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AN INVESTIGATION OF THE PLUTONIUM-SILVER SYSTEM

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AN INVESTIGATION OF THE PLUTONIUM-SILVER SYSTEM*

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Metallographic, x-ray diffraction, and differential thermal analysis have been used in a limited investigation of the plutonium-silver phase diagram. Two compounds were observed: $PuAg_{3.6}$, which melts congruently at 977°C, and $PuAg_2$, which melts peritectically at 817°C. A region of liquid immiscibility extends from about 2 to 59 at.% silver, at which composition there is a monotectic reaction at 795°C. A eutectic between $PuAg_{3.6}$ and silver was found at 801°C and 90.8 at.% silver. These results are at variance with the literature in several respects. The occurrence of liquid immiscibility is explained in accordance with the thermodynamic reasoning of Hume-Rothery and Anderson (1960).

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

Introduction

Kutaitsev et al.(1) have published a phase diagram from their investigation of the plutonium-silver system. Their phase diagram is widely different from those for other Group IB plutonium alloy systems. Aside from brief work by Cramer(2) and Runnalls(3) on individual alloys, this Russian effort is the only work available on plutonium-silver. Because the silver alloys are so different from other plutonium Group IB alloys and the Russian diagram is somewhat incomplete, this study was undertaken.

Materials and Methods

The techniques and equipment for this study were described previously in our paper on phase relations in the plutonium-lead system(4). Briefly, techniques include differential thermal analysis in sealed tantalum crucibles; x-ray diffraction from powders, polished surfaces, and single crystals; and metallography. A cathodic etcher described by Garrison et al.(5) was adapted to a gloved box and used to great advantage in supplementing the metallographic techniques. Computer programs associated with the x-ray diffraction interpretation were the same as before(4).

Silver of 99.999 wt% purity was purchased in the form of 1/4-inch rods and used without remelting. Electrorefined plutonium was obtained in the form of cast rods and machined to fit the crucibles just prior to use, to avoid tarnishing. The electrorefining, casting, and chemical analysis of the plutonium were done by Dow Chemical Company at the Rocky Flats Plant. Their results indicated a purity better than 99.9 wt%; the major impurity was the decay product, americium, which was present between 200 and 300 ppm at the time of use. Other significant impurities (in ppm by wt) were 32 iron, 9 gallium, 16 carbon, 9 copper, and 7 neptunium.

Two of the chromel-alumel thermocouples were calibrated in situ against the melting point of silver (960.8°C) in a sealed tantalum crucible. One correction was 2.2°C and the other 0.7°C, both thermocouples reading too high. A correction was applied only to data taken with a calibrated thermocouple.

Results

Thermal Analysis

Eleven different compositions were investigated by differential thermal analysis. Each melt was first taken to 1000°C and stirred by rocking the furnace through a 100-deg arc several times. The results, given in Table I, are from the cooling curves thus obtained. They are also plotted on the phase diagram (Figure 1). Slight supercooling was observed generally, but recalescence was large enough to bring the temperature back to the equilibrium point in most cases. The heating and cooling curves supported the interpretation of thermal results shown in Figure 1, with the possible exception of those for the alloys containing $PuAg_2$. These alloys were found to give small thermal indications between 760 and 780°C on heating only. The effects are not understood, but are not attributed to another phase. This conclusion is reached because neither metallography nor x-ray diffraction gave evidence

