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EVALUATION OF FUEL PARTICLES

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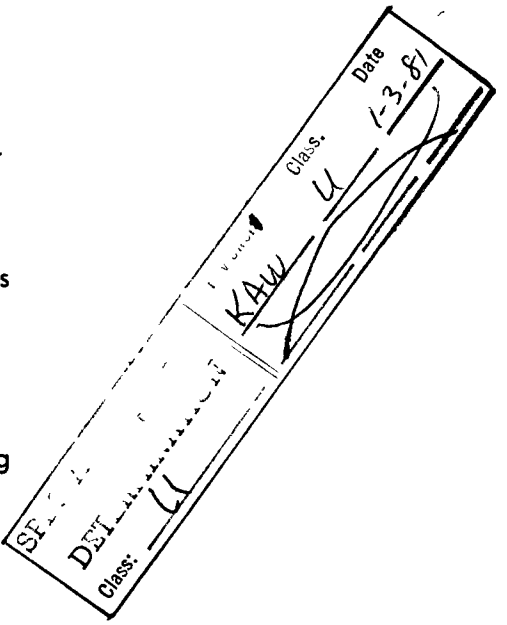

(The preliminary information presented in this report should not be published without prior written approval of the Westinghouse Astronuclear Laboratory. The work performed was supported by the Space Nuclear Propulsion Office.)

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EVALUATION OF COATED FUEL PARTICLES

Introduction

Recent results of quality control and experimental programs on pyrocarbon coated UC_2 particles are presented. Also reported are some preliminary data obtained on pyrocarbon coated mixed carbide particles.

Evaluation of Vendor Coated Particles - G. Fatzer

Evaluation of commercially available pyrocarbon coated UC_2 particles was continued. The principal objective of the study was the development of a quantitative test for uranium migration for application to quality control of production material. The migration test developed is based on microradiographic techniques as described in detail below.

1) A sample of approximately 0.5 gram weight is split out of a lot by riffling.

2) The sample is placed in a graphite crucible for heat treatment.

3) Heat-up to a specified temperature, normally in the range 2100° to 2500°C, is accomplished in 15 to 20 minutes. Time at temperature is varied from 1/2 to 4 hours, and cooldown to 1500°C is controlled at approximately 15 minutes.

4) A sample of approximately 0.05 gram is split out with a riffle and microradiographed.

5) Multiple photographs are made from the radiographic plate at approximately 150 magnifications. Fields of view are chosen from all areas of the radiograph such that no particle appears in more than one photograph.

6) Horizontal grid lines are placed at one half inch intervals on each photograph. One hundred completely visible particles are serially identified. Moving from left to right, the point at which the upper grid line first intersects the outer edge of the particle coating is the point of measurement for that particle.

Coating thickness is measured from the intersection along a line passing through the particle center. Only that part of the coating which shows no uranium present is measured.

7) The individual measurements obtained from 100 particles are averaged to obtain the "grid average" ($\bar{X}$) of the coating thickness.

8) The standard deviation (σ) of the individual measurements is computed.

9) The expression $\bar{X} - 1.6\sigma$ is used to define the residual coating thickness retained or exceeded by 95% of the particles measured.

10) To guard against an undesirably skewed distribution of migration about the "grid average," a limit is specified for the percentage of particles showing migration entirely through the particle coating.

Commercial sources are presently capable of producing pyrocarbon coated UC_2 particles to a requirement of 2300°C for four hours in an inert atmosphere with $\bar{X} - 1.6\sigma$ exceeding 10 microns and a maximum of 2% of the particles migrating completely through the coating. Results obtained from current production lots of 3M, Union Carbide, and General Atomics lots are included in Table I.

Data obtained from earlier Davison and NUMEC production lots are included in Table II. Earlier General Atomics production lots and recent development lots from Y-12 are also included in Table II.

Mechanical Damage of Coated Fuel Particles - K. Titus and M. Tobin

The extrusion mixture used in the production of the NERVA elements is composed of PyC coated UC_2 fuel particles (up to 20 v/o), graphite flour, carbon black, and varcum (a preparation of partly condensed furfuryl alcohol). It is essential to the homogeneity and strength of the fueled graphite that the four materials be thoroughly mixed and blended before extrusion, and that the three dry materials are thoroughly wetted by the varcum liquid. The blending of the dry materials is made before the varcum is added.

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Table I - Results Obtained on Current Production Lots

	As Received				2300° - 30 min.				2300° - 4 hr.				2200° - 5 hr.				2200°/5 hr. + 2100°/2 hr.			
	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated
3M																				
Lot 588	19	3.9	13	0.0	14	1.9	11	1	14	1.6	12	2	14	1.6	12	0	14	2.6	10	1
Carbon Products																				
Lot 49A	--	--	--	--	--	--	--	--	21	2.7	17	2	--	--	--	--	--	--	--	--
General Atomic																				
Lot 3100 EK	--	--	--	--	--	--	--	--	19	4.5	12	2	--	--	--	--	--	--	--	--
Lot 43 EK	25	4.2	18	0	--	--	--	--	22	5.7	13	1	--	--	--	--	--	--	--	--

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Table II - Results Obtained on Earlier Production Lots

	As Received				2300° - 30 min.				2300° - 4 hr.				2200° - 5 hr.				2200°/5 hr. + 2100°/2 hr.			
	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated	$\bar{X}$	σ	$\bar{X} - 1.6\sigma$	% Completely Migrated
Davison																				
Lot 25004	22	4.8	14	0	18	7.1	7	13	17	8.3	3	22	17	6.3	7	7	18	7.8	5	13
Lot 25011 -012	23	4.8	15	0	18	6.7	8	7	14	8.4	1	16	16	6.9	6	8	17	6.6	6	8
Y-12																				
Lot 111-L1	28	5.7	19	0	30	4.8	22	0.1	29	4.4	22	0	29	4.3	22	0.5	29	4.1	22	0
Lot 112-L2	26	7.6	14	1.8	25	7.5	13	2.8	25	7.7	13	3.5	28	7.7	16	3.5	28	5.5	19	1.6
Lot 25-L1	24	3	19	--	23	3	18	--	21	4	15	--	--	--	--	--	--	--	--	--
General Atomic (Earlier Production)																				
Lot E-30	22	1.5	19	0	20	2.4	16	4	13	8.0	0	14	20	4.0	13	1	18	3.2	13	3
Lot E-42	22	3.0	17	0	18	5.4	9	4	8	8.1	0	39	15	5.6	6	1	17	6.5	6	11
Lot 1036	24	2.2	20	0	22	5.1	14	10	17	9.5	2	41	--	--	--	--	--	--	--	--
Lot 1037	23	4.0	17	0	23	3.5	17	0.3	21	4.0	15	1	--	--	--	--	--	--	--	--
3M																				
Lot 12003	25		--	--	2	5	--	--	--	--	--	--	--	--	--	--	--	--	--	--

The resulting viscous mass is taken from the blender and ground and extruded. It is necessary to regrind and extrude the elements to get the desired quality of extruded element. The elements are cut from the second extrusion and cured to set its green strength. The fuel particles are subjected to shearing and impact forces in the steps preceding the curing of the elements, and a certain amount of mechanical damage to the coated particles can be expected.

A method of separating the PyC coated UC_2 particles from samples taken from the production line has been developed and is currently being used to determinute the extent of the mechanical damage problem in the NERVA fuel production process. The particles may be separated intact and with an efficiency of 95 to 99 per cent from the dry mix, wet mix, ground mix or the extruded, uncured element. The purpose of the separation is to determine:

1) If particles are mechanically damaged in production before the curing stage; and, if it occurs, then determine

2) at what process step or operation the damage occurs, and

3) the fraction of the particles damaged.

