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THE THERMAL EXPANSION OF PuC AND UC-PuC SOLID SOLUTION

by

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ABSTRACT

Thermal expansion characteristics for arc melted plutonium-carbon alloys containing 41.1, 43.2, 44.9, 45.4, 45.8 a/o carbon and for $\text{U}_{0.87}\text{Pu}_{0.13}\text{C}$ have been determined between room temperature and 900°C . The average coefficients of linear thermal expansion for a single phase alloy containing 45.8 a/o carbon and for single phase $\text{U}_{0.87}\text{Pu}_{0.13}\text{C}$ are presented as well as results pertaining to the plutonium-carbon phase diagram. A mechanism has been suggested to explain the unusual contraction that was observed in the dilatometric curves for the alloys that contained 43.2, 44.9 and 45.4 a/o carbon.

INTRODUCTION

Plutonium-containing ceramics such as PuC* and UC-PuC solid solutions

*The term PuC is used throughout this paper to denote the carbon deficient plutonium monocarbide phase.

are being studied for possible use as fuels in nuclear reactors. A knowledge of the thermal expansion characteristics of these potential fuels is necessary for their successful application.

Several studies have been made of the thermal expansion behavior of plutonium carbides. In various plutonium-carbon alloys containing less than 46 a/o carbon, Pascard,¹ Kruger,² and Mulford, Ellinger, Hendrix and Albrecht,³ have all observed discontinuities in their dilatometric curves. Although there is general agreement on the dilatometric curves of plutonium carbides as a function of carbon content, there are large differences in the linear coefficients of thermal expansion as shown in Table 1. Using a different approach, Pallmer⁴ observed the change in lattice dimensions as a function of temperature of a mixture containing both PuC and Pu₂C₃. The coefficients of thermal expansion obtained in this manner are also shown in Table 1.

The coefficient of linear thermal expansion of UC has been reported in the range of $10.98 \times 10^{-6}/^{\circ}\text{C}$,⁵ to $11.5 \times 10^{-6}/^{\circ}\text{C}$.⁶ The thermal expansion curves, from which the coefficients were calculated, did not exhibit any evidence of a phase transformation.

At the present time the thermal expansion of UC-PuC solid solutions has not been reported in the literature.

Table 1

*The graph is in
Table 5*

This paper deals with the use of dilatometry to determine the linear thermal expansion coefficients of PuC and $U_{0.87}Pu_{0.13}C$ and to delineate roughly the (ξ +PuC)/PuC boundary of the plutonium-carbon phase diagram. (The terminology used in this report is the same as that used by Mulford, Ellinger, Hendrix and Albrecht.)³ Dilatometric curves for the plutonium alloys containing 41.1, 43.2, 44.9, 45.4, and 45.8 at/o carbon and for the $U_{0.87}Pu_{0.13}C$ solid solution are presented. Details of the investigation, including preparation of the samples, are described.

EXPERIMENTAL

All samples were prepared by arc melting together cylinders of plutonium metal and pieces of spectrographic grade graphite rod in a zirconium gettered helium-argon atmosphere. Clean uranium sheet was added to make the $U_{0.87}Pu_{0.13}C$ alloy specimen. To obtain reasonably homogeneous samples, the ingots were inverted and remelted at least six times and were held in the molten state for about 1 min during each melting cycle. The button, weighing approximately 75 grams, was arc cast into a graphite mold, at a current of 400 amperes, and was then homogenized by annealing in vacuum at 800°C or higher (see Table 2).

The arc furnace was equipped with interchangeable water-cooled copper hearths. The casting hearth resembled that used by Secrest, Foster and Dickerson⁷ and contained a gap between the graphite mold and the water-

Table 1
 LINEAR COEFFICIENTS OF THERMAL EXPANSION
 α ($10^{-6}/^{\circ}\text{C}$)

	<u>Pascard</u>	<u>Kruger</u>	<u>Pallmer</u>
Zeta	40		
PuC	28		10.8
PuC + Pu ₂ C ₃	17	10.6	
Pu ₂ C ₃			14.8

cooled copper hearth which was evacuated to reduce the rate of cooling of the casting. Cylindrical specimens, 1 in. long by 0.250 in. in diameter were fabricated by grinding the annealed castings with silicon carbide grinding wheels. The grinding was done in a helium-filled glove box, on a lathe equipped with a tool-post grinder. Both dry grinding and wet grinding, with "Freon TF" as the coolant, were used.