Table 1. Thermal Data from Cooling Curves

Synthetic Composition (At.% Ag)	Total Charge (Gram-Atoms)	Reaction[a]						Experimental[b]
		Congruent Solidification	Liquidus	$PuAg_2$ Peritectic	Eutectic	Monotectic	Epsilon Pu Peritectic	
10.00	0.695	-	-	-	-	791°C 1.4	659°C 2.17	CHC
40.14	.698	-	-	-	-	795°C 7.1	655°C 1.3	CHC
60.16	.872	-	-	-	-	796°C 12.2	653°C 0.34	CHC
64.89	.697	-	-	817°C 8.6	-	793°C 1.9	647°C 0.1	CHC
69.70	.700	-	882°C 2.2	820°C 5.84	-	-	-	CHQ
74.99	.690	-	953°C 7.1	815°C 2.52	-	-	-	CHQ
78.45	.703	977°C 8.2	-	-	-	-	-	C-CAL
79.84	.673	-	964°C 7.8	-	795°C 1.25	-	-	CHC
85.00	.699	-	914°C 2.8	-	802°C 3.90	-	-	C-CAL
90.00	.698	-	-	-	801°C 795	-	-	C-CAL
95.00	0.691	-	891°C 3.0	-	801°C 395	-	-	C-CAL

[a] Value denotes area under differential curve of stipulated reaction (an approximation of the heat evolved).

[b] Extent of experimental work as follows: CAL = calibrated chromel-alumel thermocouple used; C = cooling curve only; CHC = cooling curve, heating curve, and a second cooling curve; CHQ = cooling curve, heating curve, and rapid cooling by removal of Inconel tube from furnace.

of a third intermetallic compound, and because the temperatures and magnitudes of the effects do not seem consistent with a peritectic reaction or phase transformation in $PuAg_2$.

The δ to δ′ transformation was observed in the 10 at.% silver alloy. The normal transformation temperatures were observed for the other phases of plutonium.

Areas under the differential curves for the monotectic and eutectic reactions were plotted against composition and extrapolated to indicate the composition of each reaction. The results indicate a eutectic composition of 90.8 ± 0.3 at.% silver and a monotectic composition of about 59 at.% silver. The latter value agrees exactly with a chemical analysis of the supernatant portion of the 10 at.% silver alloy. Extrapolation of the areas to the plutonium-rich end of the monotectic horizontal gives about 2 at.% silver for that limit. Chemical analysis of the bottom portion of the 10 at.% silver alloy gave 0.7 at.% for the same limit. However, careful examination of the microstructure revealed that most of the $PuAg_2$ compound had floated up to the region of the interface where it was not taken into the sample. Therefore, the 0.7 at.% silver result is probably better associated with the liquid solubility at the 659°C peritectic.

Metallography

Routinely, a vertical section of each melt was examined by metallography. This technique confirmed the existence of the liquid immiscibility, the two compounds, and the eutectic. These are illustrated in Figures 2, 3, and 4, respectively.

The following observations were made from metallographic examination. The alloy at 78.45 at.% silver was seen to contain a trace of eutectic when observed at high magnification. There is no tendency for the eutectic to degenerate. The alloy at 10.00 at.% silver contained a small amount of primary $PuAg_{3.6}$ as long needles or plates, confirming the thermal data regarding the location of the eutectic. This can be seen in Figure 4. The alloy at 64.89 at.% silver consisted mostly of primary $PuAg_2$ with a small amount of monotectic product, consistent with the thermal data in indicating the approximate composition of the compound we have called $PuAg_2$. Coring (ultrafine precipitation of $PuAg_2$) was observed in the plutonium phase near the $PuAg_2$ interface. This is attributed to the solubility of silver in the epsilon phase. This coring cannot be seen in Figure 2 because it has been masked with oxide.

Microhardness observations using a 25 g load indicated that the alpha plutonium in the monotectic structure had a hardness of 270 ± 5 DPHN and the $PuAg_2$ in this structure had a hardness range of 82 to 98 DPHN. $PuAg_2$ formed in the peritectic reaction had a somewhat higher hardness, however, with values of 111, 143, and 167 being recorded. We do not feel that this difference indicates another phase. $PuAg_2$ possesses some ductility, and it does not have the clean conchoidal fracture usually associated with intermetallic compounds. $PuAg_{3.6}$ with a hardness of 292 ± 5 DPHN is quite brittle.