The separation of the varcum is accomplished by dispersing the mixes in acetone and filtering the solids from the acetone. This is repeated three times to completely wash the varcum from the mix. The solids are then dried in a low low temperature furnace (150°C).

The fuel particles are separated from the carbon particulates by sedimentation techniques using a high density brominated hydrocarbon, dibromoethane (ethylene bromide). The basis of the technique is the density difference between fuel particles and carbon particulates. In a liquid medium of density 2.17 g/cc, the carbon particulates of density 1.8 g/cc would be expected to float or disperse; and coated fuel particles of density 5.0 g/cc to settle rapidly by gravitational sedimentation. Several factors contributed to initial difficulties in applying this technique:

1) Relative wettability of carbons and fuel particles in liquid medium

2) Viscosity effects on buoyancy force of liquid medium.

3) Entrapment of air bubbles around fuel particles.

4) Adsorption of surface film of water on fuel particles, resulting in floating.

5) Agglomeration of graphite flour and thermax resulting in settling.

These problems were resolved by using the following steps:

1) Pre-heat fuel mix to approximately 150°C to remove adhered H_2O vapor.

2) Immerse fuel mixture in boiling ethylene bromide to liberate entrapped air from fuel particles. Time: 4 hours.

3) Filter dispersed particulates on Whatman No. 5, unwashed retentive filter paper, by decanting off liquid from settled fuel particles.

4) Wash precipitated fuel particles alternately with ethylene bromide and acetone to remove non-fuel impurities.

5) Dry and weigh fuel particles.

After the coated particles have been separated from the fuel mix, the separated fuel particles are leached in 1:1 HNO_3 - H_2O (distilled) at 90°C for four hours. Hagar boiling chips were used to minimize bumping effect during heating of solutions. After four hours the HNO_3 leach solution was filtered. The remaining particles were washed with distilled H_2O, and the washings added to the leach solution. The leach solution was then diluted to 100 ml in a volumetric flask and analyzed for uranium by means of a colorimetric spectrophotometer.

The results of analysis of leach solutions from eight steps in two separate runs have been obtained (see Table III). The analysis shows less than 0.4 w/o of the uranium is leachable from the NUMEC beads which were sampled. There is evidently little damage (cracking) of these particles in the steps leading to the extruded elements. Further chemical analyses are in progress to determine the quantity of fragmented coated particles which may be dispersed in the flour and thermax.

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TABLE III - Per cent of Uranium Leached from Processed NUMEC Fuel Particles*

Process Step	Lot 11111-1111 (% U Leached)	Lot 11112-1115 (% U Leached)	Lot 11113-1119 (% U Leached)
Dry blend	0.039	0.021	0.006
Wet mix	0.023	0.029	0.006
First chop			
Pass 1	0.023	0.053	0.007
Pass 2	0.19	0.047	0.14
First extrusion	0.15	0.078	0.09
Second chop			
Pass 1	0.23	0.123	0.36
Pass 2	0.32	0.068	--
Final extrusion	0.32	0.27	0.22

*Similar data obtained on Davison and 3M coated particles show 0.14 and 0.17% uranium leached after the final extrusion.

Coated Particle Fabrication - M. Monkelis and A. Feild

Facilities are available at WANL to pyrocarbon coat 10 gram batches of carbide particles in a small fluidized bed (5/8-inch diameter) coating furnace. The equipment is used to prepare special lots of material for exploratory investigations (e.g., thick PyC coatings or PyC coated mixed carbide particles) and to perform development studies of improved coated particles. Single and multiple PyC coatings have been prepared at 1200°, 1400°, and 2200°C with methane partial pressures varying from 0.01 to 0.2 atmosphere at total flow rates varying from 1700 to 2900 cc per minute. Coating rates varied from 5 to 80 microns per hour at each temperature. Further coating experiments are planned to achieve correlations of process variables and coating rates.

Alpha Count Analysis - L. Cadoff, W. Brizes, and L. Fleischer

An analytical expression has been derived to correlate alpha count data to the extent of migration in pyrocarbon coated UC_2 fuel particles. It has been evaluated by means of a comparison of alpha count rates and accurate measurements of the extent of migration obtained from microradiographs. The basic assumptions in the analysis are:

1) Spherical core and particle geometry.

2) A spherical migration zone moving out symetrically from the core into the pyrocarbon.

3) A uniform uranium concentration, homogeneously distributed in the migration zone.

4) A discontinuous drop in the uranium concentration to zero at the leading edge of the migration front, at a radius equal to "T". This approximation is an attempt to describe the metallographic and radiographic observations of a sharp demarcation between the migration zone and the unaffected PyC coating.

5) Only alpha particles generated in the migration zone can escape from the fuel particle.

The derived equation takes into account the factors of instrumental counting efficiency, the geometric probability of alpha escape in a spherical system and the alpha particle range as a function of the uranium concentration through which it passes on its escape path. The derived expression is extremely cumbersome and will be discussed in detail in a future report. Figure 1 shows the calculated relationship of alpha counts (dpm)/particle as a function of the radial extent of migration, "T". The values shown were calculated using nominal fuel particle parameters, e.g.,

Fuel particle radius, R = 75 microns; range of 4.75 MeV alpha in uranium, r_u = 12.55 mg/cm^2; range of 4.75 MeV alpha in carbon, r_c = 3.85 mg/cm^2; density of carbon, $_c$ = 1.6 g/cc; specific activity of enriched UC_2, λ = 133 dpm/mg; weight fraction of uranium in migration zone, W_u = 0.20.

Ideally then, if one knows the concentration of uranium (W_u) in the migration zone, the extent of migration, "T", in a single fuel particle can be obtained from the number of alphas counted. Conversely, if the extent of migration and the number of emitted alphas are measured, the value of W_u can be determined.

The problem of correlating the extent of migration with alpha counts, becomes more complex when we deal with a large number of particles. It is known that heat-treating a sample of fuel particles results in a distribution of the extent of migration among the particles. As can be seen from Figure 1, particles emitted from a few completely migrated fuel particles can heavily outweigh those emitted from many lesser migrated fuel particles. In addition, the number of alphas emitted is not a linear function of extent of migration. It is, therefore, obvious that, in general, no correlation exists between the measured number of alphas and the extent of migration that has been averaged over all fuel particles.

To demonstrate the validity of our equation, it is necessary to determine the distribution of migration in a sample of heat-treated fuel particles. The total number of alphas emitted by this sample per minute would then be the weighted sum of the product of the distribution function and the derived expression.

