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ADVANCED CONCEPTS FOR FUTURE APPLICATION-
REACTOR EXPERIMENTS (M-3679, 38th Ed.)

(Title Unclassified)

ADVANCED, GRAPHITE-MATRIX, DISPERSION-TYPE FUEL SYSTEMS

FIRST ANNUAL REPORT

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ABSTRACT

A program of research is being conducted under Contract AT(04-3)-167 with the U.S. Atomic Energy Commission with the objectives of advancing the technology of graphite-matrix fuel systems and developing improved fuel compacts for advanced high-temperature reactor concepts. Classified work conducted in this program is described in this report.

A hot-working device for the deformation of graphite bodies in compression has been developed to investigate the feasibility of applying hot-working techniques to the fabrication of graphite-matrix fuel bodies with improved properties. This device has been used to deform cylindrical specimens of matrix graphite containing ZrC or UC-ZrC particles to strains of the order of 30% at temperatures of 2400° to 2900°C. The graphite bodies containing ZrC particles (chosen as representative carbide particles) have been found to be more plastic near 2500°C than similar bodies containing no carbide particles. This result is favorable in view of the limit on hot-working temperatures imposed by eutectic reactions between graphite and the fuel-carbide systems.

Microradiographic techniques have been developed to study the migration (at elevated temperatures) of uranium and thorium through pyrolytic-carbon (PyC) coatings on fuel particles. This has permitted the determination of diffusion (migration) coefficients on actual coated particles by nondestructive means. A tentative energy of activation for the migration of uranium from UC₂ particles into PyC coatings has been determined over the temperature range 1850° to 2300°C. Electron-microprobe analyses are in progress on annealed coated particles to determine the concentration of uranium which is visible by microradiography and the concentration gradient across the migration zone. The penetration of uranium into the coatings is not uniform but occurs radially in localized positions, and then spreads circumferentially, creating a banded structure. These results help illustrate the importance of the structure of PyC in regard to the diffusion of both fuel and fission-product materials. It has also been observed that the diffusion of uranium is considerably more rapid in the direction parallel to the layer planes in the PyC than it is in the perpendicular direction. Tests with PyC-coated (U, Zr)C particles in graphite-matrix compacts have shown that the addition of zirconium to the uranium carbide greatly improves the thermal stability. In general, the coatings on these particles retained their integrity for several hours at 2300° and 2500°C.

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INTRODUCTION

The present research program is directed toward improving the thermal stability and fission-product retention of graphite-matrix fuel systems in order to extend the application of these important reactor materials by permitting their use at higher temperatures and for longer times.

These studies are based initially on the hot-pressed graphite-matrix fuel compacts developed for the Peach Bottom High-temperature Gas-cooled Reactor (HTGR). ⁽¹⁾ In the process employed to produce these compacts, the fuel particles are mixed with graphite and pitch and this material is then hot-pressed to form the compacts. Coated fuel particles are readily incorporated into these bodies, and the results of detailed radiation and fission-product-retention testing has shown that these graphite-matrix fuel compacts are adequate for the first generation of high-temperature reactors. With the hot-pressed graphite-matrix compacts as the basis, therefore, a program of research was formulated to advance the technology of such systems and to develop improved fuel compacts for advanced high-temperature reactor concepts.

In addition to the studies reported in the unclassified portion of this report,* the following methods for improving hot-pressed graphite-matrix fuel compacts are currently being investigated:

Application of Hot-working Techniques to Fuel Compacts

The feasibility of applying the concept of hot-working to the fabrication of graphite-matrix fuel bodies with improved properties is being investigated. The initial studies are directed toward learning the conditions under which a graphite matrix containing carbide particles can be hot-worked without adversely affecting the particles, so that the improved properties of hot-worked graphite can be realized in the immediate neighborhood of the carbide particles.

In addition to the physical- and mechanical-property testing that is being conducted as an integral part of the development program outlined above, and that reported in the unclassified portion of this report,* evaluations are being made of the thermal-stability characteristics of fuel compacts selected as representative of an advancement in the technology. These

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evaluation techniques are also being used to study the basic behavior of graphite-matrix fuel-system materials, both to improve our knowledge of these materials and to guide the development studies.

