Behavior of Some Delta-Stabilized Plutonium Alloys at High Pressures*

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Abstract

Delta-phase, Pu-rich, binary alloys containing Al, Zn, In, and Ce were observed at pressures up to 11,000 atm at 24 ± 1°C. Some of these alloys transformed under compression, and their transformation pressures and volumes, densities, compressibilities, and hardnesses were determined as a function of composition. The natures of the observed high-pressure transformations are discussed and related to their respective binary alloy phase diagrams with plutonium.

Introduction

Bridgman[1] did the first work (in 1945) toward determining the effects of high pressures on pure plutonium and plutonium alloys. Recently, his data on pure plutonium were declassified and published in an unclassified journal.[2] Nothing more was done with plutonium in this field until 1956, when Hughes[3] made a study of two delta-stabilized plutonium alloys at high pressures. His results were incomplete, and so a number of additional delta-stabilized Pu-rich binary alloys were investigated at high pressures by the authors, and the results reported here.

The high-temperature, delta allotrope of plutonium can be easily retained to room temperature by the proper combination of alloying and heat treating. Alloys of this type are generally referred to as delta-stabilized alloys although the delta phase in many such alloys is actually metastable and will transform to a more stable state when the

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alloy is thermally treated or compressed. A number of delta-stabilized alloys containing Al, Zn, In, and Ce were observed at pressures up to 11,000 atm. Many of these alloys transformed under compression and their transformation pressures and volumes, compressibilities, densities, and hardnesses were determined as a function of composition. Other plutonium alloys containing Cu, Ge, Cd, and Sn were prepared, but no delta phase was found in any of these systems at room temperature.

The main objective of the present investigation was to examine the behavior of delta-phase alloys at high pressures in order to obtain new data to aid in the theoretical explanation of the anomalous properties of delta plutonium. A secondary objective was to determine the effects of these alloying elements on the stabilization of delta phase, and to correlate the results with the respective binary Pu-rich phase diagrams.

Experimental

Specimen Preparation

The alloys were made by melting and casting weighed amounts of the component metals *in vacuo* in an induction furnace to form ingots about 0.5 in. OD by 1.75 in. long. These ingots were homogenized at 450°C for at least 200 hr, air-quenched to room temperature, and, finally, machined to right cylinders 0.434 in. diam and 1.5 to 1.7 in. long. All alloy compositions given in this paper are nominal except those of the Pu-Zn alloys, which are analyzed compositions.

Procedure

The specimens were examined using metallographic and x-ray diffraction methods both before and after compression. The densities of these alloys were also measured before and after a run.† Several of the alloy specimens were found to be cored or inhomogeneous. These specimens were heat-treated for an additional 200–400 hr at 450°C.

The alloys were subjected to high pressures in the simple piston and cylinder device shown in Figure 1. The stationary piston is placed in one end of the high-pressure cylinder, and the specimen,

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† Precision of density measurements is ±0.03 g/cu cm.

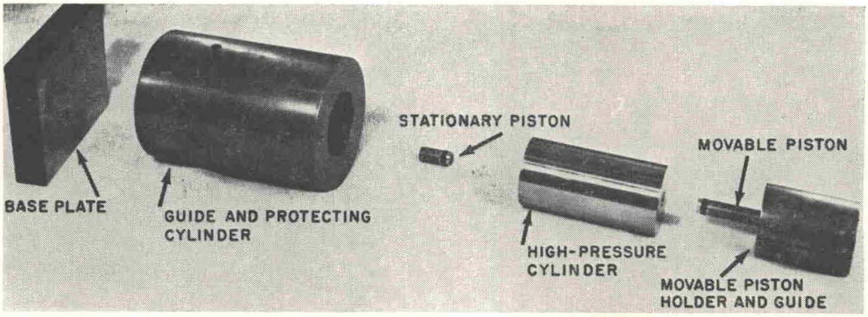

Fig. 1. Exploded view of 10 kbar high-pressure chamber.

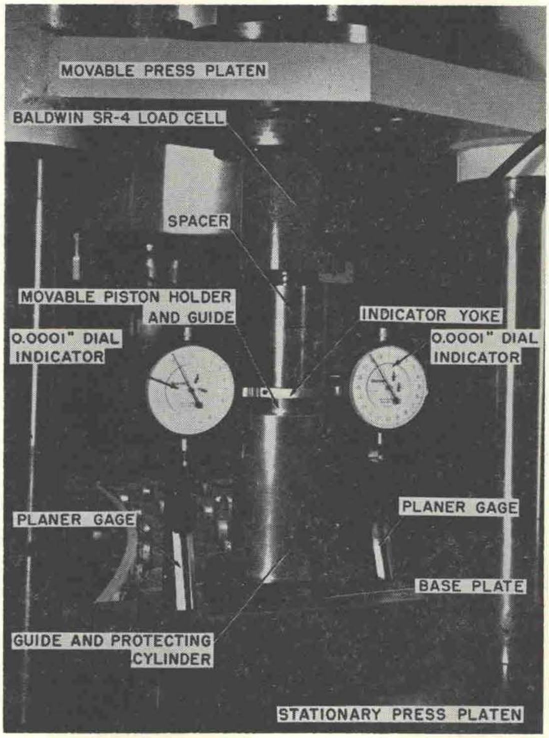

Fig. 2. Photograph of 10 kbar high-pressure apparatus.