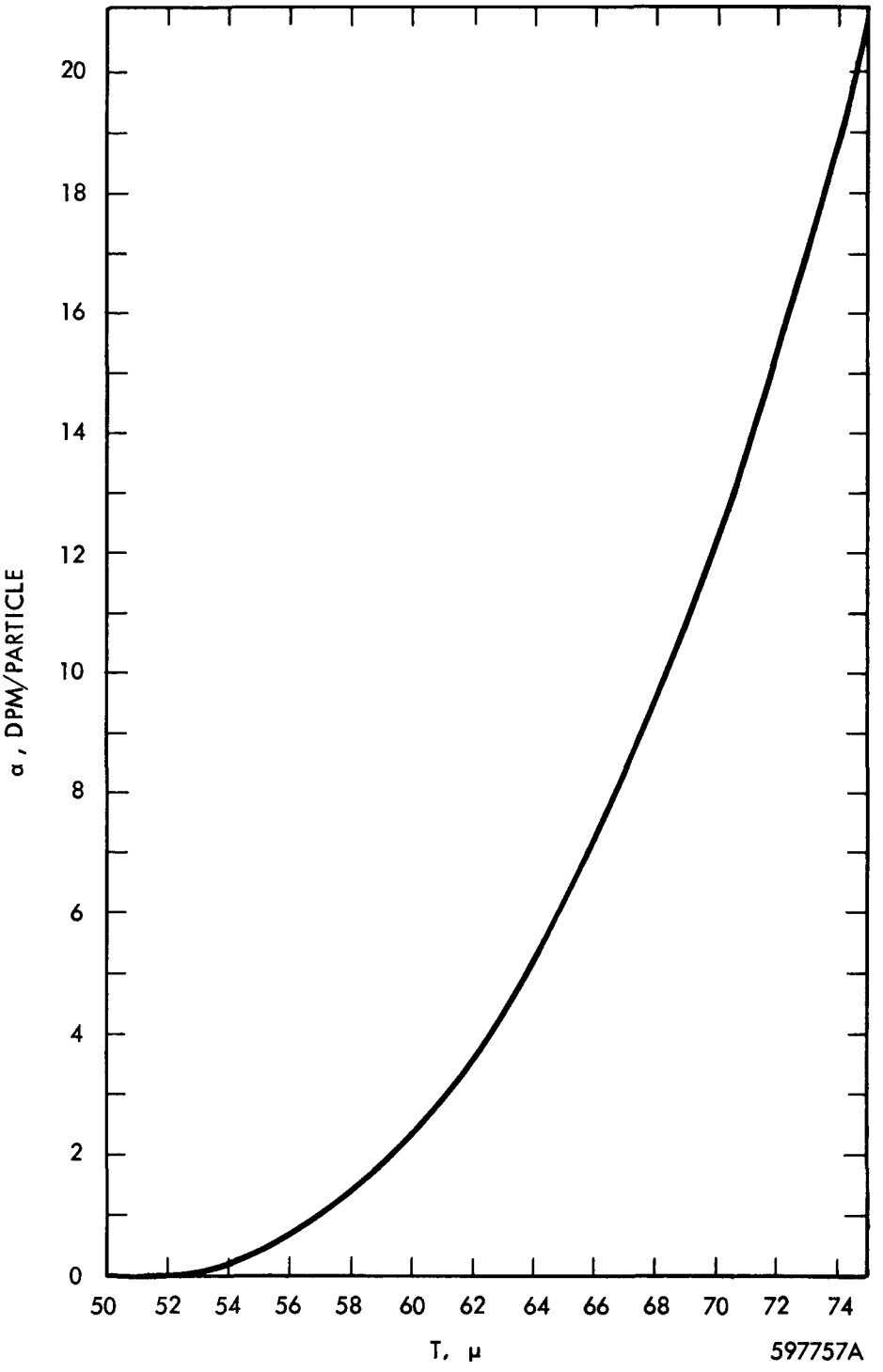


Figure 1 - Alpha Counts Emitted vs. Extent of Migration
(UC_2 particle radius = 50 μ, PyC coating thickness = 25 μ)

Samples of NUMEC and 3M enriched fuel particles (nominal radius = 75 μ) were heat treated for various temperatures and times as indicated in Table IV. Alpha count measurements were made on 0.05 gm samples using a flow counter with P-10 gas. Estimated counting efficiency is about 0.30. Measurements of extent of migration were made from microradiographs of 50 particles from each sample.

The experimental alpha-count data and the values calculated from the migration distribution function are shown in Table IV. Values of W_U, the weight fraction of uranium in the migration zone were determined from best fit considerations. For comparison purposes, calculated values of the number of alpha counts/gm based on the value of the extent of migration averaged over all particles measured, are also shown.

Table IV indicates that in general, at temperatures below 2400°C, very good agreement is achieved between experimental alpha values and those calculated on the basis of the distribution function. Values of the uranium concentration in the migration zone, W_U, were found to be about 0.20 and 0.10 for NUMEC and 3M particles, respectively, to give good correlation with experimental alpha values. Microprobe data obtained on the uranium concentration in the migration zone of the same lot of NUMEC particles confirms that the value of W_U is approximately 0.2. Microprobe data is not available on the uranium concentration in 3M particles.

The correlation using an averaged value of the extent of migration is in error at all temperatures. This error can be traced to the fact that a non-linearity exists between alpha counts and extent of migration.

At 2400°C, the particle migration behavior is inhomogeneous. The migration zone is now comprised of large discrete granules of UC_2 embedded in the PyC coat. It is apparent that an equation which assumes a uniform uranium concentration in the migration zone is not applicable for this type of behavior.

TABLE IV - Comparison of Experimental and Calculated Values of α Counts on PyC Coated Fuel Particles

Supplier	Heat Treatment Schedule	Experimental α counts/ min gm	Calculated[1] α counts (dpm)/ min gm	Calculated[2] α counts (dpm)/ min gm	Wt. Fraction of Uranium in Migration Zone
NUMEC	as received	3,000	6,500	---	0.20
	2000°C, 1 hr.	36,800	21,000	8,200	
	2100°C, 1 hr.	34,500	26,200	8,200	
	2200°C, 1 hr.	48,300	54,500	19,500	
	2300°C, 1 hr.	57,200	55,000	19,500	
	2400°C, 1 hr.	1,200,000	275,000	581,000	
3M	as received	3,600	582	---	0.10
	2100°C, 6 hr.	84,250	83,400	72,500	
	2200°C, 6 hr.	149,400	125,500	107,000	
	2300°C, 6 hr.	153,000	129,200	107,000	

(1) based on migration distribution function

(2) based on averaged extent of migration

It may be concluded that:

1) An equation has been derived which adequately describes the relationship between alpha counts emitted from a coated fuel particle and the extent of fuel migration provided that the migration behavior is uniform.

2) Alpha count measurements combined with the experimentally determined migration distribution function, may permit determination of the concentration of uranium in the migration zone.

3) The use of alpha-count measurements on a large sample of fuel particles, as a tool in the evaluation of the average extent of migration can yield misleading results. This is because the alpha values obtained are so dependent on the migration distribution in the sample.

Behavior of Coated Particles with Molten Cores - M. Tobin and W. Brizes

Nuclear rocket applications of fueled graphite require nominal maximum fuel element temperatures of the order of 2200°-2300°C.

Hot channel analysis of the reactor core indicates that a considerable volume of the fuel will be required to operate at temperatures above 2500°C. Thus, for fuel elements containing pyrocarbon coated UC_2 particles, some of the cores will be molten during reactor operation.

Most of the recent studies of the behavior of pyrocarbon coated UC_2 particles has been limited to the temperature range between 1900°-2300°C. Coated particles are now commercially available with excellent migration resistance at 2300°C for four hours. Consideration is now being directed towards the development of migration resistant pyrocarbon coated UC_2 particles at temperatures above the melting point of UC_2. Preliminary data will be presented on experiments involving molten core particles.