Thermal Stability

The rate and mechanism of migration of uranium and thorium in graphite-matrix fuel systems are being studied under both isothermal and thermal-gradient conditions. Graphite-matrix fuel compacts containing PyC-coated fuel particles are being subjected to various thermal treatments, including annealing in a temperature gradient and thermal cycling. Short-time tests at high temperature (1800° to 2300°C) are being performed to obtain data to permit calculation of the energy of activation of the carbide-particle-carbon-coating reaction process. From these data, fuel lives at other temperatures may then be predicted.

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II. THE APPLICATION OF HOT-WORKING PROCESSES TO THE FABRICATION OF GRAPHITE-MATRIX FUEL BODIES

J. L. White, J. M. Pontelandolfo, L. C. Foster

INTRODUCTION

The general purpose of this portion of the program is to determine the feasibility of employing the concept of hot-working to fabricate a graphite-matrix fuel body of improved properties. The immediate objective is to learn the conditions under which a graphite matrix containing carbide particles can be hot-worked without adversely affecting the particles, so that the improved properties of hot-worked graphite can be realized in the immediate neighborhood of the carbide particles.

The specific areas toward which the experimental work is directed are as follows:

Determination of the optimum conditions for the hot-working of typical matrix graphite.

Definition of the properties achieved by hot-working matrix graphite.

Investigation of the influence of carbide particles in the matrix graphite on the hot-working characteristics.

Exploration of the process variables and limiting conditions for the hot-working of carbide-loaded matrix graphite.

Determination of the properties of hot-worked bodies of carbide-loaded matrix graphite.

The experimental results obtained to date and reported in GA-4022, Part 1, are believed to provide substantial evidence to support the feasibility of hot-working carbide-loaded graphite-matrix bodies. Bodies of a typical warm-pressed matrix graphite containing ZrC particles (chosen as representative carbide particles) have been found to be more plastic at hot-working temperatures than similar bodies containing no carbide particles. This result is of significance to the present program because of the limit on hot-working temperatures imposed by the eutectic reactions between graphite and the various fuel-carbide systems.

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HOT-WORKING OF FUELED GRAPHITE BODIES

Some preliminary experiments have been conducted to explore any special characteristics associated with the deformation of a matrix graphite containing fuel carbides. A body of matrix graphite containing approximately 9 vol-% of UC-ZrC particles was prepared by the usual hot-pressing technique. The particles were approximately 400 μ in diameter and were prepared at General Atomic by sintering in a graphite bed to a maximum temperature of 2775°C. The particles were coated to a thickness of approximately 45 μ with pyrolytic graphite deposited from methane at 1400°C. By chemical analysis the Zr/U atom ratio was found to be 6.05. The average density of the coated particles was found to be 4.47 g/cm³.

The deformation characteristics of this body were similar to those of the ZrC-loaded matrix-graphite bodies discussed in GA-4022, Part 1. Microstructures at 150 $\times$ before and after deformation at 2550°C to a strain of 35% are shown in Fig. 2.1. The hot-worked matrix graphite has a structure which is almost indistinguishable from that of the hot-worked pyrolytic coating. The coatings have been deformed, though apparently without rupture. It is not clear whether the small apparent deformation of the UC-ZrC particles is due to actual deformation or to an orienting effect on particles which are not perfectly spherical.

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Fig. 2.2--Photomicrographs (150 $\times$, bright-field) of matrix graphite loaded with UC-ZrC particles coated with pyrolytic graphite. Upper photomicrograph: no deformation. Lower photomicrograph: After deformation at 2550 $^{\circ}$ C to a strain of 35% (longitudinal sections)

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III. STUDIES OF FUEL MIGRATION IN COATED PARTICLES

W. V. Goeddel, N. L. Sandefur, P. R. Macy

Early studies of the thermal stability of PyC-coated metal-carbide fuel particles revealed that the coatings failed owing to reaction with the fuel at temperatures well below the melting point of the latter. (2, 3, 4) The mechanism of this attack was not known, but it was assumed to be solution of the carbon in the metal carbide. This rapid migration of uranium and thorium through the coatings at temperatures above 1700°C imposed severe limitations on the maximum use of these promising new fuel systems. The present studies were therefore undertaken to establish the upper operating temperatures for graphite-matrix fuel systems employing PyC-coated particles, and to determine the mechanism and rate of the diffusion and penetration processes so that more stable systems could be developed and the operating temperatures of the reactors employing these fuels thereby extended.

