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HOT-HARDNESS TESTING OF URANIUM-PLUTONIUM CERAMICS

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ABSTRACT

The microindentation hardnesses of some uranium-plutonium carbides and of plutonium mononitride have been determined as a function of temperature. The hot-hardness behavior is discussed in terms of possible deformation mechanisms.

I. INTRODUCTION

For several years the Los Alamos Scientific Laboratory (LASL) has been involved in the determination of various high-temperature properties of several plutonium-containing ceramic compounds which are of interest as potential fuel materials for advanced liquid metal fast breeder reactors (LMFBR). The major emphasis in this program has been on the carbides of plutonium and uranium, especially the solid solution which has a nominal composition of UC-20 mol% PuC. Some work was also done on the uranium-plutonium nitrides.

II. MATERIALS

In the Pu-C system the major compounds of interest, as far as the hardness testing program was concerned, were the monocarbide and the sesquicarbide. The carbon-rich boundary of the plutonium monocarbide phase field occurs at a C/Pu ratio of approximately 0.9; at higher carbon-to-metal ratios the specimen will contain Pu₂C₃ as a second phase.¹ The solidus temperature of Pu₂C₃, 2010°C, is about 400°C higher than for PuC_{1-x}, 1600°C.

UC melts at a much higher temperature, 2525°C,² than does PuC_{1-x}. UC and PuC_{1-x} form isomorphous solid solutions having the NaCl structure, but at concentrations of PuC_{1-x} greater than about 50 mol% the UC-PuC_{1-x} equilibrium diagram becomes more complex than a simple binary and has not been defined in detail. Solid-solution specimens of (U,Pu)C which contain (U,Pu)₂C₃ as a second phase exhibit a U-Pu partition between the two

phases, with the sesquicarbide being enriched in plutonium relative to the monocarbide matrix.

The goal of the program for the solid-solution carbides was the determination of the temperature variation of the hardness as a function of both carbon composition and U/Pu ratio and the correlation of these data with possible deformation mechanisms. In the case of PuN, hardness data were obtained as a function of temperature and are herein compared to literature values for UN and (U, Pu)N.

A. Specimen Preparation and Analysis

Hot-hardness specimens were fabricated by cold pressing and sintering techniques.³ A typical spectrochemical analysis for carbide specimens is given in Table I. The analysis of the PuN used in this study is given in Table II, along with a comparative analysis of the UN tested by Harrison, of the Atomic Energy Research Establishment (AERE) at Harwell.^{4,5} No information is available on the U_{0.7}Pu_{0.3}N tested by French and Hodkin.⁶

III. EQUIPMENT

The handling of plutonium-containing materials is complicated by their high toxicity. Virtually all operations must be conducted in gloveboxes maintained at negative pressure with respect to the operating area.

A schematic diagram of the hot microhardness apparatus is shown in Fig. 1. The furnace chamber bottom

TABLE I

TYPICAL SPECTROCHEMICAL ANALYSIS OF URANIUM-PLUTONIUM CARBIDE SPECIMENS^a

Element	ppm	Element	ppm
Li	< 2	Ni	< 10
Be	< 1	Cu	< 2
B	< 1	Zn	< 20
Na	< 5	Sr	< 10
Mg	< 5	Zr	< 100
Al	< 10	Nb	< 100
Si	< 20	Mo	< 5
Ca	< 5	Cd	< 10
V	< 5	Sn	< 5
Cr	< 10	Ta	< 1000
Mn	< 5	W	< 100
Fe	< 20	Pb	< 5
Co	< 5	Bi	< 2

^aThe analysis shown here is for a U_{0.47}Pu_{0.53}C specimen.

plate rests on the glovebox floor. The furnace heating element consists of a 0.030-in.-diam molybdenum wire wound inside an alumina tube. The specimen rests on a tantalum anvil that can be raised, lowered, or rotated from outside the glovebox by a push-rod which passes through a vacuum gland and water-cooled jacket below the glovebox. For an indentation to be made, the specimen is raised until the indenter is contacted and lifted off its support. Rotation of the table below the vacuum chamber also causes the anvil to rotate, thus allowing a series of indentations to be made without cooling the furnace. The tests were conducted *in vacuo* (1×10^{-6} Torr at temperature).