X-Ray Diffraction

The compound we have designated $PuAg_{3.6}$ was first reported by Runnalls(3) and called $PuAg_3$. We isolated a single crystal of this material and took diffractometer data. Before starting the crystal structure determination, we learned that the structure had been solved by Bailey and Kline(6) for the $GdAg_{3.6}$ compound. A powder pattern calculated on the basis of the Bailey – Kline structure is compared in Table II with our observed diffractometer pattern. The intensity agreement is fair. The differences can be explained on the basis of preferred orientation, which for $PuAg_{3.6}$ was observed to an even greater extent in our powder photographs of 0.3 mm quartz capillaries. The lattice parameters for $PuAg_{3.6}$ in an 80 at.% silver alloy were

$$a = 12.727 \pm 0.006\ \text{Å}$$
$$c = 9.392 \pm 0.004\ \text{Å, and}$$
$$c/a = 0.74,$$

with a calculated x-ray density of 11.15 g/cc. The silver lattice parameter in the same alloy was 4.0857 ± 0.0003 Å at 22°C. This result indicates minimal plutonium solubility in silver at room temperature.

The powder patterns for $PuAg_2$ have not been indexed, and single crystals have not been isolated because of the ductility of this compound. The structure remains unknown.

Discussion

No details were given of the Russian experiments, except that their thermal analysis points are plotted on their phase diagram and their melts weighed at most a few grams(1). The Russians reported liquid immiscibility, one compound ("$PuAg_3$") formed in a syntectic reaction, and a eutectic between that compound and silver. Our work confirms the liquid immiscibility and the eutectic. However, major discrepancies are evident in the thermal analysis results. We observed a deeply penetrating corrosion when the alloys were exposed to air, which might be a contributing cause. Unless a protective atmosphere were provided, corrosion could seriously alter the experimental results from small samples. However, corrosion alone does not explain the differences in the results from thermal analysis. Without more detail about the Russian experimental methods and results, it is hard for us even to speculate concerning reasons for the differences between their phase diagram and ours.

The existence of liquid immiscibility in this alloy system is surprising but can be rationalized in the following way. The thermodynamic conditions leading to liquid immiscibility have been studied by Hume-Rothery and Anderson(7). They divide the conditions causing immiscibility into two types. Type 1 is the common type where there is little or no tendency toward bonding between unlike atoms. Examples of this type are found in the plutonium alloys with the alkali metals, the alkaline earths, europium, and ytterbium. A type 2 condition is that in which a tendency toward molecular bonding or ordering exists in a localized composition region of the liquid, associated with the impending solidification of a highly stable compound. This condition causes a sharp localized drop in the liquid free energy curve, sometimes resulting in an inflection in the curve on one or both sides of the compound. Associated with any such inflection are two stable liquid phases. The plutonium-silver system appears to be of this latter type, as does the plutonium-cadmium system. The most significant consideration is that these systems would be completely miscible in the liquid if it were not for an ordered structure postulated to exist in the liquid. Waber(8) suggests this by reporting a "Mott Number" of -1.91 for the Pu-Ag system, indicating complete miscibility. Mott's theory, being prior to the work of Hume-Rothery and Anderson, does not formally consider the possibility of two types of liquid immiscibility.

Table II. Powder Diffraction Pattern of $PuAg_{3.6}$

$PuAg_{3.64}$ ($Pu_{14}Ag_{51}$) $GdAg_{3.6}$ Type

Diffractometer data from 78.4 at.% Ag DTA sample. Alloy was crushed, sieved to -200 mesh, and cast into thin epoxy layer for scanning.