TABLE I

Summary of Data on Delta-Stabilized Pu-Rich Binary Alloys at High Pressures

System	Composition	Max. press. (atm)	Transformation press. (atm)	Transformation vol. $\Delta V/V_0$ (%)	Permanent vol. change[a] $\Delta V/V_0$ (%)	Compressibility ($\times 10^6$/atm)	Density	
							Before compression (g/cu cm)	After compression (g/cu cm)
Pu-Al	1.7 a/o Al	8,880	2040	16.0	16.0	4.1	15.73	18.67
	2.5 a/o Al	8,920	4340	11.8	10.9	3.8	15.66	17.70
	3.4 a/o Al	8,920	7020	6.8	6.7	4.0	15.60	16.71
	4.0 a/o Al	10,060	N.T.[b]	—	—	3.4	15.50	15.49
	5.0 a/o Al	8,670	N.T.[b]	—	—	4.5	15.31	15.26
	7.5 a/o Al	8,470	N.T.[b]	—	—	3.9	15.38	15.48
	10.0 a/o Al	8,670	N.T.[b]	—	—	3.4	15.04	15.07
	12.5 a/o Al	8,670	N.T.[b]	—	—	3.1	14.87	14.87
Pu-Zn	1.51 a/o Zn	10,000	1200	17.3	17.1	4.7	15.94	19.08
	1.79 a/o Zn	9,250	950	16.7	16.6	2.4	15.85	19.08
	2.16 a/o Zn	9,250	2520	16.2	15.7	2.0	15.75	19.08
	2.92 a/o Zn	9,100	4210	15.3	14.8	3.8	15.71	18.53
	3.35 a/o Zn	9,880	5290	15.8	15.3	4.0	15.70	18.29
	3.89 a/o Zn	9,250	6650	13.8	12.4	3.2	15.64	17.82

Pu-In	3.4 a/o In	9,100	1520	13.1	12.4	2.5	15.56	17.83
Pu-Ce	3.4 a/o Ce	10,600	I. ≤ 60	≥ 8.6	—	—	15.63	—
	3.4 a/o Ce	10,600	II. 3000	9.1	16.3	—	—	18.76
	4.0 a/o Ce	9,880	I. 500	8.4	—	I. 1.9	15.56	—
	4.0 a/o Ce	9,880	II. 4380	8.3	15.5	II. 4.2	—	18.55
	5.0 a/o Ce	9,250	I. 1460	7.9	—	I. 1.9	15.46	—
	5.0 a/o Ce	9,250	II. 6470	7.8	15.8	—	—	18.02
	6.0 a/o Ce	11,000	I. 1920	7.8	—	I. 3.0	15.31	—
	6.0 a/o Ce	11,000	II. 8220	6.2	14.6	II. 6.0	—	17.86
	8.0 a/o Ce	10,000	I. 3230	6.9	—	I. 5.4	15.13	15.16
	8.0 a/o Ce	10,000	II. N.T.[b]	—	—	II. 6.5	—	—
	10.0 a/o Ce	10,000	I. 4400	5.7	—	I. 8.4	14.96	14.93
	10.0 a/o Ce	10,000	II. N.T.[b]	—	—	II. 6.8	—	—

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[a] Values obtained by extrapolation of pressure-volume curves.

[b] N.T. means no transformation.

glycerine, and movable piston are inserted at the opposite end. This assembly is then fitted into the guide and protecting cylinder. Dial indicators, which measure linear displacement of the movable piston, are attached to the piston holder and guide.

The apparatus* is shown assembled in Figure 2. Force is applied to the movable piston by means of a 50-ton press, and the resulting pressure within the high-pressure cylinder is transmitted hydraulically to the specimen by the glycerine. This liquid was used because it does not react with plutonium and because it is relatively incompressible. A Baldwin SR-4 load cell, calibrated for pressure measurement at the solidification point of mercury, 8850 atm and 7.5°C, was used to measure the pressures.† Dial indicators located on opposite sides of the cylinder measure linear displacement of the movable piston. Volume changes in the specimen, however, cannot be calculated directly from the dial indicator readings because the glycerine compresses, the cylinder expands, and the pistons shorten as the pressure increases. Corrections for the compression of the glycerine were made from values published by Bridgman,[4] and for the dimensional changes of the cylinder and pistons from calculations based on elastic theory. The volume measurements were checked with an aluminum standard.‡ All measurements were taken at 24 ± 1°C unless otherwise noted.

Results and Discussion

The results obtained with delta-stabilized Pu-rich binary alloys containing Al, Zn, In, and Ce are summarized in Table I. Transformation pressures listed in this table were obtained by extrapolating the pressure-volume curves at the transformation breaks; volumes of transformation are the percentage volume changes at the pressures of transformation; and permanent volume changes are the percentage volume changes of the alloy after compression and return to ambient pressure. Most of the values given in Table I are mean values.

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* The maximum pressure to which the apparatus can be repeatedly subjected is about 10,000 atm; slightly higher pressures can be attained but only at the expense of great reduction in the life of the high-pressure cylinder and pistons.

† Accuracy of pressure measurements is estimated to be ±200 atm.

‡ Accuracy in determining volume changes is estimated to be ±10% of the value reported.

