UAC-6408

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JUL 6 1962

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TE 5-28-62 Hoylande D Young

ANL-FGF-345

To be submitted to Program
Chairman for presentation at
Nuclear Ceramics Session of
American Ceramics Society
Meeting, October 17-19
Seattle, Washington

May 2, 1962

PuC

The Uranium Monocarbide-Plutonium Monocarbide System

by

S. Rosen and M. V. Nevitt

Abstract

The (U,Pu)C phase field of the U-Pu-C ternary system for temperatures below 635°C has been constructed from metallographic and x-ray diffraction data. Uranium monocarbide forms a complete series of solid solutions with plutonium monocarbide. The (U,Pu)C phase is stoichiometric as regards its carbon content in a composition range from 0 to 35 a/o Pu. With a further increase in Pu content it deviates from ideal stoichiometry toward greater metal to carbon ratios to form the defect (U,Pu)C phase. Pu expands the unit cell of the monocarbide over the composition range in which it retains its stoichiometric character. In the region of the defect structure the lattice parameter decreases with increasing Pu content, the extent of the decrease being dependent upon the carbon content. Metallographic observations on cast alloys show that a transition occurs in the microstructures between U-rich alloys which show a homogeneous carbide phase and Pu-rich alloys which show a cored carbide phase.

Summary

Introduction

The investigation of U-Pu-C alloys containing a concentration of carbon around 50 a/o was undertaken as part of a program to establish the phase

diagram of the U-Pu-C ternary system. The constitution of these alloys is of interest because of their potential as reactor fuel materials. The structure of UC is face-centered cubic with the carbon atoms located in the octahedral interstices forming a NaCl structure which contains 8 atoms per cell. PuC is isostructural with UC, but exists at low temperatures as a phase deficient in carbon rather than as the stoichiometric compound.

Experimental

The principle method used to determine the phase boundaries was metallographic examination of isothermally annealed and quenched specimens. The alloys were processed within glovebox enclosures containing either a helium or nitrogen atmosphere which analyzed less than 300 ppm oxygen.

The concentration of analyzed impurities in the Pu used in preparing alloys was less than 550 ppm. Uranium of 99.96 w/o purity, and spectroscopic carbon rod were the other starting materials. Alloys were prepared by arc-melting. The alloy compositions which are reported are those of the charges prepared for melting. Chemical analyses made on a large number of the cast alloys showed that in most cases the concentration of any component did not differ by more than 1 a/o from the intended concentration.

All alloys were given a preliminary homogenization anneal at 1050°C for 3 days prior to the equilibrating anneal of one to three weeks duration. Standard methods of metallographic preparation were used. Two swab etches found to be most successful were: (a) nitric acid, acetic acid, distilled water (equal parts by volume), and (b) orthophosphoric acid (85%), ethylene glycol, ethyl alcohol (in the ratio 5:5:8 parts by volume, respectively). A 5 to 30 second swab was required. X-ray diffraction patterns were obtained with a 114.6 mm Debye-Scherrer camera using filtered CuK-α radiation.

Lattice parameters were obtained with the aid of an IBM 704 computer using a program devised by Mueller and Heaton(1). Nitrogen and oxygen contamination in annealed alloys was less than 100 ppm.

Metallographic Results

The (U,Pu)C phase boundary has been determined at 400, 570, and 635°C. Because of the near equivalence of the phase boundary at the three temperatures, only the pertinent portion of the 570°C U-Pu-C isothermal section is shown in Figure 1.

The solidification process for Pu-rich alloys results in cast microstructures containing a cored carbide phase. The presence of this coring is probably related to the fact that the PuC phase forms from the peritectic reaction, liquid + $Pu_2C_3 \rightleftharpoons PuC$ at 1654°C(2), and that the peritectic type of solidification extends into the ternary system. The range of compositions of ternary alloys in which cast microstructures showed coring is indicated in Figure 2. In many of the high-carbon alloys the coring could not be removed with the available high temperature homogenization treatment (12 hours at a maximum temperature of 1500°C). The only portion of the phase boundary that was based principally upon observations of these non-equilibrium structures is the high-carbon side of the (U,Pu)C phase boundary in the region where the deviation from stoichiometry occurs, and for this reason the boundary has been indicated by a dashed line on the isothermal section. The low-carbon boundary of the same phase field can be placed with more confidence and is given as a solid line, since an independent determination of its location was made by an analysis of the microstructures of alloys containing between 7 and 35 a/o carbon based on the method of quantitative metallography.