High-temperature, short-term tests are being made to obtain data to permit calculation of the energy of activation of the migration process. By this means, it may be possible to predict fuel lives of many years at temperatures below 1700°C from data obtained in relatively short times at higher temperatures.

Coated fuel particles are suspended in graphite powder for many of these tests to simplify sampling and examination. UC₂-C eutectic particles are being used to further simplify examination, with occasional duplicate tests being conducted with (Th, U)C₂-C eutectic particles to obtain correlations. Large (100- to 400-μ) particles with thick (50-μ) coatings are being employed so that more-accurate measurements of reaction distances can be made.

As the first step in these tests, the time-dependence of the reaction is being determined at a series of high temperatures (1850° to 2300°C) by measuring the thickness of remaining intact coatings as a function of time. These data will be extrapolated to higher or lower temperatures to ascertain fuel lives at various proposed reactor operating temperatures.

Microstructural techniques are extensively employed for evaluation of fuel migration. Optical metallography is useful for gross migration effects, while microradiography has increased resolution for detecting small migrations and localized intrusions of metal into the coatings. In

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the present studies, electron-beam microanalysis techniques are being employed to obtain quantitative measurements of metal concentrations and locations.

In addition to these studies of mechanism, new and advanced fuel systems are being tested to evaluate their thermal stability and guide the development of more stable systems.

EXPERIMENTAL TECHNIQUES

The equipment and techniques used for heating the coated particles have been described previously⁽²⁾⁽³⁾ and will only be briefly reviewed in this report. An isometric drawing of a fuel-migration furnace is shown in Fig. 3.1; photos of furnaces are shown in Figs. 3.2 and 3.3. A graphite crucible containing the coated fuel particles is placed in a tubular graphite heater (Fig. 3.4), and the particles are heated in vacuum under isothermal conditions. Close temperature control is maintained through an optical-pyrometric control system. Temperatures are measured with the aid of a calibrated optical pyrometer by sighting on the crucible through small holes in the radiation shields and graphite resistance heater.

Previous evaluations of thermally treated coated particles have depended primarily on optical-metallographic techniques. These examinations indicated that the carbide particle reacted with the carbon coating, and eventually penetrated the coating. In order to study the mechanisms of this reaction and migration, more-sensitive tools were needed to follow the metal concentration in the coating, since by optical means alone it was difficult to observe low metal concentrations in the PyC. One such tool which has been extremely valuable in improving definition of the low metal concentrations in the carbon is X-ray microradiography.

In microradiography, a radiograph is made by the usual method of shadow projection, and the X-ray image so obtained is examined under a microscope. A radiograph can be taken either by bringing the object and the film into close contact or by placing the film some distance behind the object. In the first case, the X-ray image is as sharp as it can be; in the second case there is some magnification. Both procedures were investigated for the examination of coated fuel particles.

Point-projection X-ray microradiography was performed with an electron microscope. The coated particles were sprinkled onto cellophane tape, and exposed to the X-radiation from an iron target. For purposes of resolution, an electron acceleration potential of 75 kv was used. The basically spherical carbide particles were shown as the opaque centers within the radiographically homogeneous carbon coating of the normal particle.

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Fig. 3. 1--Isometric drawing of furnace used in studies of thermal stability of coated fuel particles

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Fig. 3.2--Fuel-migration test furnaces (MG-1465-8195)

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Fig. 3. 3--Group of furnaces used in fuel-migration studies of coated particles (MG-1465-8194)

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Fig. 3.4--Arrangement of graphite crucible containing coated fuel particles within fuel-migration furnace

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Any heavy metal which migrated into the coatings appeared as less transparent (darker) areas. The photographs were projections of the complete particle, not of a section as is the case with optical metallography. Magnifications of as much as 175 diameters were obtained, but the resolution was only of the order of a few microns.

X-ray contact microradiography was employed for the balance of the present work to obtain high resolution. A Norelco CMR-5 microradiographic unit, which is equipped with a small, sealed-off X-ray tube having a beryllium window only 50 μ thick, was used. This tube was suitable for producing very soft X-rays at voltages of 5 kv or less. The sample chamber was evacuated to reduce air absorption and scattered radiation.

The resolution, which was determined by the film, was 0.5 to 1 μ and hence was close to that which can be achieved visually with an optical microscope (about 0.3 μ). High-resolution (>2000 lines/mm) film supplied by Eastman Kodak and Gevaert was employed. The radiograph was the same size as the specimen and therefore had to be examined with a microscope.