Limited studies of molten core operation on UC_2 particles with approximately 25 microns of duplex (1400° and 2200°C) coatings indicate severe migration at 2500°C for 1/2 hour (see Figure 2). Similar duplex coatings approximately 50 microns thick were deposited on Davison UC_2 cores. For comparison, a 50 micron

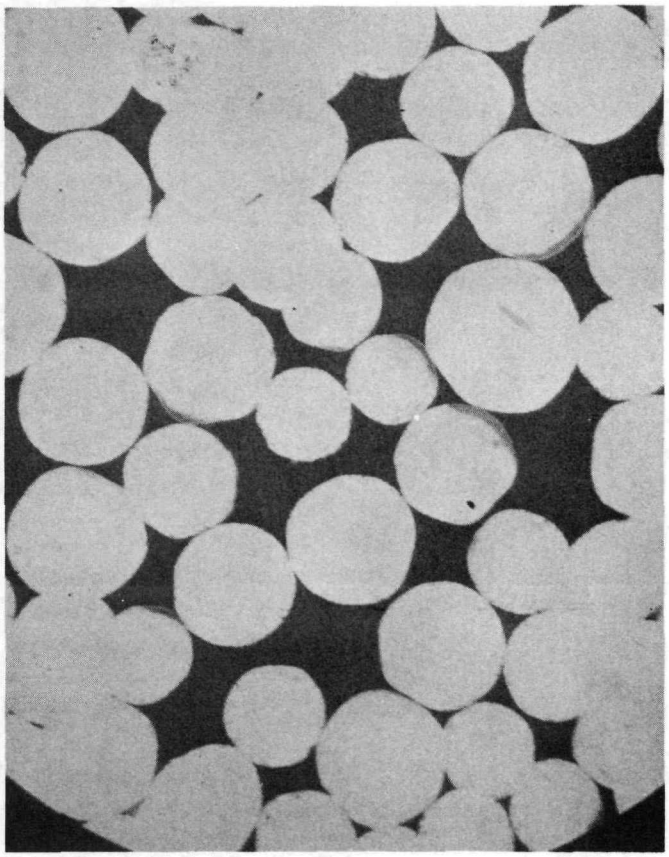


Figure 2 - Microradiograph of 3M Pyrocarbon Coated Particles
(Lot 588, see Table I) after 1/2 Hour at 2500°C

thick coating deposited at 1400°C was also prepared on Davison cores. The results of high temperature heat treatment on these coated particles are shown in Figures 3 and 4. Comparison of the behavior of the 25 and 50 micron duplex and 50 micron single coating indicates:

1) Increasing duplex coating thickness improves uranium retention for molten core operation.

2) Duplex coating offers greater resistance to uranium migration than the same thickness coating deposited at 1400°C.

The observed results may be examined in terms of the expected behavior of UC_2 and pyrocarbon as they are heated above the melting point of UC_2:

1) UC_2 ($UC_{1.9}$) dissolves carbon as it approaches melting

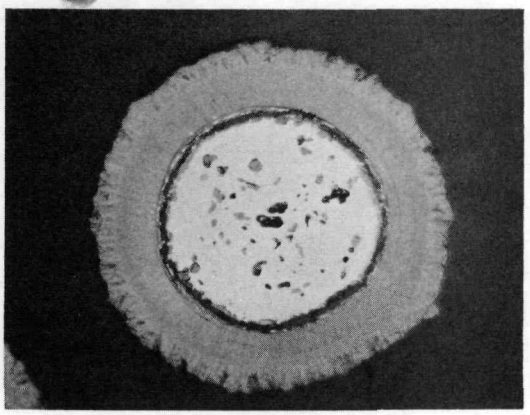
2) When melting occurs the UC_2 expands and dissolves carbon until an equilibrium composition is attained.

3) The process of thermally activated ordering of the pyrocarbon begins throughout the coating.

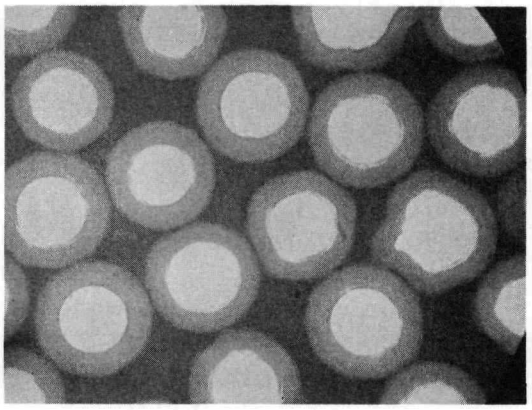
4) The pyrocarbon dissolves uranium. The uranium probably accelerates the ordering reaction.

In terms of the phenomena expected above the UC_2 melting point, a migration resistant pyrocarbon coating must be capable of absorbing the UC_2 solid to liquid volume change; the pyrocarbon coating must be thick enough to provide the carbon required by the liquid UC_2 solubility; and sufficient highly ordered pyrocarbon coating must remain to resist the migration of uranium at the new liquid-solid interface. Thus, the observed results on the 25 and 50 micron coatings are generally consistent with the expected behavior.

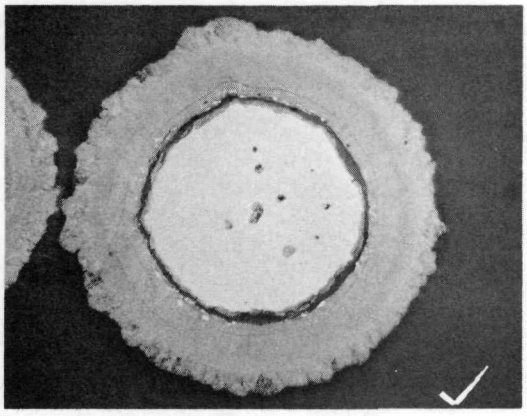
Finally, it has been observed that coarse graphite flakes (or blocks) form in molten UC_2 in contact with carbon. The quantity of the coarse graphite flakes found within or on the surface of UC_2 generally increases with time and temperature. It appears that the graphite flakes form at constant temperature by solution of carbon (such as pyrocarbon or lamp black) and precipitation of graphite. The net result of