Transformation Pressures and Volumes of Transformation

The compression curves of some of the Pu-Al alloys containing between 1.7 and 12.5 a/o Al are shown in Figure 3. Irreversible transformations occur in the 1.7, 2.5, and 3.4 a/o Al alloys but no transformations were observed in the alloys containing from 4.0 to 12.5 a/o Al when compressed at pressures up to 10,060 atm. The transformations in the three alloys mentioned above result from changes of the metastable delta phase into either alpha phase or a mixture of alpha and beta phases plus some untransformed delta. Figure 4 shows that the transformation pressures and volumes of transformation of these Pu-Al alloys vary linearly with atom per cent aluminum over the range of experimental measurements. The linear extrapolation to zero transformation pressure is interpreted as determining the minimum amount of aluminum, 1 a/o, required to retain delta phase at room temperature with the heat treatment being used. In order to verify this assumption, two alloys containing 0.8 and 1.2 a/o Al were heat-

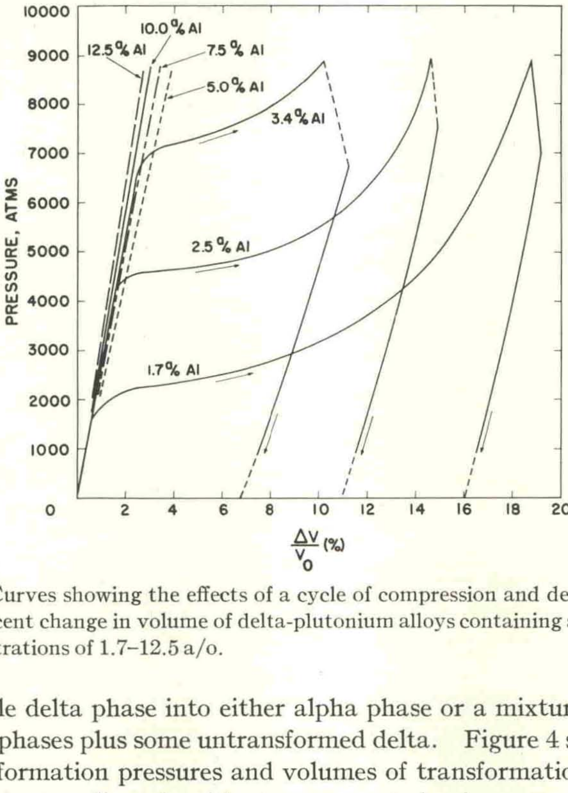

Fig. 3. Curves showing the effects of a cycle of compression and decompression on the per cent change in volume of delta-plutonium alloys containing aluminum in the concentrations of 1.7–12.5 a/o.

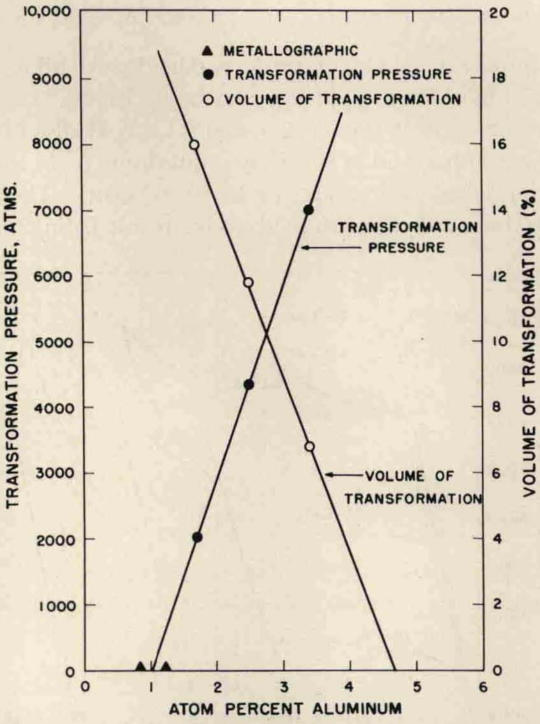

Fig. 4. Curves showing the effect of aluminum content on the pressure necessary to cause plutonium-aluminum alloys to transform from delta to lower allotropes and on the per cent change in volume associated with the transformation.

treated and examined. Upon examination, the 0.8 a/o Al alloy was found to consist mostly of alpha phase plus some beta and gamma phases and had a density of 17.7 g/cu cm. On the other hand, the 1.2 a/o Al alloy consisted of delta phase and had a density of 15.7 g/cu cm. Thus, this simple experiment provided additional justification for the meaning ascribed to the extrapolated composition at zero transformation pressure.

The compression curves of some of the Pu-Zn delta-stabilized alloys containing between 1.8 and 3.9 a/o Zn are shown in Figure 5. All of the metastable delta-phase Pu-Zn alloys transformed under compression. Their microstructures after compression showed them to be composed predominantly of alpha phase with traces of beta and usually some untransformed delta. Traces of the intermetallic