Indentations made with this hardness tester cannot be measured *in situ* because there is no viewing system. After the specimen is cooled, it is cleaned ultrasonically to remove loose contamination, and is then transferred out of the plutonium glovebox on a clean glass plate into the operating area, where a standard Leitz microhardness tester is used to measure the indentations.

The hardness indentations were made with a load of approximately 200 g, which is the minimum weight of the indenter and holder. The hardness numbers were calculated from the standard formula for a Vickers 136° diamond pyramid indenter. Diamond or alumina indenters were used to 1000°. B₄C indenters were used at higher temperatures.

TABLE II

COMPOSITION OF URANIUM-PLUTONIUM NITRIDE SPECIMENS

Element	PuN, ppm, unless otherwise stated (LASL)	UN, ppm (AERE)
N	5.49(wt%)	4.95 + 0.05
C	-	250
Si	10	30
Ti	< 50	< 10
Sn	< 1	< 2
Mg	-	< 5
Cu	1	< 2
Ta	< 1000	-
O	223	p ^a
U	26	-
Th	< 75	-
W	< 30	-
Pb	1	-
Cd	< 3	-
Zn	< 5	-
Zr	< 300	-
B	< 0.5	-
Mo	< 30	< 0.5
Ni	< 5	--
Bi	< 0.5	--
Fe	< 5	--
Nb	< 300	-

^aProbably about 2000.

IV. RESULTS AND DISCUSSION

Hot-hardness curves for a series of uranium-plutonium carbide compositions are shown in Fig. 2. Each point represents the mean of from 5 to 20 measurements taken in from one to four separate experiments. The shapes of the curves for the monocarbides are similar. The hardness values decrease gradually with increasing temperature up to about 400 to 500°C; there is then an increase in the softening rate over a relatively narrow temperature range, after which the materials again soften less rapidly with increasing temperature. For some of the compositions tested, at relatively high homologous (T/T_m) temperatures the relative hardnesses then again decrease at a

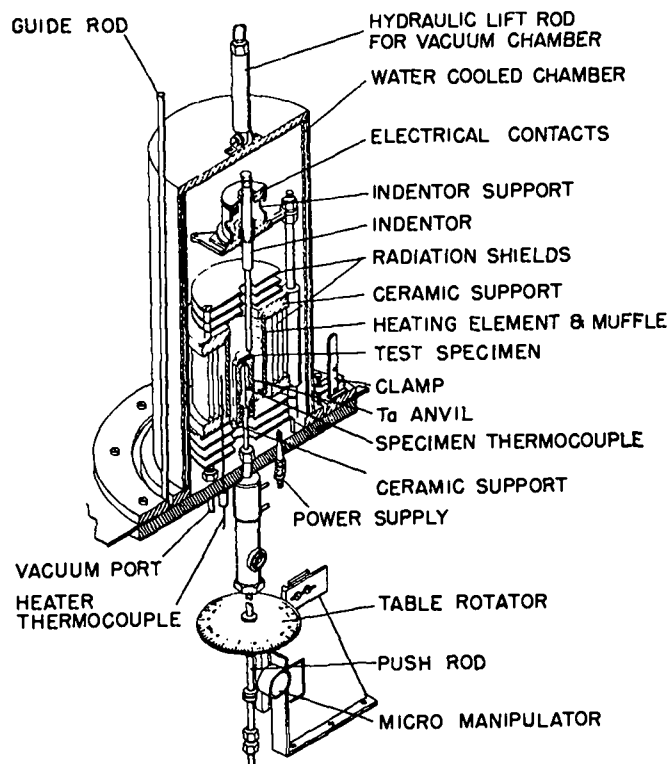


Fig. 1
Diagram of the microhardness apparatus.

greater rate. In the example of $\text{PuC}_{0.931}$, the hardness decreases from DPH 777 at room temperature to approximately DPH 600 at 400°C . The softening rate then increases, and from 400 to 600°C the hardness drops from approximately 600 to 200 DPH. From 600 to 800°C the hardness values again decrease less rapidly, while at temperatures greater than 800°C the relative hardness again decreases rapidly.