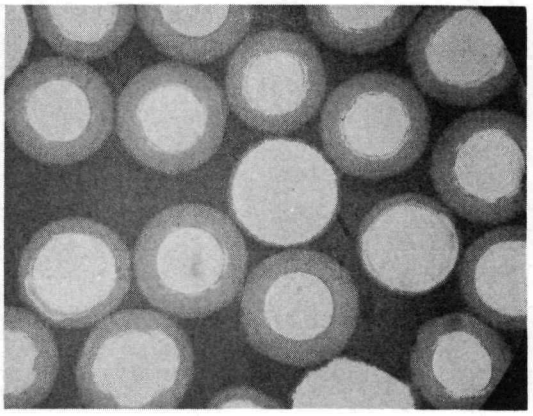
A 2300°C - 4 hours



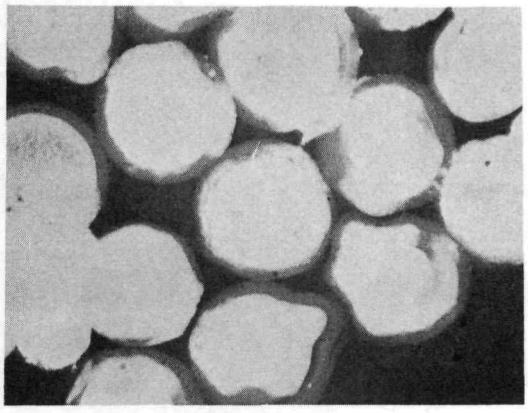
B 2300°C - 4 hours



C 2500°C - 1/2 hour

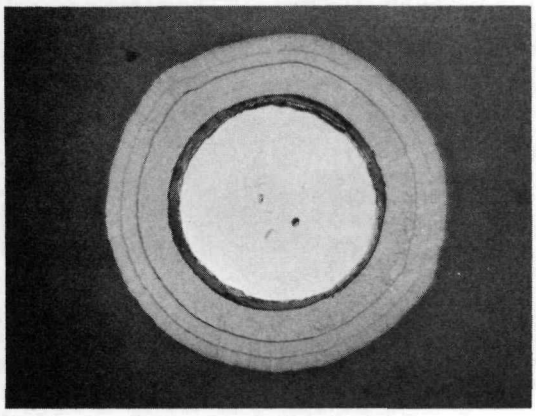


D 2500°C - 1/2 hour

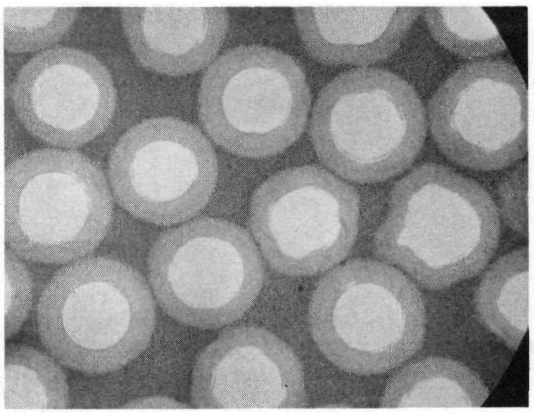


E 2600°C - 1/2 hour

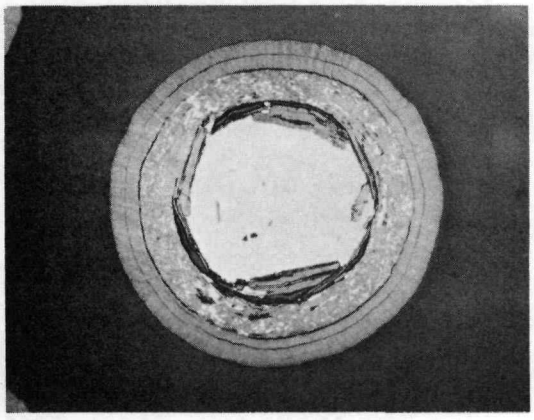
Figure 3 - Photographs of Duplex Pyrocarbon Coated (50 microns thick) UC_2 Particles after Indicated Heat Treatments



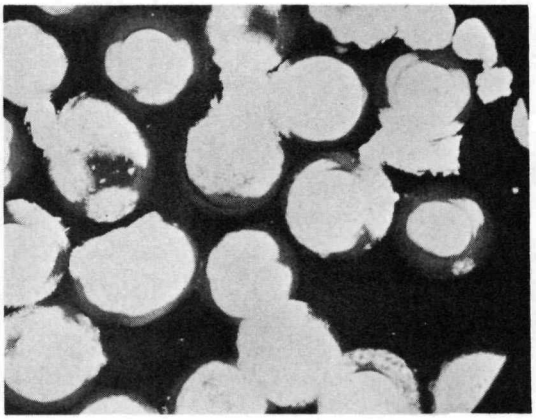
A 2300°C - 4 hours



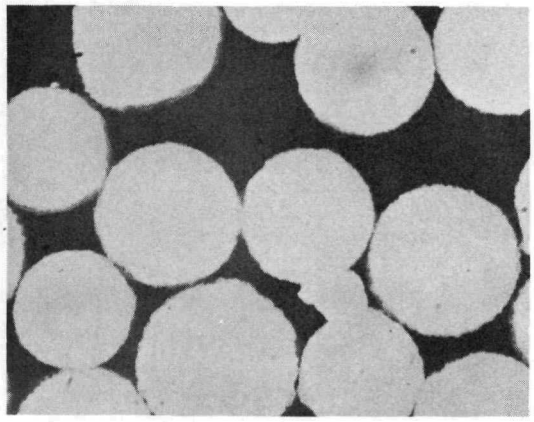
B 2300°C - 4 hours



C 2500°C - 1/2 hour



D 2500°C - 1/2 hour



E 2600°C - 1/2 hour

Figure 4 - Photographs of Pyrocarbon Coated (50 microns thick) UC_2 Particles after Indicated Heat Treatments

the reaction is the transformation of carbon to graphite. This result indicates that the solubility of carbon in molten UC_2 is greater than that of graphite. Further work is required to confirm these preliminary results.

Pyrocarbon Coated Mixed Carbide Particles - W. Brizes

In the ternary system, involving C, U, and refractory-metal carbides (such as Zr, Nb, Ta, or Hf), there is a region where the mixed carbide is stable with carbon* (see Figure 5 for example). Alloys of this type appear favorable for application in pyrocarbon coated particles since UC_2, which is known to severely migrate through pyrocarbon coatings, is not thermodynamically stable for certain compositions and temperatures. For this reason alloys of 25 UC-75 ZrC and 10 UC-90 ZrC have been made into 100 micron spherules and pyrocarbon coated (25 microns of duplex coating, 1400° and 2200°C). The particles were given migration tests at 2300°C for four hours and 2500°-2800°C for 1/2 hour. Alloys where UC_2 was not thermodynamically stable showed superior migration resistance. Photomicrographs and microradiographs of these tested particles are given in Figures 6, 7, 8, and 9.

Figure 10 is a plot of the (U, Zr)C solid solution in equilibrium with UC_2 as a function of temperature as determined both experimentally and thermodynamically by Benesovsky and Rudy. As can be seen in Figure 10, the 10 UC-90 ZrC does not form UC_2 until approximately 2600°C. This is a stable alloy and has a melting point of approximately 2750°C.

Limited migration is observed in the 10 UC-90 ZrC core particles, as shown in Figures 7 and 8 at 2500° and 2600°C for 1/2 hour heat treatment times. However, at 2700°C, the migration is quite pronounced. These observations are in good agreement with the results of Benesovsky and Rudy shown in Figure 10.

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* Benesovsky and Rudy, Planseeberichte fur Pulvermetallurgie 9, (1961), 65.