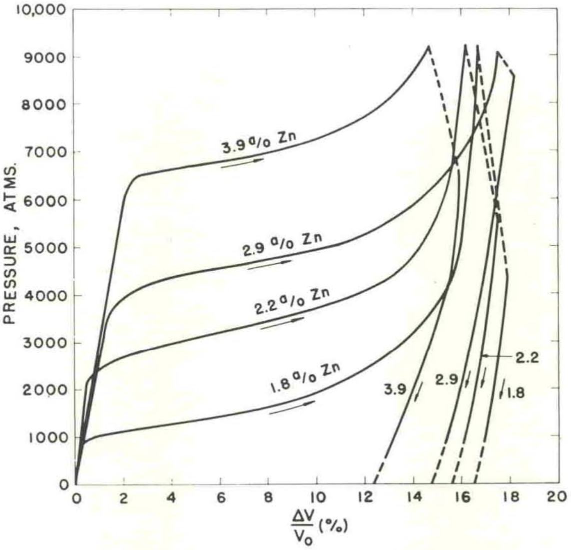

Fig. 5. Curves showing the effects of a cycle of compression and decompression on the per cent change in volume of delta-plutonium alloys containing zinc in the concentrations of 1.8–3.9 a/o. All of these alloys transform, at least partially, from delta to lower allotropes.

compound, $PuZn_2$, were also seen in the microstructures, but there was no definite evidence that the amount of this phase increased after transformation. Figure 6 shows the transformation pressures and volumes of transformation of the Pu-Zn alloys plotted against atom per cent zinc. Again, these transformation pressures and volumes are seen to vary linearly with zinc content over the range of the experimental measurements, and extrapolation shows that the zero transformation pressure occurs at about 1 a/o Zn. It is expected that the transformation pressure will increase linearly with atom per cent zinc up to the limit of solid solubility of zinc in delta plutonium. The transformation pressure should then remain constant with increasing zinc content throughout the two-phase region, delta plus $PuZn_2$.

The compression curve of a delta-stabilized Pu-In alloy, containing 3.4 a/o In, is not illustrated, but it is similar in appearance to the curve of the 1.7 a/o Al alloy shown in Figure 3. This metastable delta phase Pu-In alloy transformed at 1520 atm, and the transformation

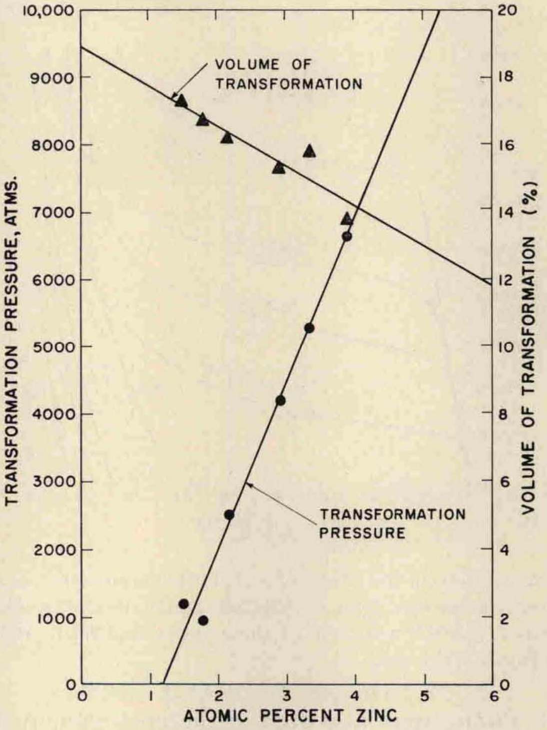

Fig. 6. Curves showing the effect of zinc content on the pressure necessary to cause plutonium-zinc alloys to transform from delta to lower allotropes and on the per cent change in volume associated with the transformation.

was found to result from the irreversible change of delta into a mixture of alpha plus delta. Experiments were also made on other Pu-In alloys containing more than 3.4 a/o In, but the results are not meaningful because the alloys were inhomogeneous.

Figure 7 shows the compression curves of some of the Pu-Ce delta-stabilized alloys containing between 3.4 and 6.0 a/o Ce. Note that these alloys undergo double transformations under compression. The transformation pressures and volumes of transformation of the Pu-Ce alloys are shown in Figures 8 and 9, respectively, plotted against atom per cent cerium. Extrapolations show that zero transformation pressures occur at 3.4 a/o Ce for the lower pressure transition, and at 1.9 a/o Ce for the higher pressure transition. When a

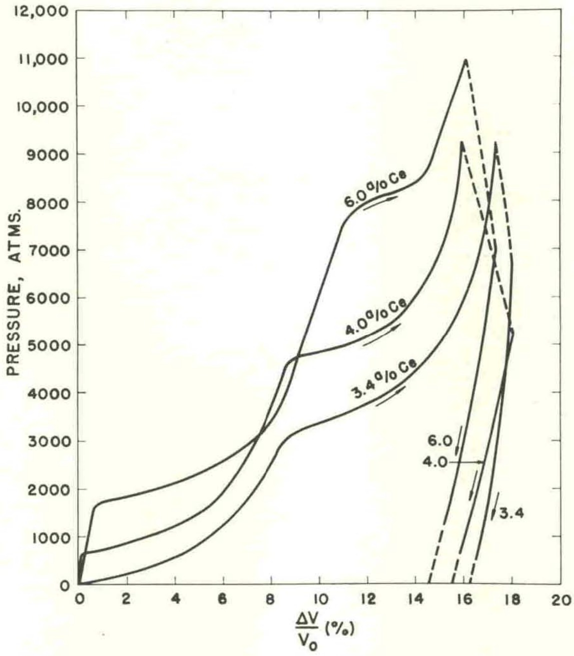

Fig. 7. Curves showing the effect of a cycle of compression and decompression on the per cent change in volume of delta-plutonium alloys containing cerium in the concentrations of 3.4–6.0 a/o.

plutonium alloy containing between 1.9 and 3.4 a/o Ce is heat-treated at 450°C and air-quenched, it should consist mostly of beta phase. The minimum amount of cerium required to retain delta phase at room temperature with the heat treatment being used is 3.4 a/o Ce.