	d (Å)		Intensity	
(hkl)	Observed	Calculated	Observed[a]	Calculated[b]
(201) (002)	4.725	4.753 4.696	8	10.3 2.5
–	4.623	–	5	–
–	4.547	–	4	–
(211)(121) (112)	3.814	3.808 3.779	11	18.1 2.6
(212)(122)	3.125	3.116	4	4.6
(310)(130)	3.064	3.057	20	10.2
(221) (103)	3.028	3.014 3.012	7	2.7 1.1
(131) (302)	2.903	2.907 2.894	2	0.6 2.4
(400)	2.761	2.755	7	5.6
–	2.754	–	5	–
(401) (222)	2.642	2.644 2.634	4	2.4 7.1
(312)(132)	2.571	2.562	65	45.6
(320)(230)	2.534	2.529	13	6.8
(213)(123)	2.508	2.503	46	100.0
(321)(231)	2.444	2.442	14	10.3
(410)(140)	2.412	2.405	100	70.7
(303) (402)	2.381	2.383 2.377	15	19.4 3.3
(004)	2.361	2.348	11	10.3
(411)(141)	2.334	2.330	58	29.5
(104)	2.299	2.296	3	3.4
–	2.266	–	2	–
–	2.244	–	3	–
(223) (322)(232)	2.229	2.232 2.226	14	6.8 10.7
(500)	2.204	2.204	9	5.5
(313)(133)	2.188	2.187	7	8.4
(204)	2.159	2.160	4	5.7
(412)(142)	2.145	2.141	3	4.6
(330)	2.131	2.121	2	1.0
–	2.098	–	3	–
(420)(240)	2.085	2.083	3	0.9
(403)	2.067	2.068	3	1.1
(214)	2.050	2.045	2	0.1
–	2.020	–	1	–
(502)	2.002	2.000	2	1.1
(510)(150)	1.980	1.980	5	3.1

Table II (continued)

(hkl)	d (Å)		Intensity	
	Observed	Calculated	Observed[a]	Calculated[b]
(323)(233)	1.969	1.967	5	5.9
–	1.948	–	1	–
(511)(151)	1.936	1.937	11	1.8
(332)		1.933		3.1
(143)	1.905	1.907	3	0.9
(422)(242)		1.904		2.3
(600)	1.837	1.837	2	0.5
(430)(340)	1.814	1.812	5	4.2
(601)	1.803	1.803	12	2.9
(115)		1.802		1.1
(431)(341)	1.782	1.779	1	0.8
(205)		1.778		0.8
–	1.746	–	2	–
(521)(251)	1.735	1.735	8	1.8
(423)(243)		1.734		9.2
(324)(234)	1.725	1.721	2	0.8
(215)(125)	1.712	1.712	3	3.1
(432)(342)	1.689	1.691	3	4.4
(414)(144)	1.681	1.680	3	3.6
(513)(153)	1.674	1.673	8	2.8
(522)(252)	1.653	1.652	2	1.3
(603)	1.584	1.584	3	0.5
(612)(162)		1.583		2.2
(433)(343)	1.567	1.568	7	5.0
(006)		1.565		5.5
(244)	1.554	1.558	2	2.6
(531)(351)		1.553		0.9
(106)		1.550		0.8
(523)	1.537	1.537	2	4.4
(620)(260)	1.528	1.528	2	1.8
(261)	1.508	1.509	5	2.4
(325)(235)		1.508		2.4
(442)		1.507		0.8
(206)		1.506		0.7
(532)(702)(352)	1.493	1.493	4	2.4
(613)(163)	1.482	1.481	3	2.7
(415)		1.480		9.6
(622)	1.454	1.453	4	8.1
(711)(171)	1.443	1.443	3	1.3
(344)	1.430	1.435	1	4.7
(443)	1.419	1.418	3	5.5
(540)(450)	1.412	1.411	5	6.5
(524)(254)				
(703)(533)(353)	1.408	1.407	5	2.3
(226)		1.404		0.9
(451)	1.394	1.396	13	3.1
(712)		1.394		1.9
(316)(136)		1.393		6.6

Table II (continued)

(hkl)	d (Å)		Intensity	
	Observed	Calculated	Observed[a]	Calculated[b]
(630)(360)	1.386	1.389	3	4.1
(631)(361)	1.374	1.374	22	7.1
(623)(263)				5.7
(164)	1.364	1.367	3	3.4
(801)(155)		1.363		2.9
(720)	1.345	1.347		2.9
(721)(271)	1.333	1.333	4	1.3
(632)		1.332		0.8
(Plus 93 more observed lines to d = 0.817)				