Some of the microstructures used to bracket the phase boundaries are shown in Figures 3 through 6. The microstructures of alloys whose carbon compositions placed them on the low-carbon side of the (U,Pu)C phase field always showed a second phase which could be identified from x-ray diffraction patterns as a metallic U-Pu phase. For example, Figure 3 shows the U-Pu zeta phase disposed interdendritically in the monocarbide structure of the U-13 a/o Pu-46 a/o C alloy quenched from 400°C. U-rich alloys containing more than 50 a/o C were easily identified metallographically due to a characteristic Widmanstatten precipitate of the $(U,Pu)_2C_3$ phase, Figure 4. The microstructure of many high-carbon alloys of intermediate U-Pu composition contained a cored carbide constituent as may be seen from the etched appearance of the dendrites, shown in the microstructure of the U-24 a/o Pu-51 a/o C alloy, Figure 5. The occurrence of weak $(U,Pu)_2C_3$ lines on the diffraction pattern of this alloy, suggests that the interdendritic constituent is the $(U,Pu)_2C_3$ phase [probably resulting from a Class II ternary reaction: liquid + $(U,Pu)C_2 \rightleftharpoons (U,Pu)C + (U,Pu)_2C_3$]. Figure 6 shows a Pu-rich alloy containing the monocarbide phase which probably resulted from the peritectic reaction: liquid + $(U,Pu)_2C_3 \rightleftharpoons (U,Pu)C$. The dendrites appear to be remnants of the primary crystallization of $(U,Pu)_2C_3$.

X-Ray Results

Pu expands the unit cell of UC. The lattice parameters, measured at room temperature, of alloys quenched from 400 and 570°C are plotted against Pu composition in Figure 7. The parameters in the composition range 0 to about 35 a/o Pu are for monocarbides of ideal stoichiometry. At higher Pu concentrations the values are for carbides which lie either on the high- or low-carbon boundary in the region of the defect structure. The Pu concentration scale has been extended beyond 50 a/o so that the plot may include data for the binary monocarbide of Pu which at the temperatures of interest occurs in the composition range 52 a/o to 57 a/o Pu. A linear extrapolation of these binary data back to 50 a/o Pu yields a lattice parameter for PuC of ideal stoichiometry which is larger than any of the measured values, and which can be joined by a straight line to the lattice parameter of UC to show that large deviations from Vegard's Law characterize this solid solution.

In many cases, the Debye-Scherrer powder diffraction patterns of cored alloys revealed the presence of two face-centered cubic monocarbide phases having slightly different parameters. The square data points represent several of these alloys. The parameter values were obtained by taking the weighted average of the parameters derived from both sets of lines, the weighting being based upon relative film intensities.

The composition at which the (U,Pu)C phase field begins to deviate from stoichiometry may be estimated from the change in curvature of the lattice spacing/composition curve. 35 ± 2 a/o Pu has been chosen as the point where the defect (U,Pu)C structure forms by the rejection of carbon atoms from the lattice. This value agrees well with metallographic observations.

It may be expected, judging from the complex relationship shown in Figure 7, that mixed monocarbides of U and Pu can exhibit wide variations in unit cell dimension which are dependent upon composition and upon the conditions of preparation.

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2. R. N. Mulford, F. H. Ellinger, G. S. Hendrix, E. D. Albrecht, "The Plutonium-Carbon System" in Plutonium 1960, Cleaver-Hume Press, London (1961).