Compression curves of delta-stabilized alloys containing 4.0, 6.0, and 10.0 a/o Ce are shown in Figure 10. These alloys were compressed through the lower pressure transformation only to maximum pressures of either 10,000 or 1000 atm less than that required to attain the higher pressure transformation, whichever was lower. This figure shows that the transformations are irreversible in the 4.0 a/o Ce alloy, partly reversible in the 6.0 a/o Ce alloy, and completely reversible in the 10.0 a/o Ce alloy. Note that the extent of reversibility increases with increasing cerium content in these alloys. The trans-

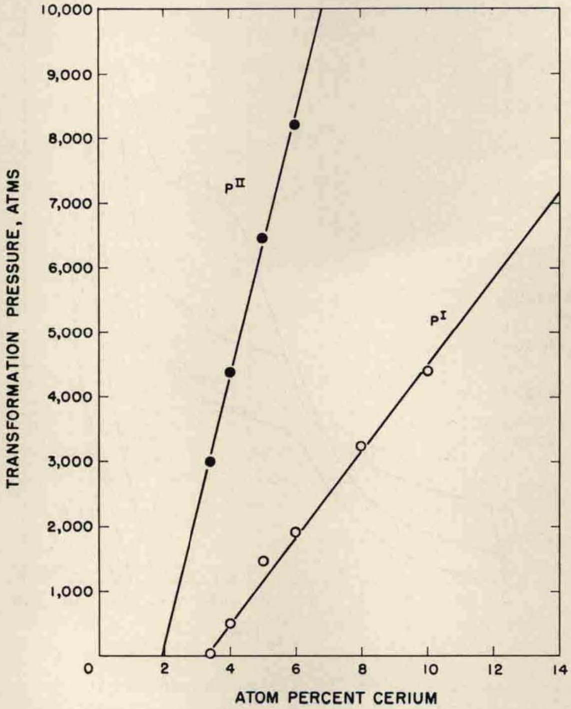

Fig. 8. Curves showing the effect of cerium content on the pressure, P^{I}, necessary to cause plutonium-cerium alloys to transform almost completely from delta to beta (plus some gamma) and on the pressure, P^{II}, necessary to cause the alloys to transform from beta (plus some gamma and residual delta) to alpha.

formation becomes completely reversible in the alloys containing more than 7.1 a/o Ce. This irreversible transformation was found to be caused by a change of the metastable delta phase into mostly beta phase plus small amounts of gamma and some untransformed delta, the amount of untransformed delta increasing with increasing cerium content. The transformation occurs rapidly at room temperature and the beta-phase microstructure in the alloy containing 4 a/o Ce resembled that of a diffusionless, martensitic transition. This high-pressure treatment can thus be used to retain beta-phase plutonium that is free of voids and microcracks at room temperature.

The second, higher pressure transformations are irreversible (see Fig. 7) and result from the change from beta to alpha. The alloys,

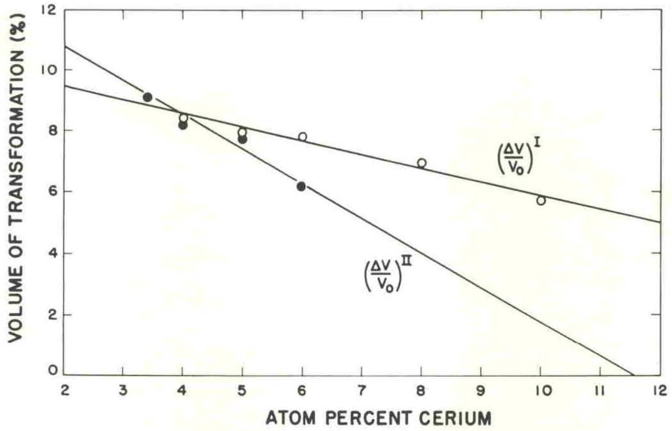

Fig. 9. Curves showing the effect of cerium content on the per cent changes in volume $(\Delta V/V_0)^{I}$ and $(\Delta V/V_0)^{II}$ associated with the transformation pressures P^{I} and P^{II} of Figure 8.

after compression through the second transition, consist mostly of alpha phase essentially free of the microcracks and voids usually found in slowly cooled Pu-rich, alpha-phase alloys.

Densities

Densities plotted against atom per cent aluminum, zinc, and cerium are shown in Figures 11(*a*), 11(*b*), and 11(*c*), respectively. The curves show the densities of the heat-treated alloys before and after compression.

