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Retention of a metastable bcc ε-Pu solid solution: ε-Pu(Ti)

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A metastable ε-Pu (bcc) solid solution has been retained to room temperature by rapid quenching of Pu-rich Pu-Ti alloys from the liquid state. Until now, ε-Pu solid solutions were limited to high temperatures and had not been successfully quenched to room temperature without transformation. The apparatus used to quench the specimens was a modified "gun-type" splat-cooling unit, capable of producing extremely high cooling rates of from 10^6 to 10^8 °C sec^{-1}. ε-Pu(Ti) was retained in the composition region from ~ 20 to more than 45 at.% Ti, and extrapolation of the lattice parameter/composition curve yielded a value of $a_0 = 3.53_0$ Å for ε-Pu at 20°C. This modification differs from the ε-Pu modification derived by extrapolating from high temperature to 20°C by a small valence increase of ≈ 0.1. Metastable δ-Pu (Ti) (fcc) solid solutions were also quenched-in with alloys containing lesser amounts of Ti, and evidence was found to indicate that the δ was probably a product of ε-Pu(Ti) solid-state decomposition.

1. Introduction

Elemental plutonium has six crystalline modifications at atmospheric pressure. Of these, the three modifications stable at the highest temperatures are: δ, Cu-A1 type (fcc), between 310 and 458°C, δ′, In-A6 type (fct), between 458 and 480°C, and ε, W-A2 type (bcc), between 480 and 641°C [1].

None of these modifications can be retained to room temperature by quenching of the pure metal. δ-Pu is stabilized by alloying additions of Al, Ga, Ce, Sc, Zr, Am, and other elements, however, and it can be obtained as an equilibrium phase at 20°C as the corresponding binary phase diagrams show [1]. ε-Pu also forms extensive equilibrium solid solutions with several of these same metals, but such ε-phase regions are always limited to high temperatures.† Hitherto, ε-Pu has not been retained at room temperature by quenching and, consequently, the lattice parameter of ε-Pu is known only at elevated temperatures [2] where extensive studies of Pu and Pu-based solid-solution alloys have been made [1-3].

The splat-cooling technique [4-6] for rapidly quenching alloys from the liquid state has been applied to plutonium systems as part of a programme to develop new Pu alloys and intermetallic compounds. By this technique we hope to lock in elements that have heretofore been insoluble in solid plutonium and to make new metastable crystalline and amorphous phases. The successful retention of ε-Pu (Ti) and δ-Pu (Ti) solid solutions at room temperature is the first result to be reported. The complete Pu-Ti equilibrium phase diagram as published by Ellinger *et al* [1] is reproduced in Fig. 1a and shows phase equilibria involving δ′-Pu(Ti) as determined by Elliott and Larson [7]. δ-Pu(Ti) was retained in alloys with more than 7 at. % Ti by quenching from the ε-phase region [8].

2. Experimental procedure

Master alloys of high-purity electro-refined Pu

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†Sc, Zr, U, and Np each form a complete series of bcc solid solutions with ε-Pu at high temperatures.

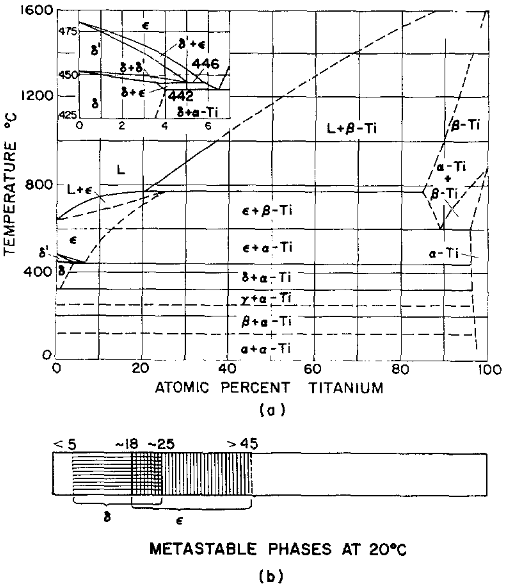

Figure 1 The Pu-Ti alloy system: (a) equilibrium phase diagram and (b) quenched-phase plot of metastable phases retained at 20° C.

and high-purity (99.96 wt %) Ti were prepared in an inert gas arc-melting furnace. Each sample to be splat-cooled consisted of a bead, weighing about 50 mg, obtained from a master alloy.

The alloys were quenched in a "gun-type" splat-cooling unit based on the design of Ruhl and Giessen [9, 10]. An important modification was enclosure of the quenching unit in a glove-box system, thus making the apparatus suitable for handling plutonium and other alpha-radioactive materials that are highly toxic. Quenching was carried out on copper target plates. The plates were cooled intermittently with liquid nitrogen to maintain their temperatures at 20° C or slightly lower.