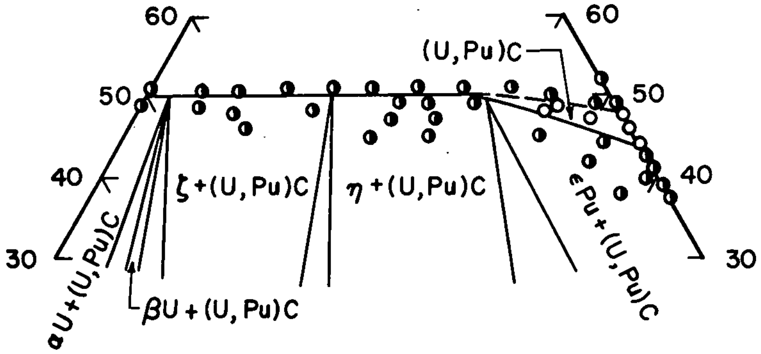

Figure 1. Partial U-Pu-C Isothermal Section at 570°C
Micro No. 34172

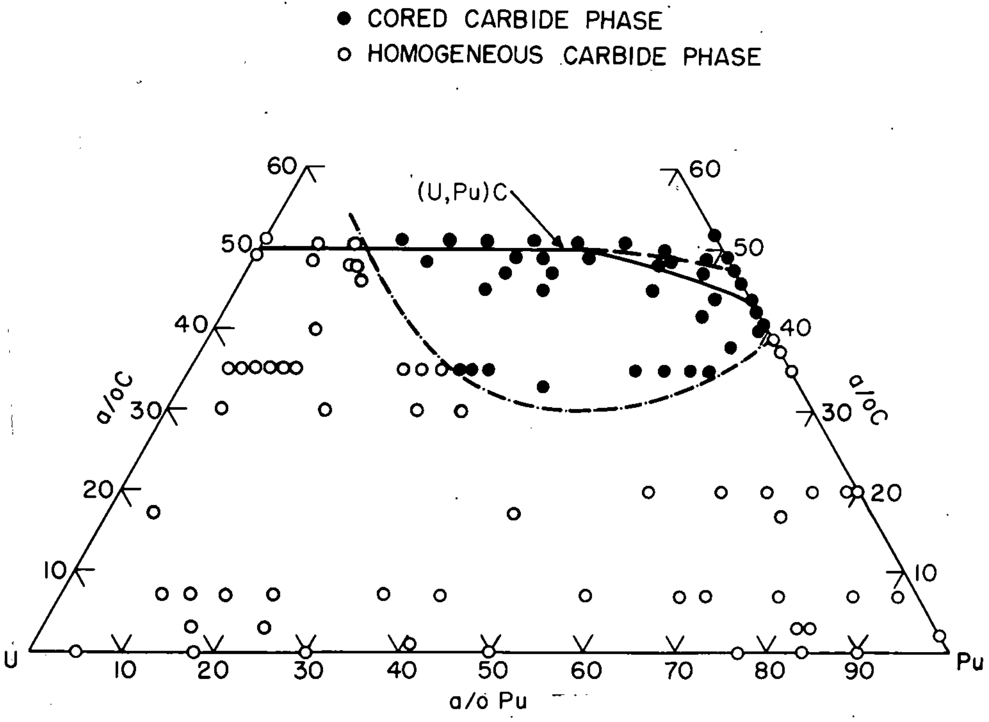

Figure 2. Concentration Triangle Showing
Presence of Coring in Cast Alloys
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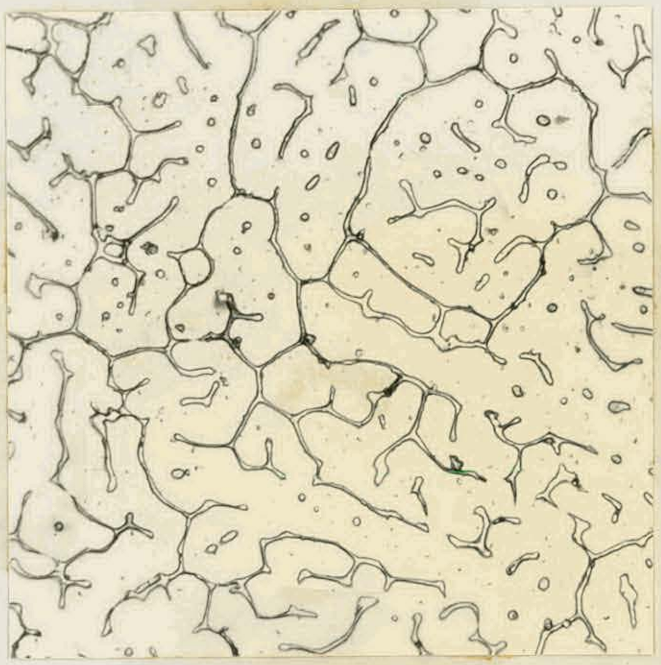

Figure 3.