In the case of the Pu-Al alloys, these density curves intersect at 4.5 a/o Al [see Fig. 11(*a*)], and this intersection is interpreted to be the composition below which delta-phase alloys are metastable at room temperature and hence will transform irreversibly under compression. The data given in this paper do not show a transformation in an alloy containing 4 a/o Al, but this alloy should transform at pressures greater than the maximum pressure to which it was subjected, 10,060 atm. Delta-phase alloys containing more than 4.5 a/o Al are thermodynamically stable at room temperature, according to this viewpoint, and although no transformations were observed in alloys containing between 4.0 and 12.5 a/o Al, it is expected that these will also transform at pressures greater than 10,200 atm (see

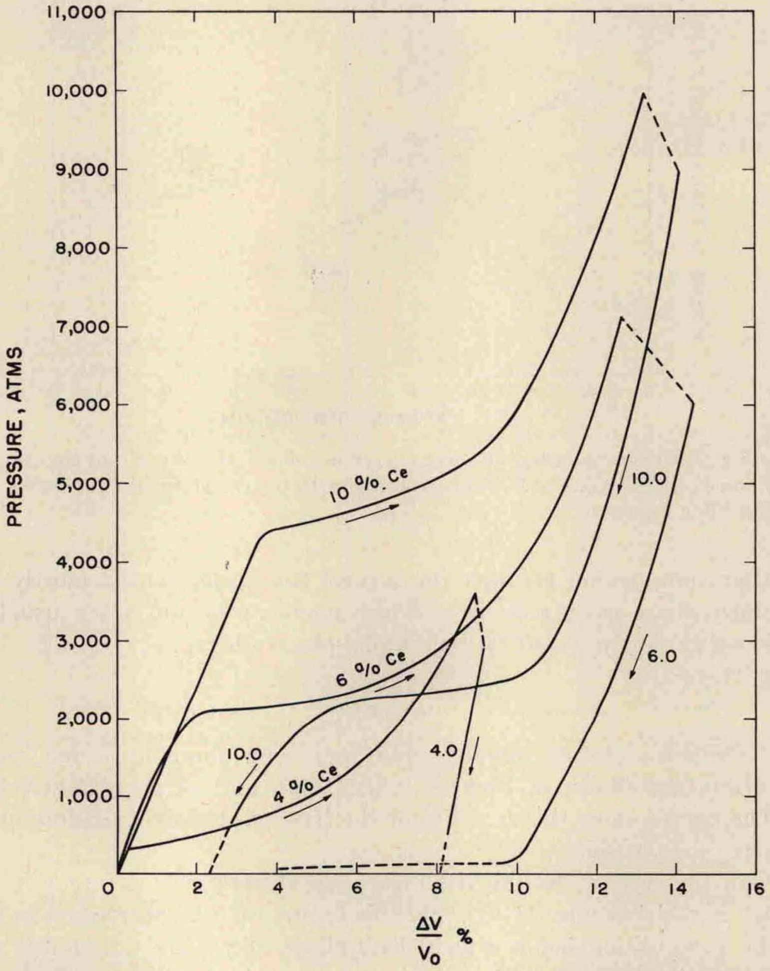

Fig. 10. Curves showing the effects of a cycle of compression and decompression on the per cent change in volume associated with the lower pressure transformation of delta-plutonium alloys containing 4.0, 6.0, or 10.0 a/o cerium.

Table II) but that the transformations will be of the completely reversible type.

Figure 11(*b*) shows that all of the delta-stabilized Pu-Zn alloys studied transformed irreversibly at pressures below 10,000 atm. Extrapolations of the before compression and after compression

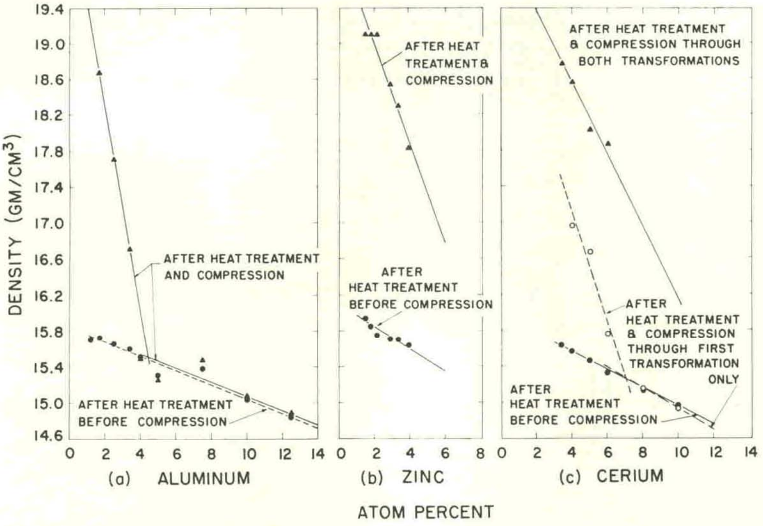

Fig. 11. The effects of composition and of compression on the density of alloys of plutonium delta-stabilized with (*a*) aluminum, (*b*) zinc, and (*c*) cerium.

curves for these alloys intersect at about 9.3 a/o Zn (see discussion on phase diagrams).