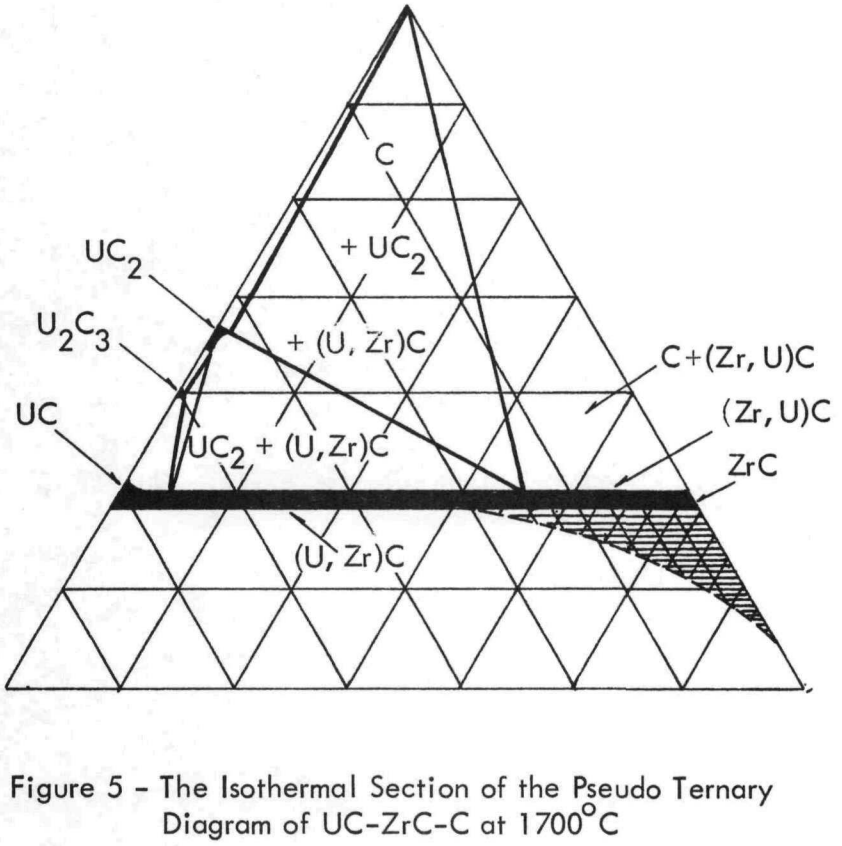
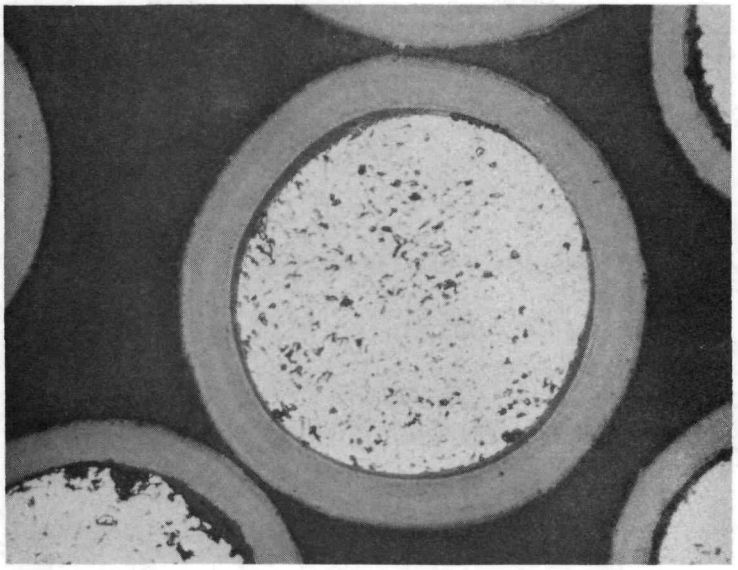
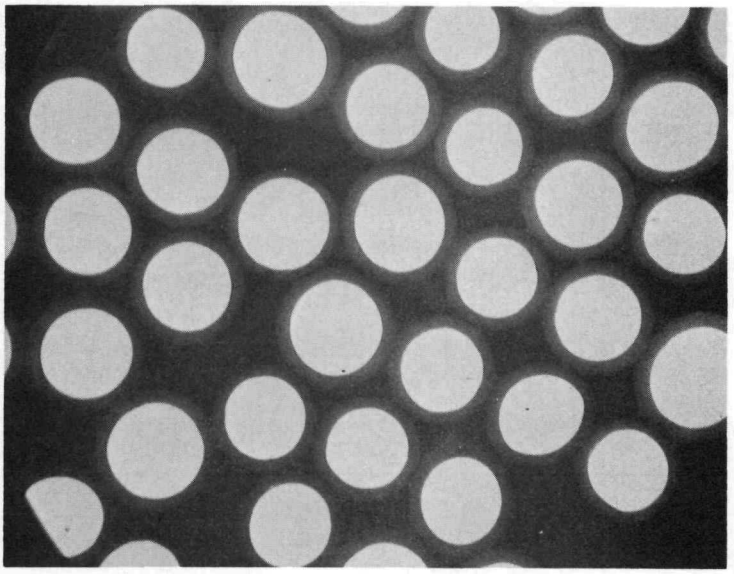


Figure 5 - The Isothermal Section of the Pseudo Ternary Diagram of UC-ZrC-C at 1700°C

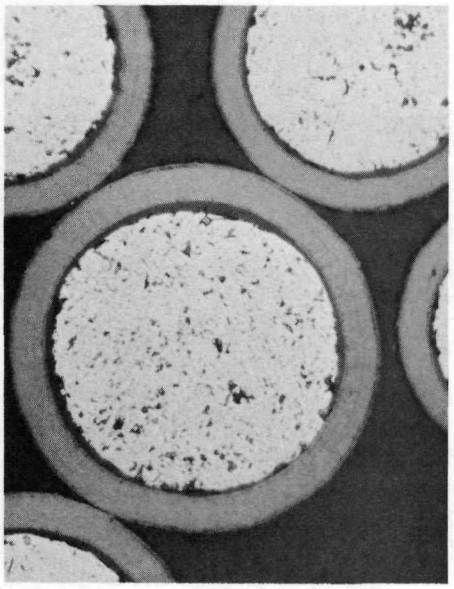


A - 400 X

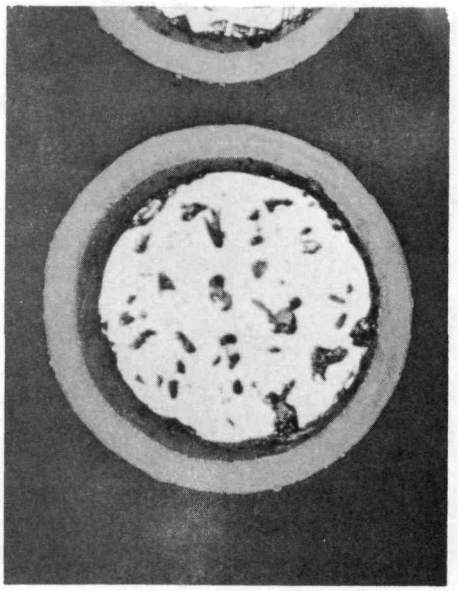


B - 100 X

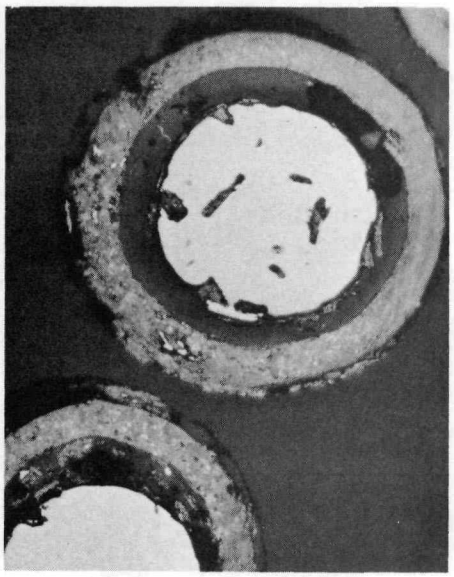
Figure 6 - Photomicrograph (A) and Microradiograph (B) of As-coated 10 UC-90 ZrC Particles