It is apparent that the curves do not follow the classic Ito-Shishokin⁷ form, viz., two straight line segments intersecting at a temperature near half the melting point, $0.5 T_m$,⁹ and 0.4 to $0.75 T_m$ for certain intermetallic compounds.¹⁰ A more detailed analysis of the general shape of the curves can be made from Fig. 3, which is a plot of hardness vs homologous temperature for the plutonium monocarbide specimen. The curve may be divided into three parts: (1) a nonlinear section, PQR, from room temperature to about $0.47 T_m$, (2) a linear segment, RS, from 0.47 to $0.57 T_m$, and (3) a linear segment, ST. The segment ST possibly corresponds to the high-temperature branch of the Ito-Shishokin curve, where diffusion-controlled processes such as dislocation climb and grain boundary sliding are believed to be the predominant deformation mechanisms. Below point S, deformation presumably occurs by slip. The behavior below point R may be due to dislocation interactions with solute impurities

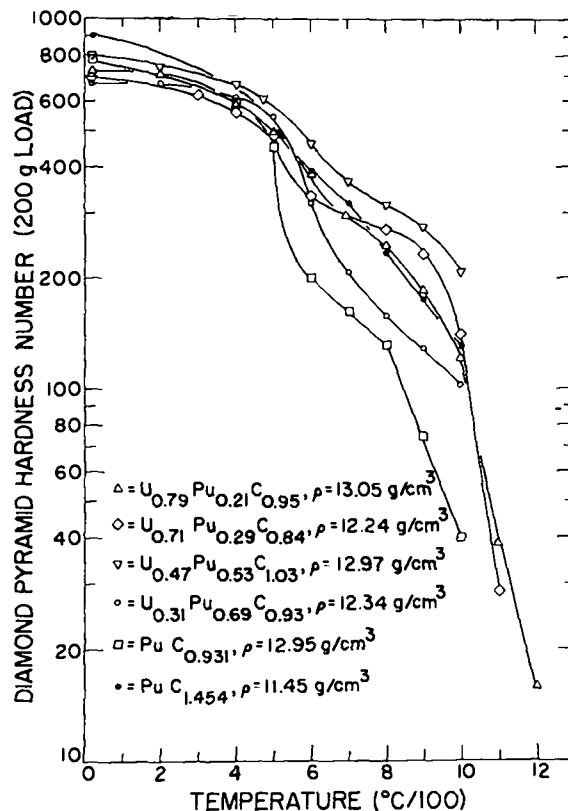


Fig. 2
Hot-hardness curves for uranium-plutonium carbides.

or to charged defect-dislocation interactions such as have been proposed by Westbrook¹¹ for nonstoichiometric compounds.

If the line segment RS is extrapolated to room temperature, a hardness is obtained near the experimentally determined value, P. It appears likely that the low-temperature branch of the curve would be PRS if there were no charged defect or impurity-dislocation interactions, but that as a result of these interactions, whatever their exact nature, the rate of softening is retarded until a temperature is reached (in this case $\sim 0.36 T_m$ at point Q) where the charged defects and/or impurities start to become mobile and the dislocations, in effect, become unpinned. At this point the softening rate increases. Finally, a temperature is reached (point R) where the defect/impurity dislocation interactions are negligible and the softening rate becomes that which would have held up to the Ito-Shishokin inflexion temperature had the interactions at lower temperatures not resulted in a hardening effect.

$\text{PuC}_{0.931}$ is the extreme in the series of carbide compositions studied, and the analysis of its hardness curve applies only qualitatively to the solid-solution carbides. The general similarity of the solid-solution hardness