Density versus composition curves for both transformations in Pu-Ce alloys are shown in Figure 11(*c*). The intersection of the after compression curves for the lower pressure transformation occurs at 7.1 a/o Ce. Delta-stabilized alloys containing less than this amount of cerium are metastable and transform irreversibly (under compression) into mostly beta phase, while delta-stabilized alloys containing more than 7.1 a/o Ce are thermodynamically stable at room temperature and undergo completely reversible delta-to-beta transformations. Intersection of the extrapolations of the before compression and after compression curves for the higher pressure transformation occurs at 16.3 a/o Ce. Delta-stabilized alloys containing from 3.4 to 6.0 a/o Ce transformed from delta to beta and from beta to alpha on increasing pressure, and these transformations did not reverse when the pressure was reduced. It is expected that all delta-stabilized alloys containing less than 16.3 a/o Ce will behave in a similar manner with the beta-to-alpha transformation becoming more completely reversible with increasing cerium content. Therefore, it is believed that delta-stabilized alloys containing more than 16.3 a/o Ce will transform from delta to beta and from beta to alpha when pressure is increased, and from alpha to beta and from beta to delta when pressure is decreased; i.e., both transformations are completely reversible. Data on these reversible transformations at high pressures are summarized in Table II. The reversible transformation pressures were obtained by extrapolating or interpolating the transformation pressure versus composition curves (Figs. 4 and 8) to the critical compositions listed in Table II.

TABLE II
Equilibrium Transformation Data for Pu-Rich Pu-Al and Pu-Ce Alloys at High Pressures

Critical composition	Transformation (reversible)	Transformation pressure (atm)
4.5 a/o Al	$\delta \rightarrow \alpha$	10,200
7.1 a/o Ce	$\delta \rightarrow \beta$	3,800
16.3 a/o Ce	$\beta \rightarrow \alpha$	29,500

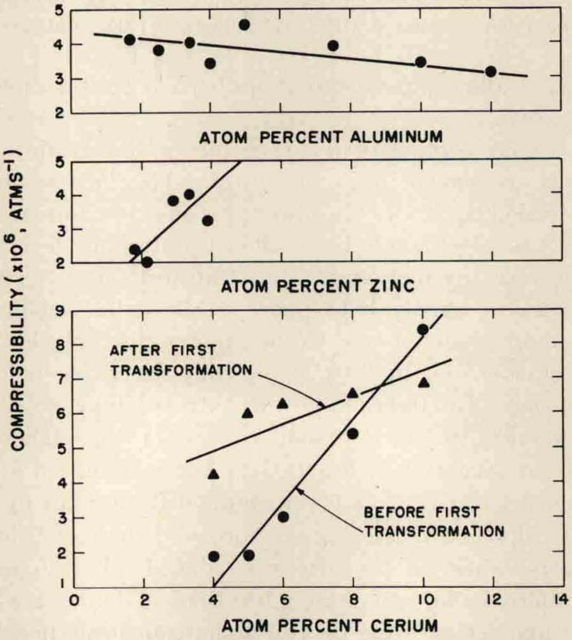

Fig. 12. The effects of aluminum, zinc, and cerium, respectively, on the compressibility of delta plutonium.

Compressibilities and Hardnesses

The compressibilities plotted against composition of delta-stabilized Pu-Al, Pu-Zn, and Pu-Ce alloys below their transformation pressures and of beta-phase Pu-Ce alloys between the first and second transformations are shown in Figure 12. Compressibilities of the Pu-Al alloys decrease linearly with increasing aluminum content at the approximate rate of 0.1×10^{-6}/atm/atom per cent, and the compressibilities of the Pu-Zn, delta-phase Pu-Ce, and beta-phase Pu-Ce alloys increase linearly with increasing zinc or cerium content at the approximate rates of 0.6, 1.1, and 0.3×10^{-6}/atm/atom per cent, respectively. The values of compressibilities are probably accurate to only ±25% of the value reported.

Figure 13 shows the variation of hardness as a function of composition in these alloys. The hardnesses can be increased and controlled

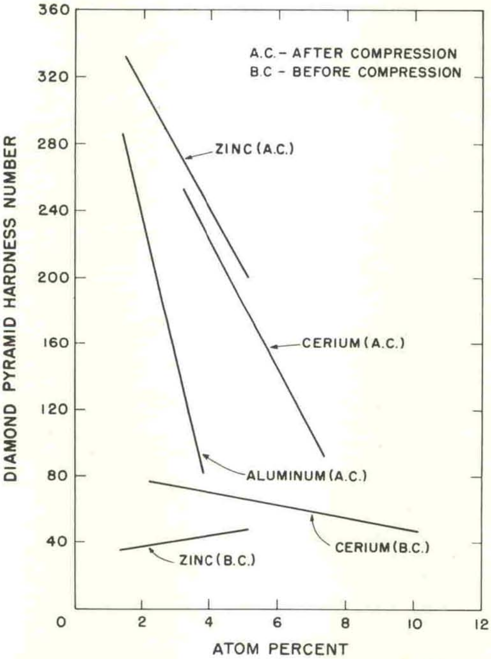

Fig. 13. The effects of concentration of alloying elements (aluminum, cerium, and zinc) and of pressures up to about 10,000 atm on the hardness of delta-stabilized plutonium alloys.

over a limited range by selecting the proper combination of alloying element and pressure. Also, less aluminum than either zinc or cerium is required in order to change the hardness by a given amount.

Phase Diagrams

Effects of pressure on metastable, single-phase, binary alloys do not appear to have been determined previously. Some interesting correlations between the behaviors of such alloys under pressure and their respective phase diagrams can be inferred from the results of this study. The Pu-rich portion of the Pu-Al,[5] Pu-Zn,[6] and Pu-Ce[7] phase diagrams are shown in Figures 14(*a*), 14(*b*), and 14(*c*), respectively.