[a] Net intensity over background normalized to $I_{(410)(140)} = 100$

[b] POWD2 intensities, Reference(4)

Acknowledgments

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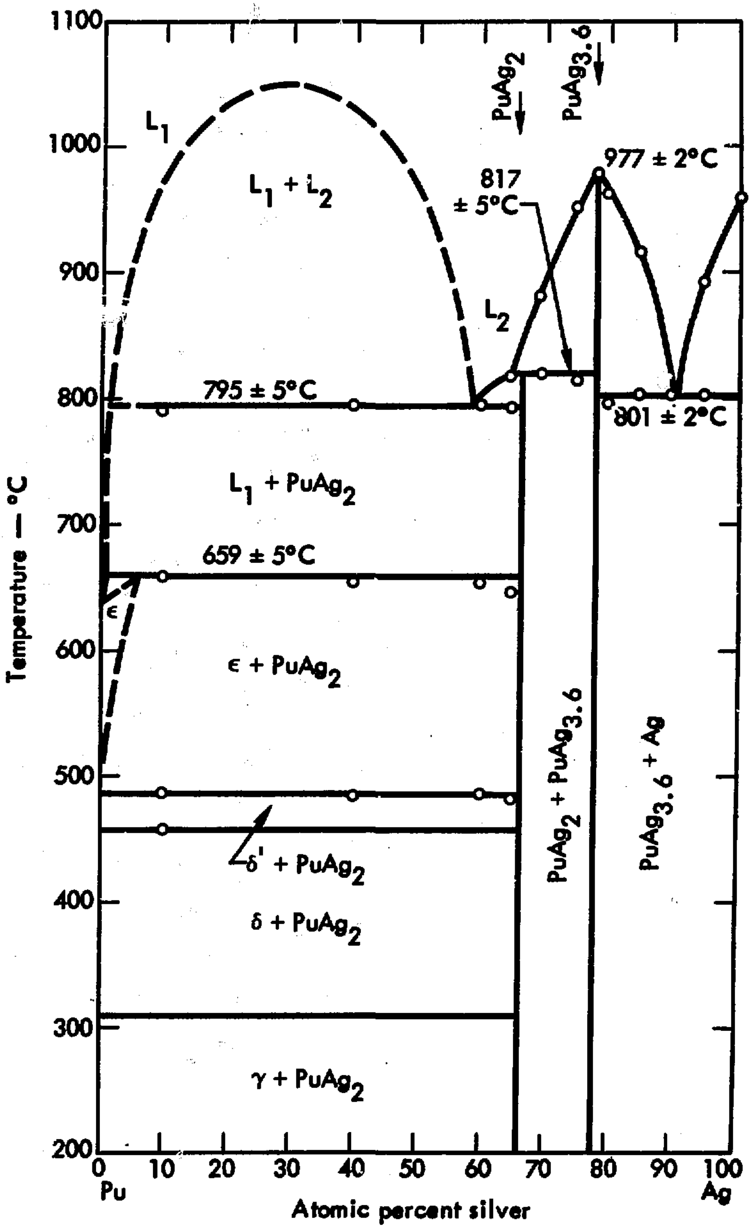
List of Figures