Samples of the annealed castings were analyzed by x-ray diffraction and chemical methods, and the results are listed in Table 2.

Table 2 →

The dilatometer used in this work was essentially that described by Elliott and Miner,⁸ except that in some of the experiments a dial gauge, rather than strain gauges, was used as the length-sensing device. Specimens were heated from room temperature to about 900°C at approximately 2°C/min. Cooling from 900°C was accomplished in two ways: (1) by cooling slowly at approximately 2°C/min or (2) by shutting off the furnace power and opening the furnace to expose the dilatometer tube to room temperature to cool the specimen rapidly.

RESULTS AND DISCUSSION

The dilatometric curves for the plutonium alloy containing 45.8 a/o carbon showed no evidence for a phase change during heating from 25° to 900°C (Fig. 1). The linear thermal expansion of this specimen (45.8 a/o carbon) can be expressed by the equation

$$\Delta l_{25-900^\circ\text{C}} = l(-4.0 \times 10^{-4} + 8.3 \times 10^{-6}t + 3.0 \times 10^{-9}t^2).$$

Table 2
ANALYSIS OF PLUTONIUM CARBIDES

Analyzed Composition a/o Carbon	Lattice Dimension a_0 , Å	Annealing Conditions	
		Temperature, °C	Time, hr
41.1	4.968 ^a	800	41 ^b
43.2	4.964 ^a	915	66 ^b
44.9	4.968 ^a	925	48 ^b
45.4	4.959	None	
45.8	4.968	1300	2.5

^aContained an unidentified second phase

^bSlowly cooled

The average coefficient of linear thermal expansion between room temperature and 900°C is $11.0 \times 10^{-6}/^{\circ}\text{C}$. This value compares quite well with the $10.8 \times 10^{-6}/^{\circ}\text{C}$ obtained by Pallmer,⁴ who used x-ray diffraction methods. The composition, however, of the PuC phase that Pallmer studied was not reported but may have been approximately 48 a/o carbon (determined from the phase diagram of Mulford, Ellinger, Hendrix and Albrecht).³ As shown in Table 2, x-ray diffraction analysis detected only single phase PuC in this alloy. Examination of its microstructure (Fig. 2) also indicated that this annealed specimen consisted of a single phase PuC of large grain size.

Fig 1 & Fig 2

Two types of dilatometric curves were obtained on alloys containing 43.2, 44.9, and 45.4 a/o carbon, depending on the heat treatment given the specimen prior to the dilatometric measurements. If the specimen had previously been heated at 900°C and then rapidly cooled to room temperature, an unusual type of thermal expansion curve was obtained upon reheating (Fig. 3). This curve is characterized by a normal expansion from room temperature to approximately 300°C, a contraction of the specimen from 300° to 430°C, an abnormally large expansion from 430° to 550°C and then a normal expansion to 900°C. If the specimen had been slowly cooled (2°C/min) after heating to 900°C, the expansion behavior during subsequent heating is characterized by a normal expansion to 405°C, an abnormally large expansion between 415° and 575°C and then a normal expansion to 900°C (Fig. 4). No contraction of the specimen was observed in this second type of curve. These two types of dilatometric curves were reproduced on the 43.2, 44.9 and 45.4 a/o carbon alloys by use of the heat treatments mentioned above.*

*For additional details on individual alloys and dilatometric curves, see A. E. Ogard, C. C. Land and J. A. Leary, "The Thermal Expansion of PuC and PuC-UC Solid Solution," Los Alamos Scientific Laboratory Report LA-2768, October, 1962.

Fig 3 & Fig 4

A suggested mechanism that may explain the two types of expansion behavior is as follows: after the specimens had been slowly cooled they may have consisted of two phases (ζ + PuC) and did not exhibit contraction when reheated. If the specimens had been rapidly cooled, however, more than the equilibrium amount of PuC might have been present at room temperature. Therefore, when these alloys were reheated (to $\sim 300^\circ\text{C}$) ζ was rapidly precipitated from the unequilibrated PuC. This rapid precipitation of the more dense ζ could have resulted in an overall contraction of the specimens and thus accounted for the behavior observed in the dilatometric curves. The density of the 43.2 a/o carbon alloy was measured both after it had been slowly cooled [$(1/4^\circ)\text{C}/\text{min}$] and after it had been rapidly cooled. The values obtained were 14.14 and 13.58 g/cm^3 , respectively. In comparison, the theoretical density for PuC is $13.59 \pm 0.06 \text{ g}/\text{cm}^3$.⁹