(U,Pu)C plus Interdendritic Zeta in U-13 a/o Pu-46 a/o C Alloy Quenched from 400°C; 500X; Phosphoric Acid Etch
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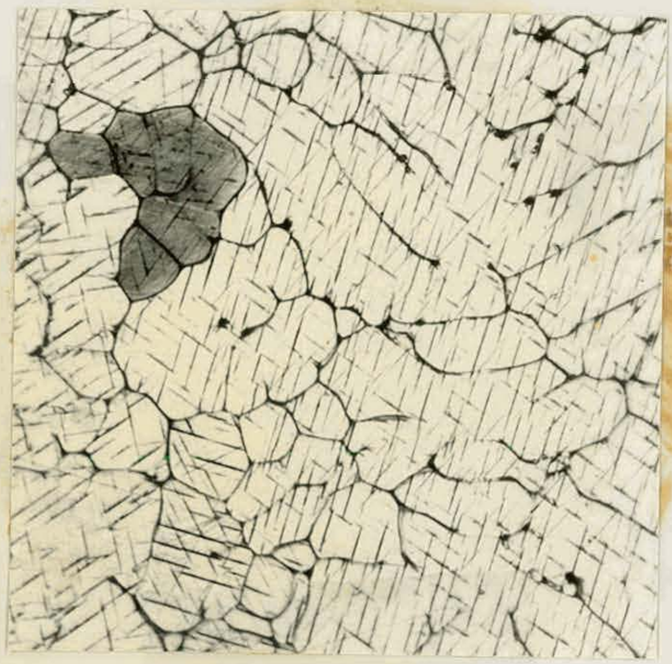

Figure 4.

(U,Pu)C plus $(U,Pu)_2C_3$ Widmanstatten Percipitate in U-6 a/o Pu-50.5 a/o C Alloy Quenched from 570°C; 500X; Phosphoric Acid Etch
Micro No. 31683

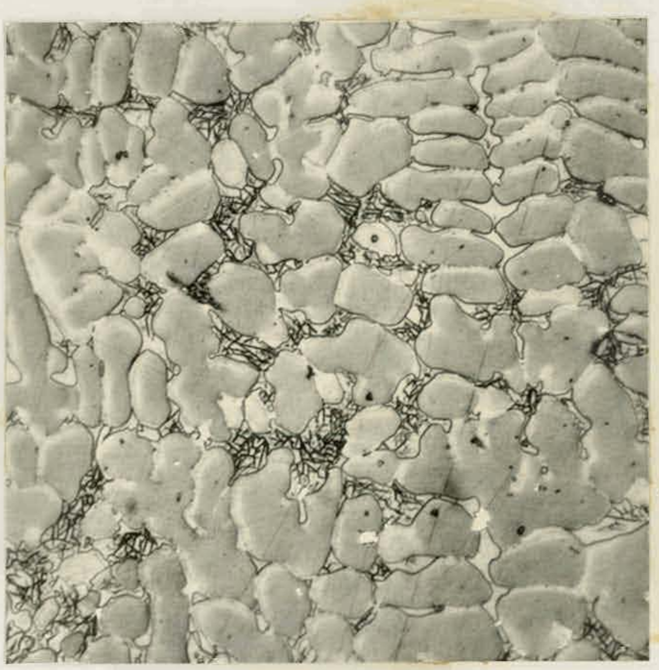

Figure 5.