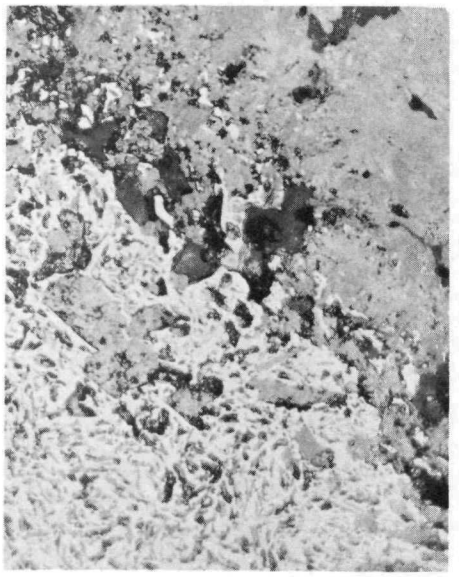
A 2500°C



B 2600°C

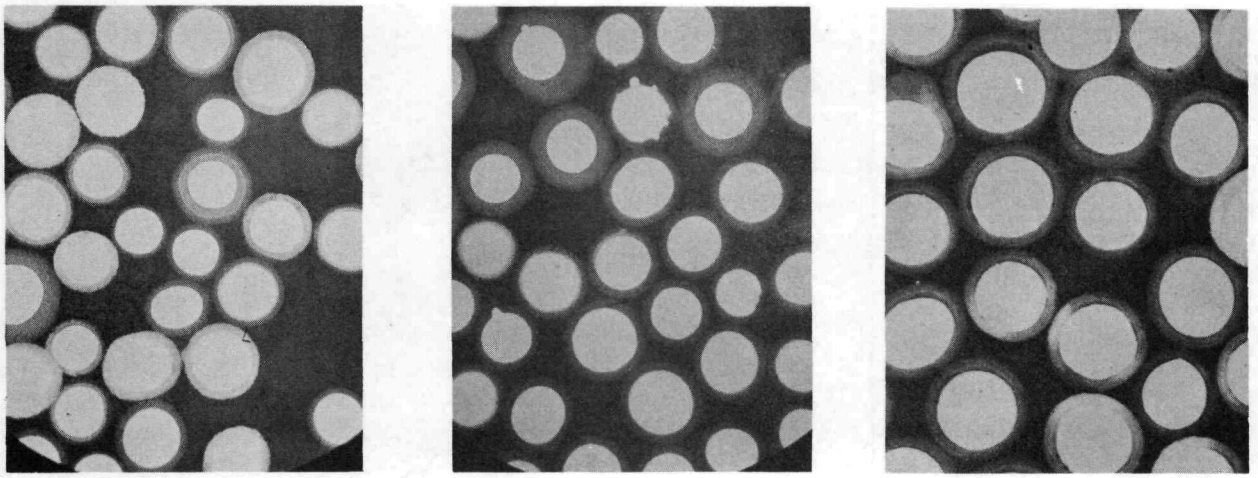


C 2700°C



D 2800°C

Figure 7 - Photomicrographs of Coated 10 UC-90 ZrC Particles after 1/2 Hour Treatment at Indicated Temperatures (400 X)

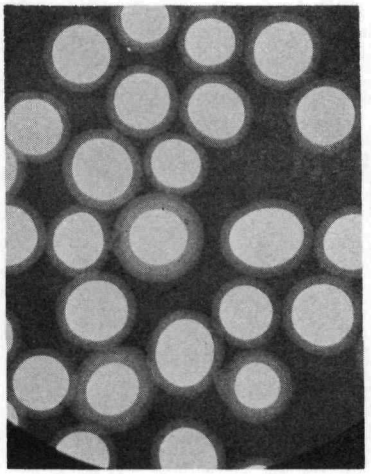


A 2300°C - 4 hours B 2500°C - 1/2 hour C 2600°C - 1/2 hour

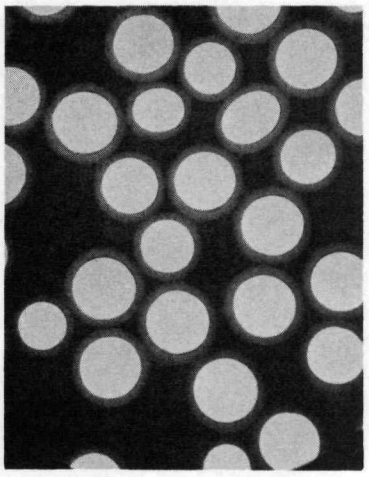
2500C - 2600C

D 2700°C - 1/2 hour E 2800°C - 1/2 hour

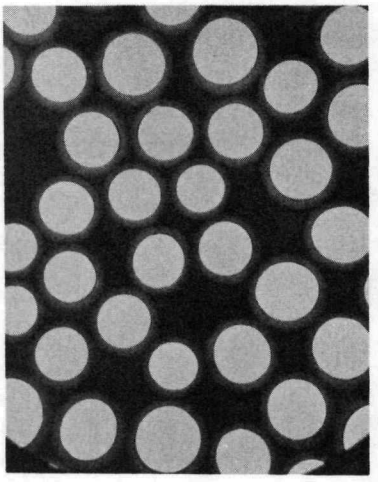
Figure 8 - Microradiographs of Coated 10 UC-90 ZrC Particles after Treatments at Indicated Temperatures and Times (100 X)



25 UC-75
As Coated

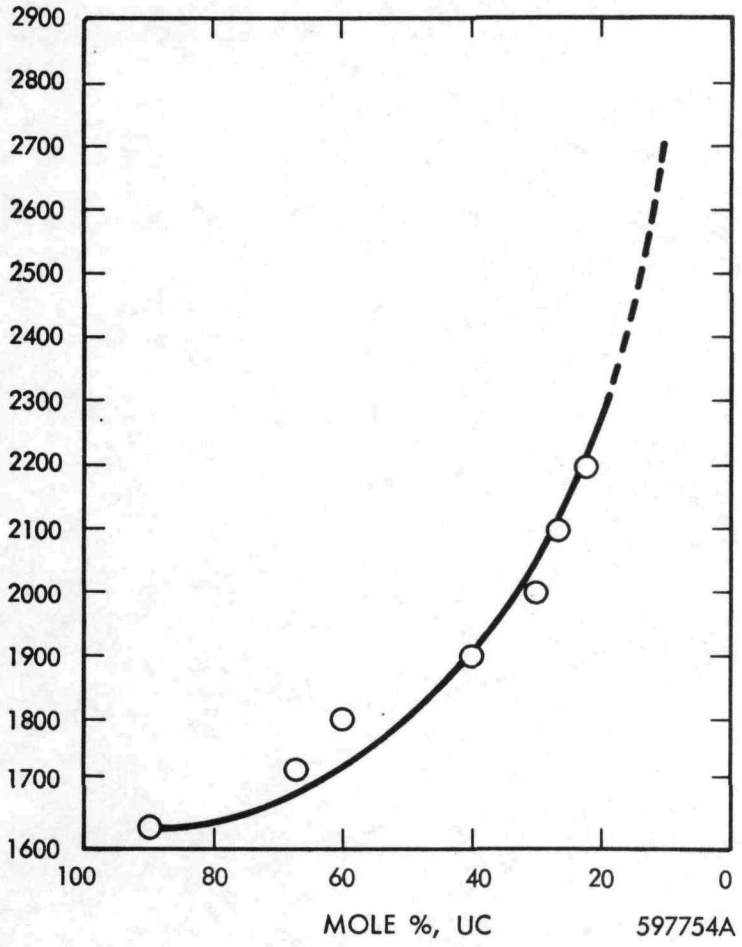


2300°C - 4 hours



2500°C - 1/2 hour

Figure 9 - Microradiographs of Coated ~~25~~ 10 UC-75 ZrC before and after Indicated Treatments (100 X)



BELOW CURVE IS REGION OF (Zr, U)C + C,

ABOVE CURVE (Zr, U) C DECOMPOSES TO FORM UC_2

Figure 10 - Decomposition Temperatures for the Formation of UC from (Zr, U)C + C Alloys

Table V - Electron Probe Results Obtained on UC-ZrC Coated Particles*

(Data of Benesovsky, Theisen, and Stecher)

Alloy Composition		Extent of Migration**			
		Uranium	Distance	Zr	Distance
(Mole Per Cent)	(Weight Per Cent)	(w/o)	(microns)	(w/o)	(microns)
ZrC	88.4 Zr			0	1
10 UC-ZrC	20.2 U - 69.6 Zr	0.2	8	0.15	5
30 UC-ZrC	48.5 U-43.3 Zr	22	2	33.7	2
		11.5	4	12.9	4
		2.6	8	0.9	8
		0.2	15	0.1	15
65 UC-ZrC	77.9 U-16.1 Zr	25.2	2	29.5	2
		4.9	8	0.8	8
		2.1	10	0.5	10
		0.25	30	0.1	30
		0.2	35	0	35
		0.2	80	0	80

* Particles were coated at 2000°C using methane. Coating thickness was greater than 200 microns.