Thermal expansion curves obtained on reheating both the slowly cooled and the rapidly cooled 41.1 a/o carbon alloy showed no evidence of the contraction that had been observed in the other plutonium-carbon alloys. The type of expansion curve obtained for this alloy was similar to that shown in Fig. 3. The large increase observed in the expansion rate of this alloy can be attributed both to the dissolution of ζ and to the formation of the less dense PuC by the peritectoid reaction ($\epsilon + \text{PuC} \rightleftharpoons \zeta$)³.

Metallography also revealed that the 45.4 a/o carbon alloy consisted of two phases at room temperature and suggested that the (ζ + PuC)/PuC boundary is between 45.4 and 45.8 a/o carbon at $< 300^\circ\text{C}$. A transformation,

which was believed to be due to the precipitation of ζ phase when the alloy specimen was cooled across the $(\zeta + \text{PuC})/\text{PuC}$ boundary, occurred at 416° and 447°C , respectively, in the slowly cooled 45.4 and 43.2 a/o carbon alloys. The $(\zeta + \text{PuC})/\text{PuC}$ boundary intersects the ζ peritectoid isotherm between 41.1 and 43.2 a/o carbon.

UC-PuC SOLID SOLUTION

The thermal expansion curves for a UC-PuC solid solution ($\text{U}_{0.87}\text{Pu}_{0.13}\text{C}$) revealed no irregularities between 25° and 900°C (Fig. 5). This solid solution was found to be single phase both by x-ray diffraction analysis ($a_0 = 4.97\text{\AA}$) and by metallography (Fig. 6). The linear thermal expansion of $\text{U}_{0.87}\text{Pu}_{0.13}\text{C}$ can be expressed by the equation

$$\Delta l_{25-900^\circ\text{C}} = l(3.8 \times 10^{-4} + 8.7 \times 10^{-6}t + 3.0 \times 10^{-9}t^2).$$

The average coefficient of linear thermal expansion is $11.1 \times 10^{-6}/^\circ\text{C}$ between room temperature and 900°C .

Fig 5 & Fig 6

CONCLUSION

The average coefficients of linear thermal expansion of single phase PuC (45.8 a/o carbon) and $\text{U}_{0.87}\text{Pu}_{0.13}\text{C}$ between room temperature and 900°C were found to be 11.0×10^{-6} and $11.1 \times 10^{-6}/^\circ\text{C}$, respectively.

The dilatometric curves of annealed alloys containing 41.1 to 45.8 a/o carbon indicated phase transformations in agreement with the published phase diagram.³ The $(\zeta + \text{PuC})/\text{PuC}$ boundary was found to be located between 45.4 and 45.8 a/o carbon at $< 300^\circ\text{C}$ and was found to intersect the ζ peritectoid isotherm between 41.1 and 43.2 a/o carbon. At 43.2 and 44.9 a/o carbon, the boundary was placed at 447° and 416°C , respectively.

The phase transformations and unusual thermal expansion characteristics of Pu-C alloys containing between 41.1 and 45.8 at/o carbon probably make these alloys unsatisfactory as possible solid reactor fuels.

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Fig. 1. Thermal expansion of PuC_{0.85} (45.8 a/o carbon).

Fig. 2. Microstructure of $\text{PuC}_{0.85}$ (45.8 a/o carbon), X500 enlarged to 1.5, single phase PuC of large grain size, small voids present.

Fig. 3. Typical thermal expansion of Pu-C alloys containing 43.2, 44.9 and 45.4 a/o carbon. Alloy rapidly cooled from 900 $^{\circ}\text{C}$ prior to dilatometry.

Fig. 4. Typical thermal expansion of Pu-C alloys containing 41.1, 43.2, 44.9 and 45.4 a/o carbon. Alloy slowly cooled from 900°C prior to dilatometry.

Fig. 5. Thermal expansion of $\text{U}_{0.87}\text{Pu}_{0.13}\text{C}$.

Fig. 6. Microstructure of $U_{0.87}Pu_{0.13}C$, X1000 enlarged to 1.5, oblique light.