EXPERIMENTS TO DETERMINE MIGRATION RATES AS A FUNCTION OF TEMPERATURE

The migration of uranium through the PyC coatings on UC₂ particles was studied as a function of time and temperature at high temperatures to furnish quantitative data for the estimation of fuel lives at lower temperatures. Samples of PyC-coated UC₂ particles were initially heated at four different temperatures (1850°, 2000°, 2150°, and 2300°C) for four different times. By means of microradiography, the distance of migration of uranium into the PyC was determined from averages of measurements on at least 50 particles for each of the time-temperature conditions. The tests were subsequently extended to higher (2500°C) and lower (1700°C) temperatures, and to longer times.

Two groups of PyC-coated UC₂ particles were used for these experiments. The pertinent characteristics of these coated particles are given in Table 3.1. (These particular coated particles were prepared using the "graphite-bed" technique⁽⁵⁾ to make round UC₂ particles and the fluidized-bed process⁽⁶⁾ to apply the PyC coatings at a temperature of 1400°C.) Photomicrographs of these coated particles are shown in Figs. 3.5 and 3.6.

For experiments to be conducted at a single temperature, 10 to 15 g of particles were placed in the crucible (Fig. 3.4). After each predetermined annealing period, the furnace was cooled and a 1- to 2-g sample of particles was removed. Microradiographs were then made of the particles to determine the extent of uranium migration into the coatings.

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(250x)

Fig. 3.5--PyC-coated UC_2 particles used for the determination of migration rates (Lot L1985-135NCR)

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Fig. 3.6--PyC-coated UC_2 particles used for the determination of migration rates (Lot L1985-147NC)

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Table 3.1

DESCRIPTION OF PyC-COATED UC₂ PARTICLES

Lot No.	Thickness of PyC Coating (μ)	Diam. of UC ₂ Particle (μ)	Carbon Content of UC ₂ Particle (wt-%)
L1985-135NCR	46	132	11.50
L1985-147NC	38	103	12.50

The way in which the measurements were made can best be described by reference to Fig. 3.7. The original thickness of the coatings was obtained by averaging (for 50 particles) $(a + b)/2$, where b equals the thinnest part of the coating and a equals the thickest part of the coating. The UC₂ kernel was measured in the same manner. The extent of migration of the uranium into the carbon coating was determined by averaging measurements of $(b - c)$, c being the thinnest part of the carbon coating remaining. This value $(b - c)$ was also compared with

$$\left(\frac{a + b}{2} - \frac{c + d + e}{3} \right), \quad (3.1)$$

$$\left(\frac{a + b}{2} - \frac{c + e}{2} \right), \quad (3.2)$$

$$\left(b - \frac{c + d}{2} \right), \quad (3.3)$$

where d and e are measurements of the coating thickness remaining at two other locations. The values determined by the three methods differed only slightly. To estimate the extent of error in the penetration values, standard deviations were determined for several sets of values used in the computation. The σ values were about 5.5 and 2.5 μ for Lots L1985-135NCR and L1985-147NC, respectively. Only measurements falling within 2σ were used in the final calculations.

Photomicrographs and microradiographs of representative annealed particles are shown in Figs. 3.8 through 3.10.

The temperatures and times of the anneals, and the distances of migration of the uranium into the PyC coatings, are given in Tables 3.2 and 3.3. These data are shown plotted in Figs. 3.11 through 3.20. From curves drawn through these data points, "migration" coefficients were calculated using the relationship $M = x^2/4t$, where M is the migration coefficient, x is the distance of migration, and t is time.

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Fig. 3.7--Measuring scheme used to determine extent of fuel migration in coated particles

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(a)

(b)

(c)

(d)

Fig. 3.8--Microradiographs (150x) of PyC-coated UC_2 particles annealed at $2300^{\circ}C$: (a) control; (b) 1/2 hr; (c) 1 hr; (d) 3 hr (Lot L1985-135NCR)

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(a)

(b)

(c)

(d)

Fig. 3.9--Photomicrographs (150x) of PyC-coated UC₂ particles annealed at 2300°C: (a) control; (b) 1/2 hr; (c) 1 hr; (d) 3 hr (Lot L1985-135NC)

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(a)

(b)

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(c)

(d)