For safety in handling, the target plates with their splatted samples were sealed in plastic prior to examination on a General Electric XRD-5 diffractometer with Cu*K*α radiation. Samples were first X-rayed about 1 h after splatting and were subsequently re-examined at various times over a period of several weeks storage at room temperature to search for possible changes in the diffraction patterns. Scanning speeds of 2° min^{-1} and 0.2° min^{-1} were employed. Lattice parameters were evaluated by internally calibrating the patterns with the copper target diffraction peaks [11] and forming weighted averages of the lattice parameters derived from the observed peaks, placing maximum weight on peaks with $2\theta = 50$ to 70°. Owing to peak broadening at higher angles, extrapolation to $2\theta = 180°$ does not increase the accuracy of the result. Lattice parameters have a fractional accuracy (maximum confidence limit) of $\pm 1.5 \times 10^{-3}$, corresponding to $\Delta a < \pm 0.006$Å and $\Delta \bar{V} < \pm 0.09$Å^3 for ε-Pu(Ti).

3. Results

A quenched-phase plot [12] showing the retained metastable phases is given in Fig. 1b. Alloys with 5 to 45 at. % Ti were studied; the results are presented in Table I and the resulting mean atomic volumes, $\bar{V}$, are plotted in Fig.2.

3.1. δ-Pu(Ti) solid solution

Fig. 1b and Table I show that a single-phase δ-Pu(Ti) solid solution has been retained in alloys with 10 and 15 at. % Ti. In alloys with 5, 20 and 25 at. % Ti, δ was also retained, as a mixture with other phases. In the Pu + 5 at. % Ti alloy an unidentified phase, probably a low-temperature Pu modification, co-existed; at 20 and 25 at. % Ti, ε-Pu(Ti) was found as a second phase.

The diffraction patterns of δ show strong peak broadening which increases with increasing Ti content and varies considerably for different *hkl* sets within each pattern. An analysis of the strain and particle-size components of this effect will be undertaken and will be reported later. The presence of either broadening component indicates that δ does not form directly from the melt but is the product of a solid-state transformation from ε-Pu(Ti). This observation, in conjunction with the phase diagram, Fig. 1a, suggests that the supercooling of Pu-Ti alloys in this composition range was < ~ 200° C, in agreement with general observations on splat-cooled metastable phases [5].

Because of the peak broadening, lattice parameter determinations are not as accurate for δ as for ε; in addition, the data in Table I show considerable scatter in the lattice parameters and the mean atomic volumes of δ-Pu(Ti). Values for $\bar{V}$ are plotted against alloy composition in Fig. 2. The room temperature value for δ-Pu extrapolated from δ-Pu(Ga) alloys [13] agrees well with the present values for metastable δ-Pu(Ti), as shown in Fig. 2 and Table II. It is not known at present whether δ-Pu(Ti) in two-phase alloys is altered in composition as a result of the transformation process, or whether this or

TABLE I Results of rapid quenching experiments on Pu-Ti alloys

Composition (at. % Ti)	Equilibrium structure at 20°C	Structure after splat-cooling*	Lattice parameter (Å)	Mean atomic volume (Å^3)	No. of determinations	Comments
5	α-Pu + α-Ti	δ(~ 80) + other phase	4.610	24.50	2	
10	as above	δ(100)	4.559	23.69	1	
15	as above	δ(100)	4.588; 4.572	23.68; 23.89	3	Erratic results, very strong peak broadening.
20	as above	δ(50)	~ 4.505; 4.515; 4.533	22.8$_0$; 23.01; 23.29	3	Erratic results for δ.
		ε(50)	3.473	20.95	2	
25	as above	δ(40)	4.50$_2$	22.82	2	
		ε(60)	3.463	20.76	2	
30	as above	δ(15)	—	—		
		ε(85)	3.458	20.67	2	
35	as above	ε(100)	3.445	20.45	1	
45	as above	δ(25)	—	—		
		ε(75)	3.420	20.00	1	

*Numerical values are estimated percentages. δ = δ-Pu(Ti) solid solution; ε = ε-Pu(Ti) solid solution, isostructural with β-Ti(Pu) solid solution.

