2.776	1	321	0.13001	0.13066	0.00065
2.714	< 1	3 $\bar{2}$ 3	0.13596	0.13648	0.00052
2.650	< 1	50 $\bar{4}$	0.14268	0.14241	-0.00027
2.599	9	123	0.14830	0.14813	-0.00017
2.584	29	305	0.15006	0.15011	0.00005
2.514	100	030	0.15854	0.15868	0.00014
2.456	12	13 $\bar{1}$	0.16600	0.16601	0.00001
2.386	1	23 $\bar{1}$	0.17595	0.17574	-0.00021
2.325	7	520	0.18523	0.18519	-0.00004
2.285	1	231	0.19190	0.19186	-0.00005
2.270	9	614	0.19443	0.19438	-0.00005
2.174	5	521	0.21196	0.21211	0.00015
2.138	7	033	0.21923	0.21962	0.00039
2.131	7	3 $\bar{2}$ 5	0.22062	0.22063	0.00001
2.090	4	224	0.22922	0.22943	0.00021
2.051	5	4 $\bar{1}$ 6	0.23817	0.23806	-0.00011
1.981	5	51 $\bar{6}$	0.25522	0.25516	-0.00006
1.953	1	233	0.26275	0.26214	-0.00061
1.947	< 1	125	0.26435	0.26452	0.00017
1.863	1	04 $\bar{1}$	0.28875	0.28887	0.00012
1.834	< 1	141	0.29767	0.29749	-0.00018
1.827	1	531	0.30003	0.30026	0.00023
1.810	< 1	14 $\bar{2}$	0.30579	0.30571	-0.00008
1.803	1	702	0.30829	0.30823	-0.00006
1.797	< 1	417	0.31011	0.30996	-0.00015
1.779	4	424	0.31663	0.31670	0.00007
1.739	1	007	0.33124	0.33175	0.00051
1.735	1	801	0.33264	0.33255	-0.00009
1.723	1	63 $\bar{4}$	0.33534	0.33543	0.00010
1.666	4	81 $\bar{6}$	0.36094	0.36152	0.00058

TABLE IV. Proposed monoclinic lattice parameters for the Pu-U zeta-phase solid-solution. A bulk density of 18.44_5 was measured for the Pu-32 wt% U alloy. The other two alloys were microcracked and could not be measured.

Parameter	Pu-32 wt% U	Pu-40 wt% U	Pu-50 wt% U
a_0 (Å)	15.87 ± 0.01	15.86 ± 0.01	15.85 ± 0.02
b_0 (Å)	7.535 ± 0.005	7.524 ± 0.007	7.516 ± 0.007
c_0 (Å)	13.06 ± 0.01	13.06 ± 0.01	13.03 ± 0.01
β (deg.)	111.17 ± 0.02	111.19 ± 0.03	111.17 ± 0.03
V (Å ³)	1457	1452	1448
ρ_x (g/m ³) (based on 68 atoms per unit cell)	18.50	18.55	18.60

TABLE V. Resultant diffraction pattern obtained by summing nine diffractometer traces of a deliberately banded Pu-15 wt% U alloy. Though the zeta phase lines are readily identified, the balance of the pattern does not completely fit eta Pu-U, δ -Pu or α -Pu singly or in combination. Microprobe evidence indicates the balance of the pattern should be single phase. In the listing below, the zeta-phase lines are marked.

d(Å)	I/I ₀	Iden.	d(Å)	I/I ₀	Iden.
2.98	< 1	zeta	2.598	6	zeta
2.954	< 1	-	2.587	9	-
2.93	2	-	2.580	3	-
2.91	< 1	-	2.569	9	-
2.89	1	-	2.55	9	-
2.87	< 1	zeta	2.539	1	-
2.86	1	zeta	2.536	17	-
2.85	< 1	PuO	2.527	75	zeta +
2.84	< 1	-	2.516	5	-
2.836	3	-	2.499	1	-
2.819	2	-	2.49	2	-
2.80	< 1	zeta	2.479	6	-
2.78	1	-	2.473	1	PuO
2.755	1	-	2.466	1	zeta
2.67	< 1	zeta	2.457	2	-
2.65	< 1	-	2.440	< 1	-
2.63	< 1	-	2.426	1	-
2.620	2	-	2.415	24	-
2.603	4	zeta	2.406	4	-

TABLE V. (Continued)

d(Å)	I/I ₀	iden.	d(Å)	I/I ₀	iden.
2.402	1	zeta	2.157	8	-
2.396	25	-	2.144	4	zeta
2.392	21	zeta	2.140	7	-
2.371	100	-	2.123	< 1	-
2.347	8	-	2.116	1	-
2.341	5	zeta	2.111	2	-
2.335	41	-	2.107	1	-
2.330	1	-	2.102	8	zeta
2.325	16	-	2.099	14	zeta
2.320	30	-	2.093	2	-
2.297	7	zeta	2.084	2	-
2.289	6	zeta	2.069	1	zeta
2.242	2	zeta	2.066	4	zeta
2.234	1	-	2.058	2	zeta
2.229	2	-	2.027	1	-
2.220	2	-			
2.216	1	-			
2.195	7	-			
2.188	2	-			
2.183	1	zeta			
2.178	1	zeta			
2.162	2	-			

TABLE VI. The effect of uranium on the lattice parameters of α -Pu and β -Pu.

Material	a_0 (Å)	b_0 (Å)	c_0 (Å)	β (deg)	Ref.
Pure α -Pu at 21°C	6.183	4.822	10.963	101.79	8
α -Pu with 5 wt% U at 23°C	6.193	4.828	10.977	101.78	This work
Pure β -Pu at 23°C	9.221*	10.448*	7.819*	92.54*	8
β -Pu with 7 wt% U at 21°C	9.211	10.417	7.812	92.52	9
β -Pu with 9 wt% U at 23°C	9.179	10.377	7.763	92.47	This work

* Parameters obtained by extrapolating higher temperature data to ambient temperature.

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