Fig. 3.10--Microradiographs (150x) of PyC-coated UC_2 particles annealed at $1850^{\circ}C$: (a) control; (b) 4 hr; (c) 9 hr; (d) 25 hr (Lot L1985-147NC)

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Table 3.2

MIGRATION OF URANIUM INTO PYROLYTIC-CARBON COATINGS UNDER VARIOUS ANNEALING CONDITIONS
(Coated-particles Lot L1985-135NCR)

Temp. (°C)	Time (hr)	Migration Distance (μ)
1700	81	1
	196	9
	356	9
	569	11
1850	4	5
	9	7
	16	10
	25	14
2000	2	5
	4	5
	7	14
	10	14
2150	1.5	11
	2.5	11
	4.5	15
	6.5	14
2300	0.5	5
	1.0	11
	2.0	12
	3.0	12
2500	0.2	33

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Table 3.3

MIGRATION OF URANIUM INTO PYROLYTIC-CARBON
COATINGS UNDER VARIOUS ANNEALING CONDITIONS
(Coated-particles Lot L1985-147NC)

Temp. (°C)	Time (hr)	Migration Distance (μ)	Temp. (°C)	Time (hr)	Migration Distance (μ)
1700	81	8	2150	0.5	10
	196	11		1.0	9
	361	13		2.0	12
1850				3.3	11
	4	6		4.8	13
	9	9		6.8	13
	16	10		9.0	12
	25	12		11.5	13
	36	11	2300	0.5	11
	49	13		1.0	11
	64	13		1.5	11
2000	81	13		2.0	12
	1.5	7		2.5	12
	2.5	10		3.3	13
	4.5	12		4.0	12
	6.5	11		4.8	14
	8.5	12	2500		
	11.0	12		0.2	31
	14.0	12			
	17.0	12			

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Fig. 3.11--Time-penetration curve for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-135NCR) at 1700°C

Fig. 3.12--Time-penetration curve for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-135NCR) at 1850°C

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Fig. 3.13--Time-penetration curve for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-135NCR) at 2000°C

Fig. 3.14--Time-penetration curve for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-135NCR) at 2150°C

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Fig. 3.15--Time-penetration curve for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-135NCR) at 2300°C

Fig. 3.16 --Time-penetration curves for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-147NC) at 1700°C

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Fig. 3.17--Time-penetration curves for migration of uranium into pyrolytic-carbon coatings on UC₂ fuel particles (Lot L1985-147NC) at 1850°C

Fig. 3.18--Time-penetration curves for migration of uranium into pyrolytic-carbon coatings on UC₂ fuel particles (Lot L1985-147NC) at 2000°C

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Fig. 3.19--Time-penetration curves for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-147NC) at $2150^{\circ}C$

Fig. 3.20--Time-penetration curves for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-147NC) at $2300^{\circ}C$

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The time-penetration profiles for the coated particles of Lot L1985-147NC (which were annealed for longer times) show that the rate of migration decreases with time. There is an initial, rather rapid penetration of uranium into the coating, followed by a considerably slower migration to greater distances. There are several possible explanations for this behavior: depletion of uranium at the UC_2 -PyC interface, the process then being limited by the diffusion of uranium in the UC_2 particle; structural changes in the coating due to chemical effects or to the high-temperature annealing; and rapid saturation of microcrack migration paths in the inner layers of the PyC, with resultant impeded transport of uranium beyond this range. The validity of these explanations is under investigation.

Migration coefficients have been estimated for both the initial (shallow) penetration (Table 3.4) and the subsequent (deep) penetration (Table 3.5). The dependence of these migration coefficients on temperature is shown in the Arrhenius plots of Figs. 3.21 and 3.22.

The log M versus $1/T$ plots are quite linear over the temperature range 1850° to $2300^\circ C$. However, at 1700° and $2500^\circ C$, the migration rates show an appreciable departure from this linear relationship. At $1700^\circ C$ the observed migration rate is less than predicted by extrapolation of the 1850° to $2300^\circ C$ Arrhenius plots. This may possibly be related to the phase change of UC_2 from tetragonal to cubic which is reported⁽⁷⁾ to occur around $1800^\circ C$. (This temperature region was also found to be critical in previous studies of the "amoeba" effect.⁽²⁾ In these earlier studies, the "amoeba" effect was observed at temperatures above $1800^\circ C$; it was not observed at $1700^\circ C$.) At $2500^\circ C$ the migration rate was found to be considerably faster than predicted, but this might well be expected because of the formation of a liquid phase at $2450^\circ C$ (UC_2 -U eutectic).