1. Plutonium-silver phase diagram resulting from this work.

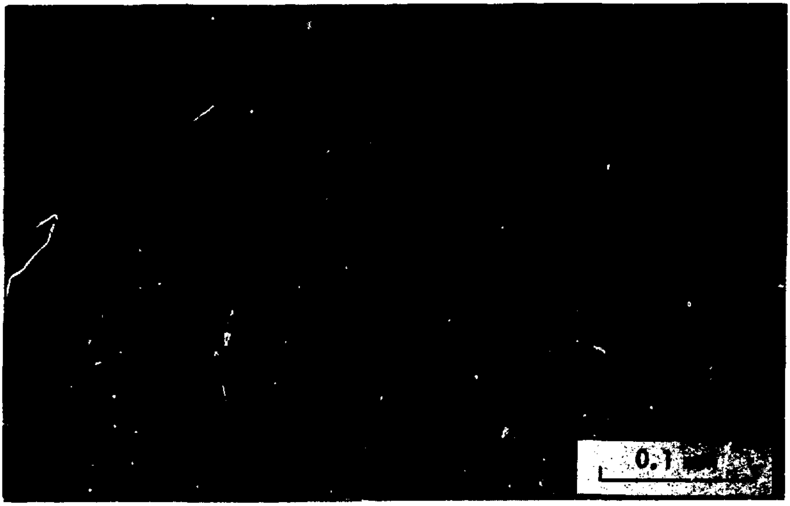
2. Interface structure resulting from immiscible liquids in an alloy containing 10 at.% silver. The supernatant monotectic liquid reacted at 795°C to form $PuAg_2$, entrapping globules of plutonium-rich liquid. The latter (bottom and globules) rejected $PuAg_2$ before freezing, becoming alpha plutonium. (Original magnification X250, unetched.)

3. Primary $PuAg_{3.6}$ in a matrix of $PuAg_2$, the result of a peritectic reaction at 817°C in an alloy containing 69.7 at.% silver. A slight amount of plutonium-rich liquid was entrapped in the $PuAg_2$. (Original magnification X250, cathode etch.)

4. Primary $PuAg_{3.6}$ in a eutectic mixture of $PuAg_{3.6}$ and essentially pure silver, the result of the eutectic reaction at 801°C in an alloy containing 90 at.% silver. (Original magnification X250, cathode etch.)


1100
1000
900
800
700
600
500
400
300
200
Temperature — °C
0
10
20
30
40
50
60
70
80
90
100
Pu
Ag
Atomic percent silver
L_1
$L_1 + L_2$
L_2
$PuAg_2$
$PuAg_{3.6}$
977 ± 2°C
817 ± 5°C
795 ± 5°C
801 ± 2°C
$L_1 + PuAg_2$
659 ± 5°C
ε
$\epsilon + PuAg_2$
$\delta' + PuAg_2$
$\delta + PuAg_2$
$\gamma + PuAg_2$
$PuAg_2 + PuAg_{3.6}$
$PuAg_{3.6} + Ag$

Wood - Fig. 1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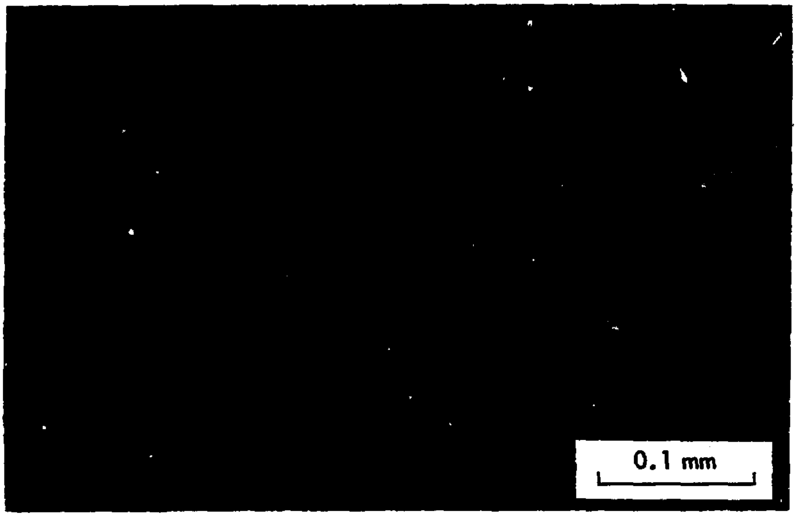
Wood - Fig. 3



Wood - Fig. 4