The intersection of the Pu-Al density curves at 4.5 a/o Al, referred to earlier in this paper, can be extrapolated to atmospheric pressure by assuming that this composition does not vary with pressure. This composition is then interpreted to be on the alpha plus delta/delta solvus phase boundary at room temperature [see Fig. 14(*a*)]. This value, 4.5 a/o Al, is intermediate between the reported values of 2.0 ± 0.2 a/o Al[8] and about 8 or 9 a/o Al,[5] but these results are in disagreement with another version of the Pu-Al diagram.[9] This latter version shows a eutectoidal decomposition of delta phase into beta phase plus Pu_3Al at about 175°C, and on cooling to room temperature alpha phase plus Pu_3Al become the equilibrium state of such decomposed alloys.[9] No evidence was found during the present study to substantiate this type of Pu-Al diagram. The metastable delta Pu-Al alloys transformed under pressure into either alpha or mixtures of alpha plus beta with some untransformed delta, and at no time was $PuAl_3$ identified in any of the alloys by microscopic or x-ray methods, either before or after compression.

The intersection of the Pu-Ce density curves at 7.1 a/o Ce can also be extrapolated to atmospheric pressure in the same way as described above for the Pu-Al alloys. Again, this composition represents the beta plus delta/delta solvus phase boundary, and it agrees reasonably well with the value of 5 a/o Ce, obtained by extrapolation of high-temperature x-ray and metallographic data[7] [see Figure 14(*c*)].

One of the authors (K. A. G.) has calculated that pure delta plutonium will transform to either gamma or delta prime at 1300 atm and at elevated temperatures; i.e., at pressures greater than 1300

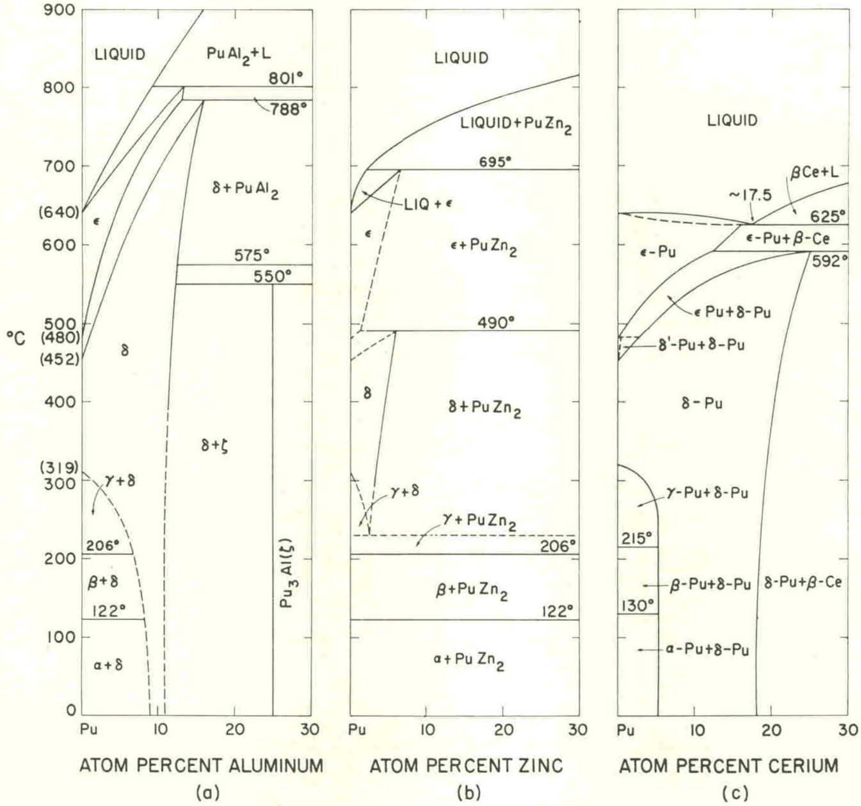

Fig. 14. Plutonium-rich regions of the (*a*) Pu-Al, (*b*) Pu-Zn, and (*c*) Pu-Ce phase diagrams.

atm *no* delta phase can be formed regardless of temperature. As can be seen in Table II, a delta-stabilized alloy containing 4.5 a/o Al should transform reversibly from delta to alpha at 10,200 atm and a delta-stabilized alloy containing 7.1 a/o Ce transforms reversibly from delta to beta at 3800 atm. These reversible transformation pressures increase with increasing alloying contents (see Fig. 8). Thus, the addition of aluminum or cerium has the effect of extending the delta-phase field with respect to pressure, similar to the effect produced by these alloy additions in extending the delta-phase field with respect to temperature [see Figs. 14(*a*) and 14(*c*)]. The stability of beta-phase

Pu-Ce alloys after compression suggests that cerium is probably more soluble in beta than in the gamma or alpha phases.

The Pu-Zn phase diagram shows a eutectoidal decomposition of delta phase into gamma phase plus $PuZn_2$ at about 235–243°C, and alpha phase plus $PuZn_2$ corresponds to the equilibrium state of decomposed alloys at room temperature[6] [see Fig. 14(*b*)]. Delta-stabilized Pu-Zn alloys are, therefore, actually metastable at room temperature and should transform under pressure to a more stable state. All delta-phase Pu-Zn alloys studied did transform under compression, substantially in agreement with this Pu-Zn phase diagram.

Acknowledgments

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