Activation energies for the initial (shallow) migration of uranium in PyC coatings were calculated from these log M versus $1/T$ plots over the temperature range 1850° to $2300^\circ C$:

Lot L1985-135NCR	60,000 cal/g-atom
Lot L1985-147NC	73,000 cal/g-atom

The slower (deep) penetration observed in the anneals of long duration (Lot L1985-147NC) gives an activation energy of 43,000 cal/g-atom, and is linear over the wider temperature range of 1700° to $2300^\circ C$.

The migration coefficients, M, in square centimeters per second, may be expressed by the following equations:

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Table 3.4
MIGRATION COEFFICIENTS FOR SHALLOW PENETRATION

Temp. (°C)	Migration Coefficient, M (cm ² /sec)	
	Lot L1985-135NCR	Lot L1985-147NC
1700	1.7×10 ⁻¹³	4.8×10 ⁻¹³
1850	4.8×10 ⁻¹²	6.4×10 ⁻¹²
2000	1.2×10 ⁻¹¹	2.2×10 ⁻¹¹
2150	3.4×10 ⁻¹¹	6.0×10 ⁻¹¹
2300	5.6×10 ⁻¹¹	1.3×10 ⁻¹⁰
2500	3.8×10 ⁻⁹	3.3×10 ⁻⁹

Table 3.5
MIGRATION COEFFICIENTS FOR
DEEP PENETRATION

Temp. (°C)	Migration Coefficient, M (cm ² /sec)
1700	1.8×10 ⁻¹³
1850	3.9×10 ⁻¹³
2000	7.2×10 ⁻¹³
2150	1.2×10 ⁻¹²
2300	2.4×10 ⁻¹²

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Fig. 3.21--Dependence of migration coefficient on temperature for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-135NCR)

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Fig. 3.22--Dependence of migration coefficient on temperature for migration of uranium into pyrolytic-carbon coatings on UC_2 fuel particles (Lot L1985-147NC); shallow penetration (upper curve) and deep penetration (lower curve)

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Shallow penetration, 1850°-2300°C

Lot L1985-135NCR $M = 6.8 \times 10^{-6} \exp(-60,000/RT)$

Lot L1985-147NC $M = 2.1 \times 10^{-4} \exp(-73,000/RT)$

Deep penetration, 1700°-2300°C

Lot L1985-147NC $M = 9.8 \times 10^{-9} \exp(-43,000/RT)$

Extrapolation of the shallow-penetration data to 1400°C gives migration coefficients of approximately 10^{-13} cm²/sec, corresponding to a penetration of about 35 μ in 8500 hr. The corresponding value from the deep-penetration curve of Fig. 3.22 is about 17 μ. However, a very long-term test such as this (8500 hr at 1400°C) has previously been made, (8) and no migration was observed. Clearly, further work is necessary before migration data obtained at high temperatures can be used to accurately predict fuel behavior at lower temperatures.

Arrangements have been made for electron-beam microanalyses of annealed coated particles to determine the concentration of uranium which is visible by microradiography, and the concentration gradient across the migration zone. These data are necessary for calculations of actual diffusion coefficients and activation energies from the penetration data.

SUMMARY OF MIGRATION-RATE EXPERIMENTS

Measurements of the rate of migration of uranium into PyC coatings on UC₂ particles have been made over the temperature range 1700° to 2500°C using microradiographic techniques. Migration coefficients and activation energies have been calculated from these data. The results show three unusual features: (1) the rate of migration decreases with time, yielding two migration curves (shallow and deep penetration) indicative of two different types of uranium transport; (2) data obtained at high (1850° to 2300°C) temperatures do not accurately predict migration rates at lower temperatures; and (3) migration rates vary between lots of supposedly similar coated particles. These results demonstrate that more than one mechanism is responsible for the observed migration, and that the structure of the coating itself may have a profound influence on the migration. Investigations are now in progress to define the mechanisms of migration and to determine the influence of coating structure.