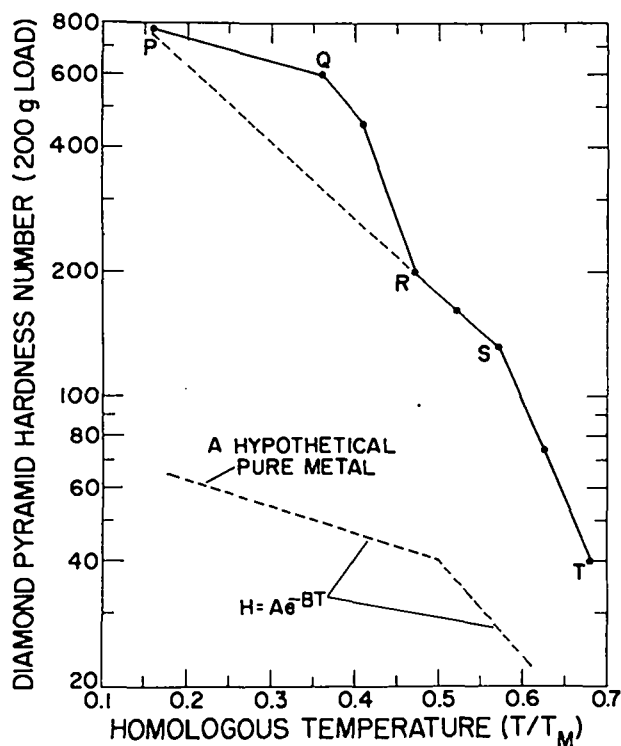


Fig. 3
Hardness of $\text{PuC}_{0.931}$ vs homologous temperature.

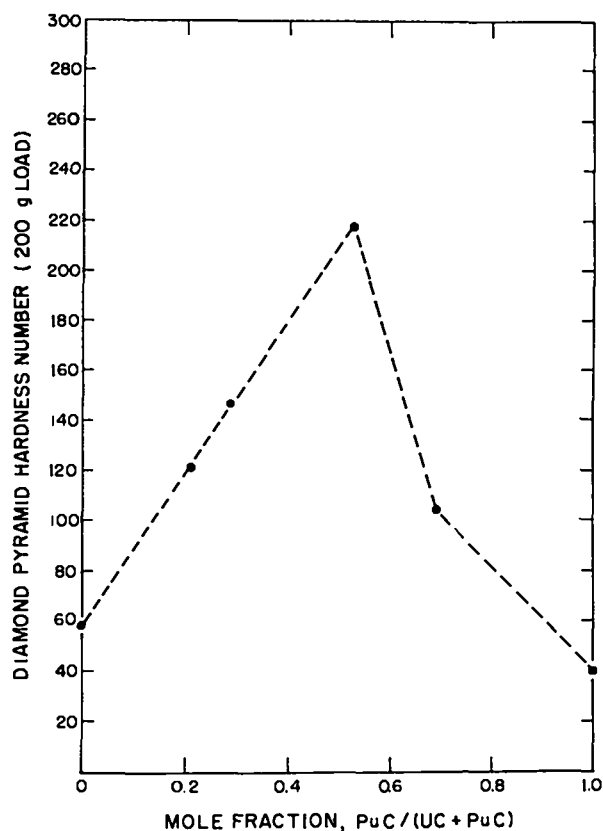


Fig. 4
Hardness of U-Pu monocarbides at 1000°C .

curves, however, makes the above admittedly speculative analysis of the shape of the $\text{PuC}_{0.931}$ curve appear reasonably applicable to the solid-solution carbides also.

Evidence for solid-solution hardening in alloys of UC and PuC can be seen in Fig. 4. The UC hardness value was taken from the work of DeCrescente and Miller.¹² Although the composition survey was not complete, it appears that the hardness at 1000°C increased with increasing PuC content up to about 53 mol% PuC. This trend was readily observed at temperatures between 600 and 1000°C . If the pattern continued at higher temperatures, namely at $\geq 1200^{\circ}\text{C}$ where creep measurements have been made for UC and (U,Pu)C, then the solid-solution carbides might be expected to be more creep resistant than UC. Yet, as shown in Fig. 5, solid-solution carbides have been reported to have higher creep rates¹³ than UC.¹⁴ Moreover, if the existing creep data are extrapolated to lower temperatures, at about 1050°C the lines would cross; that is, the creep rate of UC would be equal to that of the solid-solution carbide. This is consistent with the hot hardness which indicates that, in the temperature range from about 600 to 1000°C , the solid-solution carbides are harder to deform than is UC.

At high temperatures, $> 0.5T_M$, where diffusional processes are important, a defect structure such as that found in PuC_{1-x} might be expected to be relatively weak, whereas at intermediate temperatures charged defects or impurities could result in a strengthening effect. For

instance, if the solute plutonium is regarded as an impurity in (U,Pu)C, at intermediate temperatures the drift velocity of the solute atoms or of associated vacancies might decrease enough to impede dislocation motion and result in a higher hardness than that obtained for pure UC. Self-diffusion data for plutonium in the solid-solution carbides are so limited that independent corroboration of this mechanism is not possible at this time.