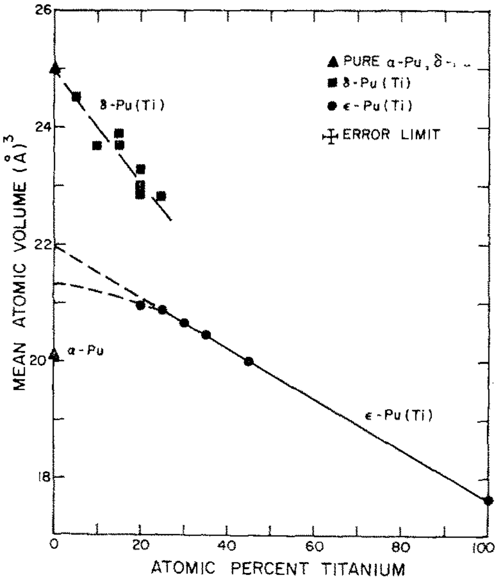

Figure 2 Mean atomic volumes of metastable Pu-Ti phases plotted against alloy composition.

another cause accounts for the erratic lattice parameters.

The apparent atomic volume of Ti in δ-Pu(Ti) of ~ 15(Å^3) (from a straight-line extrapolation in Fig. 2) is unrealistic in a hard-sphere model; if the present curve is confirmed by later, more complete measurements, it would indicate that a composition-dependent decrease of the atomic size of the Pu atoms in δ-Pu(Ti) takes place, and is probably due to a valence increase of Pu in δ-Pu(Ti) at increasing Ti contents. This size change is estimated to be complete at a Ti content of ~ 60 at. %, where δ and ε solid solutions would have approximately identical atomic volumes.

3.2. ε-Pu(Ti) solid solution

According to the data in Table I, ε is retained in alloys of Pu with 20 to 45 at. % Ti (see Fig. 1b). These ε-alloys show the expected reduction in cell size with increasing Ti content, and evidenced no decomposition of the ε-phase over periods as long as 2 weeks. At 15 at. % Ti, ε was not found. From the data it seems very probable that ε could also be retained beyond 45 at. % Ti and that ε-Pu(Ti) would be connected in a metastable solid solution range with the isostructural β-Ti(Pu) solid solution [1]; however, the higher melting points made it impossible at present to quench alloys with > 45 at. % Ti owing to alloy reaction with the crucible and other experimental difficulties. In any case, the object of the work was the retention of ε in the Pu-rich region of the diagram rather than the formation of the complete solid solution series.

The lattice parameters of ε (Table I) vary monotonically and the mean atomic volumes are plotted against composition in Fig. 2. It is shown that the values for alloys with 25 to 45 at. % Pu follow a straight line that extrapolates to the value for β-Ti, which was determined at 20°C from measurements on retained metastable β-Ti

TABLE II Extrapolated lattice parameter (a_0) and mean atomic volume ($\bar{V}$) data derived from metastable δ-Pu(Ti) and ε-Pu(Ti) solid solutions at room temperature

Phase	Pu		Ti	
	a_0 (Å)	$\bar{V}$(Å^3)	a_0 (Å)	$\bar{V}$(Å^3)
fcc	4.64 (δ)	25.0 (δ)	~ 3.91*	~ 15*†
	4.642 (δ)‡	25.0 (δ)‡		
bcc	3.53_0 (ε)	22.0 (ε)	3.279 (β)	17.65 (β)†
	(+ 0.005, − 0.038)§	(+ 0.1, − 0.7)§		

*Ti (Cu-Al type).

†Compare with $\bar{V}$(α-Ti) = 17.65 (Å^3) [18] and $\bar{V}$(β-Ti) (RT) = 17.65 (Å^3) [14].

‡Ref. 13.

§Uncertainty limits.

solid solutions [14]. The value for Pu-20 at. % Ti lies below this line; however, it was derived from a two-phase alloy with δ which possibly contains ε with ~ 22 at. % Ti. The best extrapolation to pure ε-Pu ignores this value, since the lattice parameters of ε solid solutions at high temperature [3] fall on straight or, at most, only slightly curved lines.

The high-temperature data are important because they justify the atomic volume extrapolation to ε-Pu over a range of 20 to 25 at. %. In contrast to the behaviour of the ε data, retrograde lattice parameter curves have been observed for δ solid solutions at high temperature [3]; however, plots for δ at room temperature, such as for δ-Pu(Ga) [13], are linear. This indicates that the apparent valence change with composition causing the retrograde behaviour of the atomic volume versus composition curve of δ is limited to high temperatures. At room temperature, an anomalous atomic volume curve for ε would thus be very unlikely, and the present linear extrapolation seems justified. The mean atomic volume of ε can be expressed as

$$\bar{V}[\epsilon\text{-Pu(Ti)}] = 22.0 - 0.0435\,(\text{at. \% Ti})\,. \quad (1)$$

4. Discussion

Besides the retention of an ε-Pu solid solution, an important result of this study is the extrapolated room temperature lattice parameter value $a_0(\epsilon\text{-Pu}) = 3.53_0$Å given in Table II. Other dimensional parameters derived from this value are compared with high-temperature (HT) data and extrapolated low-temperature (LT) data on ε(Pu) in Table III. In the following, the properties of ε will be discussed briefly.