OTHER HIGH-TEMPERATURE THERMAL-STABILITY STUDIES

Very High-temperature Tests

Several different lots of PyC-coated UC₂ and (Th, U)C₂ were heated at 2000° and 2300°C. Metallography and microradiography (Figs. 3.23 and

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TEST HISTORY

← Control sample

2000°C in vacuum for 6 hr

2300°C in helium for an additional 6 hr

Fig. 3. 23(a)--Photomicrographs (at 150x) of Vitro (Th, U)C₂ particles coated with General Atomic pyro-carbon (60 μ), before and after thermal testing; compare with Fig. 3. 23(b)

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TEST HISTORY

← Control sample

2000°C in vacuum for 6 hr

2300°C in helium for an additional 6 hr

Fig. 3. 23(b)--Microradiographs (at 150×) of Vitro (Th, U)C₂ particles coated with General Atomic pyro-carbon (60 μ), before and after thermal testing; compare with Fig. 3. 23(a)

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TEST HISTORY

← Control sample

2000°C in vacuum for 6 hr
2300°C in helium for an additional 6 hr

Fig. 3.24(a)--Photomicrographs (at 150×) of General Atomic (Th, U)C₂ particles with 45-μ pyro-carbon coating, before and after thermal testing; compare with Fig 3.24(b)

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TEST HISTORY

← Control sample

2000°C in vacuum for 6 hr

2300°C in helium for an additional 6 hr

Fig. 3.24(b)--Microradiographs (at 150x) of General Atomic (Th,U)C₂ particles with 45-μ pyro-carbon coating, before and after thermal testing; compare with Fig. 3.24(a)

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3.24) showed penetration of metal into the coating in a few hours. Banded concentrations of metal were found in the coatings, apparently in the laminations. (Circumferential diffusion of metal between the layers of the coatings is apparently much faster than radial diffusion.) The coatings were not destroyed in 6 hr at 2300°C, but heavy metal penetration throughout the coating was revealed by microradiography. The extent of attack varied greatly among the various samples. Evaluations of composition and structure versus stability are in progress to determine the important factors for very-high-temperature thermal stability.

Other Fuel Systems

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Operating temperatures and fuel lives of PyC-coated carbide fuel particles in graphite-matrix elements are limited by the thermal stability of these systems. This stability is, in turn, largely a consequence of the composition and structure of the fuel particle. Zirconium carbide stabilizes uranium monocarbide and forms a solid solution whose melting point is several hundred degrees higher than that of UC_2 . Use of (U, Zr)C particles therefore offers the possibility of a more stable fuel system for high-temperature operation through avoidance of low-melting eutectics. Two lots of (U, Zr)C particles were prepared, and the high-temperature stability of this system was evaluated by the fuel-migration testing.

Uncoated (U, Zr)C particles (30-70 U-Zr) were incorporated into a graphite matrix for high-temperature testing. Unfortunately, the unprotected particles reacted with the gases given off by the pitch binder during baking, and the integrity of most of the particles was destroyed. A sample with its remaining particles was heated for 5 min at 2800°C in helium. Metallographic examination revealed only slight diffusion of the fuel particles into the graphite-matrix--many of the particles retained their original shape (see Fig. 3.25). (In similar tests, UC_2 and (Th, U) C_2 particles with PyC coatings reacted completely through the coatings and dispersed into the matrix graphite, leaving only a hole to mark their original location. (See Fig. 3.26).

PyC-coated (Zr-U)C particles* were tested for various times at 2300°, 2500°, and 2700°C (see Fig. 3.27). Some reaction occurred between the particles and coatings at 2300° and 2500°, and a few of the coatings were ruptured by the 2700°C test. In general, it appeared that these coated particles were stable (retained their coating integrity) for several hours at 2300° and 2500°C.

*PyC coatings were applied at 1400°C.

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M1210-1-1

Fig. 3.25--Photomicrograph of uncoated
(U, Zr)C particles in a graphite-matrix
fuel compact after heating at 2800°C for
5 min in helium

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M1114-1-3

200×

(a)

M1083-1-4

200×

(b)

Fig. 3.26--Remains of PyC-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles in graphite-matrix fuel compacts (a) after heating at 2700°C for 5 min, (b) after heating at 2800°C for 2 min

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(a)

(150×)

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(b)

(150×)

Fig. 3.27--Photomicrographs of PyC-coated (U-Zr)C particles before and after thermal testing: (a) control sample; (b) 6 hr at 2300°C

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(150×)

(c)

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(150×)

(d)

Fig. 3.27 (continued)--Photomicrographs of PyC-coated (U-Zr)C particles before and after thermal testing: (c) 4 hr at 2500°C; (d) 1 hr at 2700°C

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