The hot-hardness data for PuN obtained in this study are compared in Fig. 6 to literature values for UN and $\text{U}_{0.7}\text{Pu}_{0.3}\text{N}$. Solid-solution hardening apparently occurs in this system also. The "bump" in the PuN hardness curve at 700°C is a phenomenon which has also been observed in UN by Harrison and Pape.⁵ They reported that the metallic impurity content did not influence the bump, and attributed the bump to a change in the deformation mechanism. French and Hodkin⁶ did not report a comparable phenomenon in their work on $\text{U}_{0.7}\text{Pu}_{0.3}\text{N}$. The sharpness of the knee or the bump appears to decrease with increasing load. This fact suggests that the inflection may be a surface effect, possibly caused by an adsorbed oxygen layer on the nitride specimens. The oxygen content of Harrison's specimen was relatively high (see Table II).

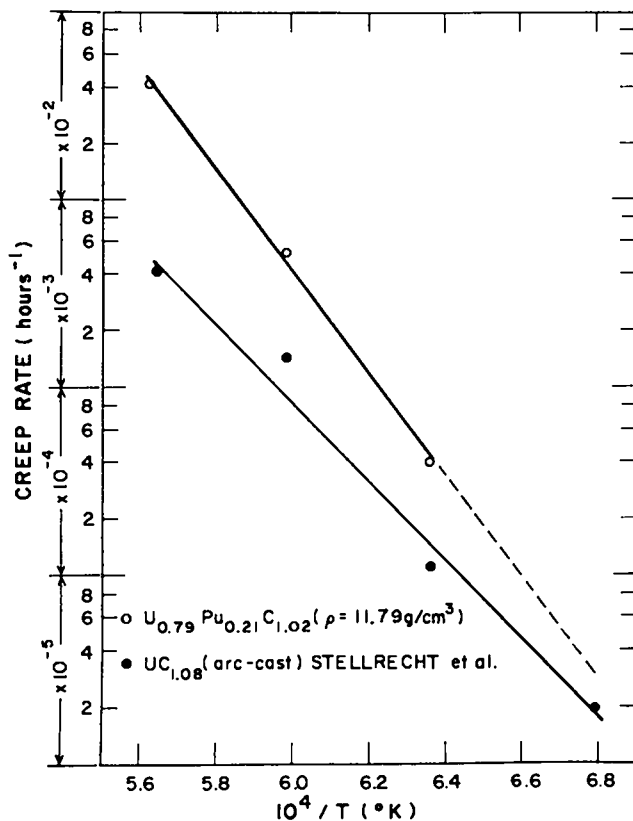


Fig. 5

Secondary creep rates of $U_{0.79}Pu_{0.21}C_{1.02}$ and $UC_{1.08}$ at 6000 psi.

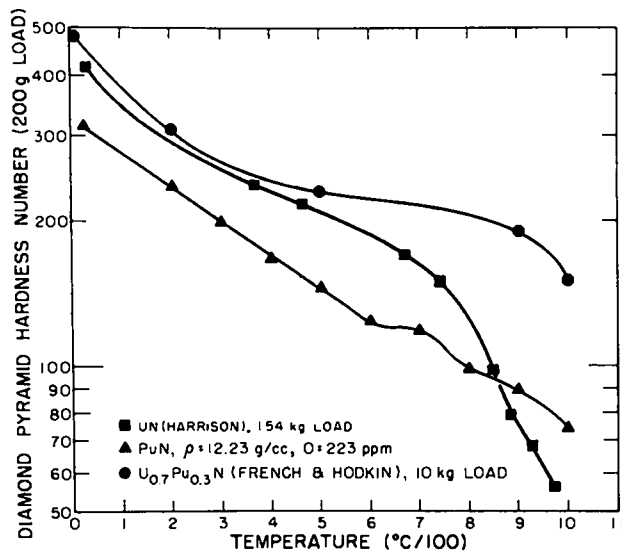


Fig. 6

Hot hardness of uranium-plutonium nitrides.

V. SUMMARY

This study has yielded information on the hardness of potential advanced LMFBR fuels. Plutonium-containing monocarbides and mononitrides do not yield the classic Ito-Shishokin hardness curves. The nonlinearity of the carbide curves at low homologous temperatures may be caused by impediments to dislocation motion of the vacancy-impurity type.

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