Comparison of $\bar{V}[\epsilon(\text{LT})] = 22.0(\text{Å}^3)$ with $\bar{V}(\alpha\text{-Pu}) = 20.10(\text{Å}^3)$ [1] shows a volume increase for α → ε of 9.4%, far larger than is usual for the common transition to an isovalent. W-A2 type high-temperature phase (± 2%) [15]. This large value shows that the assumption [16] of a valence decrease of Pu on going from α to ε is also true if the transition takes place at room temperature. Furthermore, the rather low value of $a_0[\epsilon(\text{LT})]$ is of special interest (see Table III). The data given for the lattice parameters of ε(HT) at 20 and 500° C were calculated from a formula [2] valid between 490 and 550° C:

$$a_0(\epsilon) = 3.63479 + 13.25 \times 10^{-5}\,(T\text{-}480)\,. \quad (2)$$

The twelve-fold radii given in Table III for those two temperatures are identical with those derived by Zachariasen and Ellinger [16] for 20 and 450° C, respectively, using the same extrapolation. For the temperature interval 20 to 500° C, the thermal lattice parameter contraction is, therefore, $\Delta a_\epsilon(\text{thermal}) \approx 0.063$Å, while the contraction on going from ε(HT) at 500° C to ε(LT) at 20° C (derived from Pu(Ti) alloys) is Δa_ϵ (total) = 0.107Å. Thus, only ~ 60% of the contraction is due to isovalent thermal expansion, the remaining ~ 40% must be due to an electronic transition occurring in this temperature interval. Strictly speaking, the extrapolated binary room temperature modification ε-Pu(Ti) would then really be a separate modification ε(LT) of Pu, isostructural with ε(HT) but with a lattice parameter smaller by ~ 1.25% at room temperature.

Although lattice parameter extrapolations over large temperature ranges are generally not reliable, we feel that the high quality of the data [2] used in deriving Equation 2 justifies the extrapolation used here; furthermore, the inclusion of data on the ε-Pu(Ti) alloys with 20 at. % Ti would tend rather to decrease than to increase $a_0[\epsilon(\text{LT})]$ and will thus increase the portion of the contraction due to the electronic transition.

TABLE III Comparison of dimensional properties of Pu in the W-A2 type modification

Phase	T(°C)	a_0 (Å)	r_8 (Å)	r_{12} (Å)	$\bar{V}$(Å^3)	$\bar{\alpha} \cdot 10^6$ (°C^{-1})	ρ(g cm^{-3})
ε(HT)	500	3.637_3	1.575	1.622	24.06	36.5	16.49
ε(HT)	20	3.574*	1.548	1.594	22.83	(36.5)†	17.38
ε(LT)	20	2.53_0‡	1.52_8	1.57_4	22.0	§	18.03

*Extrapolated from 500°C

†Assumed for extrapolation.

‡Extrapolated from ε-Pu(Ti) alloys.

§True value not known; the mean calculated value for the temperature interval 20 to 500°C is 63.7×10^{-6}.

Nonetheless, to be accepted, the interpretation suggested here must be confirmed by additional data, such as might be obtained by a direct measurement of the coefficient of thermal expansion of ε-Pu(Ti) and from an improved volume-composition extrapolation.

The twelve-fold metallic radius r_{12} [(εLT)] = 1.57_4Å is closer to the average metallic radius $r_{12}(\alpha) = 1.58$Å [16] than to $r_{12}[\epsilon(\mathrm{HT})]_{\mathrm{RT}} = 1.594$Å. A better picture of the crystal-chemical relationships is probably given by a comparison of the mean atomic volumes [15], which gives volume expansions

$$\bar{V}(\alpha)_{20} \xrightarrow{9.4\%} \bar{V}[\epsilon(\mathrm{LT})]_{20} \xrightarrow{3.6\%} \bar{V}[\epsilon(\mathrm{HT})]_{20}$$

placing ε(LT) nearer to ε(HT) than to α at 20°C.

We do not consider the involved question [17] of the sizes and metallic valences for the Pu modifications here, except for one comment. Using the valence assignment [17] $n(\alpha) = 5.4$ and $n(\delta) = 4.8$ and interpolating the mean atomic volumes, we find the valences of ε to be

$$n[\epsilon(\mathrm{LT})] \approx 5.1; \; n[\epsilon(\mathrm{HT})_{20}] \approx 5.0 .$$

Using other assignments, and evaluating radii instead of volumes, yields approximately the same valence difference of ≈ 0.1 between the two forms of ε.

It is likely that ε could be retained by rapid quenching in alloys from other binary Pu systems with an extended equilibrium high-temperature ε-solid solution range, and experiments to do so are in progress.

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