Cored (U,Pu)C plus Interdendritic $(U,Pu)_2C_3$ in U-24 a/o Pu-51 a/o C Alloy, As Cast; 500X; Phosphoric Acid Etch
Micro No. 32574

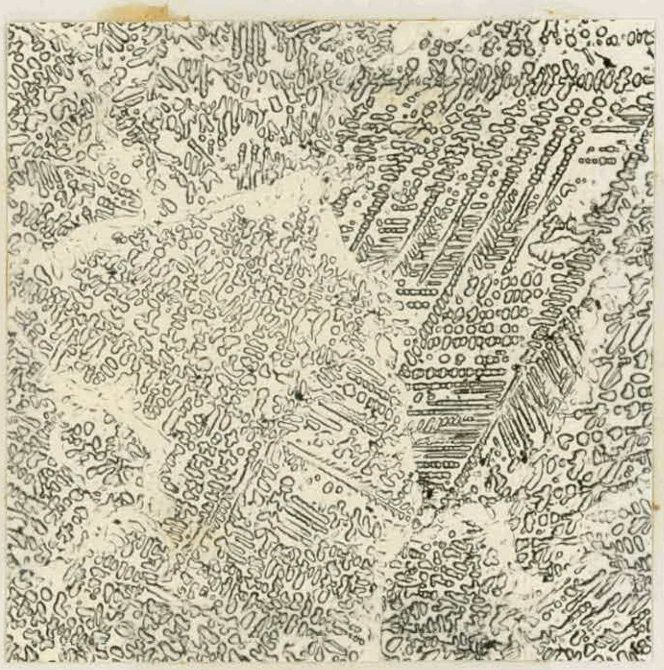

Figure 6.

Cored (U,Pu)C in U-44 a/o Pu-48 a/o C Alloy Quenched from 400°C; 200X; Nitric Acid Etch

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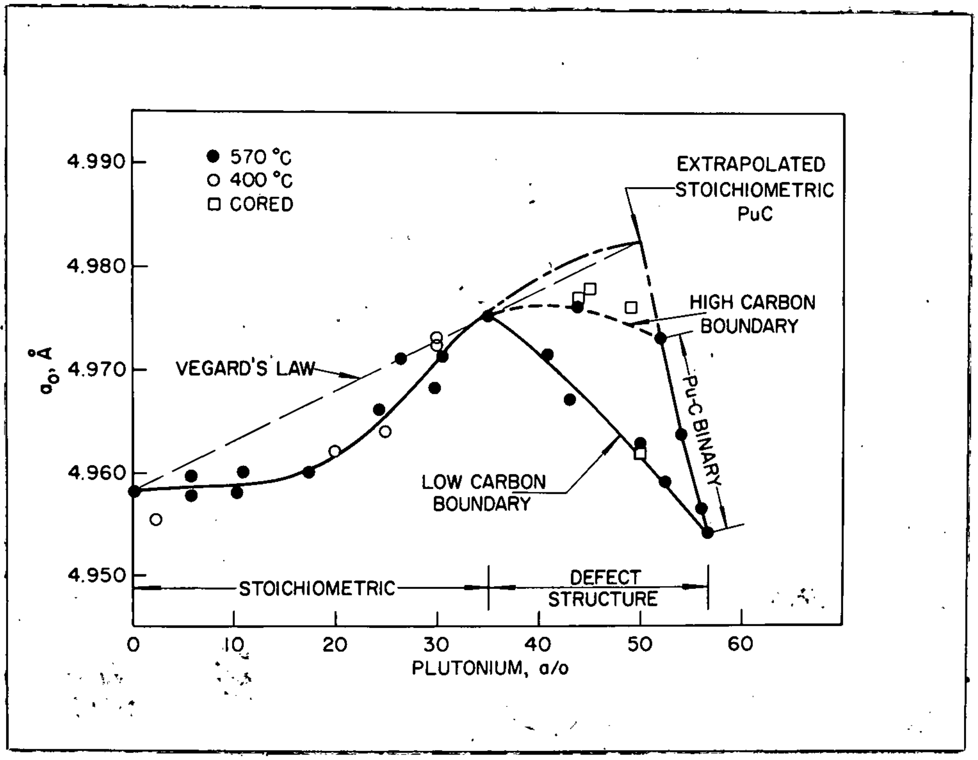

Figure 7. Lattice Parameter/Composition Curve for the (U,Pu)C Phase
Micro No. 34174