** Particles were heat treated to 2000°C for 100 hours in a vacuo.

PyC coated mixed UC-ZrC alloy fuel particles were also prepared and heat treated for 100 hours at 2000°C in vacuum by Benesovsky, et. al.*

The results obtained by electron probe examination of the heat treated particles are given in Table V. It is apparent that migration of both uranium and zirconium takes place in the samples containing 30 mole per cent UC and greater. The indicated solubility of U and Zr in pyrocarbon coatings are 0.2 and 0.1 weight per cent, respectively.

Steady-state Irradiation of NERVA Fuel Material - D. Jacobs and C. Glassmire

Introduction

The first phase of the NERVA fuel irradiation program is in progress. Its purpose is to define the various problem areas which will require detailed study during the remainder of the program. The preliminary results of this study will be described.

Experimental Procedure

A total of twelve fuel pellets were irradiated. The pellets and their associated control samples were machined from fully loaded (417 mgU^{235}/cm^3) NERVA fuel elements. Each pellet received one of the following pre-irradiation treatments:

1) heated in vacuum to 2400°C for 0.5 hour, then held at 100°C in 100 per cent relative humidity for one day.

2) machined from a NERVA fuel element which had been subjected to a 2.75 minute hydrogen corrosion test at 2500°C (surface temperature).

3) no pre-irradiation treatment.

After their treatment, the pellets and their corresponding control samples were stored in a conventional dessicator. No special precautions were taken to protect the pellets from ordinary room air during normal handling.

The irradiations were conducted within the Trail-Cable Facility of the

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* Benesovsky, Theisen, and Stecher, Planseeberichte fur Pulvermetallurgie, II, (1963), 146.

GETR. The experimental parameters are given in Tables VI, VII, and VIII. The burnup and flux wire analyses are, as yet, incomplete and consequently, all parameters were calculated on the basis of the position of the capsules within the Trail-Cable Facility.

Experimental difficulties precluded the direct measurement of temperature. Consequently, the temperatures which are given were calculated from the flux estimates. It should be noted that the reported temperatures may be higher than will be confirmed by the burnup and flux-wire analysis.

Experimental Results

The results of the post-irradiation examinations are given in Tables VI, VII, and VIII. To date, post-irradiation metallography has been completed only on pellets T-T4B, T-T4M, and T-T4T. However, it is believed that the microstructure of the other pellets resembles that of the T-T4 pellets having the corresponding pre-irradiation treatment.

The control samples were held at temperatures corresponding to the appropriate in-pile temperatures for times corresponding to the duration of exposure. In all cases, the control samples retained their structural integrity and dimensions.

Three pellets, machined from a hydrogen corroded element, were heated to 2500°C at 10°C/sec, 56°/sec and 900°C/sec. In all cases, the pellets retained their structural integrity. However, the pellet heated at the greatest rate suffered a 1.32% diametric expansion and a 0.90% longitudinal expansion.

Discussion of Results

Figures 11 and 12 show the general appearance of the pellets from capsules T-T4 and T-T5. Figures 13, 14, and 15 are photomicrographs of the fuel pellets from capsule T-T4 and their control samples.

The similarities in the behavior of the hydrogen corroded pellets and the hydrolyzed pellets are striking. It is significant that these were the pellets in which fuel migration had occurred prior to irradiation.

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Table VI - Preliminary Test Results - Pellets: T-T3B, T-T4B, T-T5B, and T-T6B

Pre-irradiation treatment: 0.5 hr at 2400°C, then held one day at 100°C in 100% relative humidity.

Pellet	Pre-irradiation Condition	Mean Flux (n/cm^2-sec)	Exposure Time (min.)	Mean Burnup ($fiss/cm^3$)	Mean C. L. Temp. (°C)	Post-irradiation Condition
T-T5B	Good structural integrity. NbC liner intact. Some fuel migration. PyC coatings intact.	3.5×10^{13}	130.8	1.4×10^{17}	2020	Pellet extremely friable; broken while still in capsule. NbC liner adhered no broken channels but covered with network of cracks.
T-T6B	Same as T-T5B.	3.6×10^{13}	270.0	2.9×10^{17}	2020	Pellet broken into small pieces, almost a powder.
T-T4B	Same as T-T5B.	4.6×10^{13}	100.2	1.4×10^{17}	2400	Similar to T-T5B. Microscopically, the sample was covered with a network of cracks. PyC coating cracked and broken. Matrix cracks associated with broken PyC coatings.
T-T3B	Same as T-T5B.	4.7×10^{13}	25.2	3.5×10^{16}	2420	Similar to T-T5B.

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Table VII - Preliminary Test Results - Pellets: T-T3M, T-T4M, T-T5M, and T-T6M

Pre-irradiation treatment: None

Pellet	Pre-irradiation Condition	Mean Flux (n/cm^2-sec)	Exposure Time (min.)	Mean Burnup ($fiss/cm^3$)	Mean C. L. Temp. (°C)	Post-irradiation Condition
T-T5M	Good structural integrity. No fuel migration. PyC coatings intact. No NbC liner.	3.2×10^{13}	130.8	1.2×10^{17}	1860	Pellet intact and showed good structural integrity. Pellet underwent no dimensional changes.
T-T6M	Good structural integrity. No fuel migration. PyC coatings intact. NbC liner intact.	3.3×10^{13}	270.0	2.6×10^{17}	1980	Similar to T-T5M.
T-T4M	Same as T-T6M.	4.1×10^{13}	100.2	1.3×10^{17}	2220	Similar to T-T5M. Microscopically, PyC coatings intact. No fuel migration. NbC liner intact.
T-T3M	Same as T-T6M.	4.2×10^{13}	25.2	3.1×10^{16}	2250	Similar to T-T5M.

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Table VIII - Preliminary Test Results - Pellets: T-T3T, T-T4T, T-T5T, and T-T6T

Pre-irradiation treatment: Machined from element which had been given a 2.75 minute hydrogen corrosion test, surface temperature: 2500°C.

Pellet	Pre-irradiation Condition	Mean Flux (n/cm^2-sec)	Exposure Time (min.)	Mean Burnup ($fiss/cm^3$)	Mean C. L. Temp. (°C)	Post-irradiation Condition
T-T5T	Good structural integrity. NbC liner intact. Some fuel migration. PyC coatings intact.	2.8×10^{13}	130.8	1.1×10^{17}	1700	Pellet was initially intact but broke during normal handling. Time cracks on surface. NbC liner covered with network of cracks.
T-T6T	Same as T-T5T.	3.0×10^{13}	270.0	2.4×10^{17}	1740	Pellet intact. Fine cracks on surface. No NbC liner visible. Increase in diameter: 4.3%, increase in height: 3.4%.
T-T4T	Same as T-T6T.	3.6×10^{13}	100.2	1.1×10^{17}	2040	Pellet intact. Fine cracks on surface. Increased in diameter: > 4%. Microscopically, sample covered with network of cracks. Sample ultimately broke. PyC coatings cracked and broken. Matrix cracks associated with broken PyC coatings.
T-T3T	Same as T-T6T	3.7×10^{13}	25.2	2.7×10^{16}	2080	Similar to T-T6T. Increase in diameter: 4.3 %.

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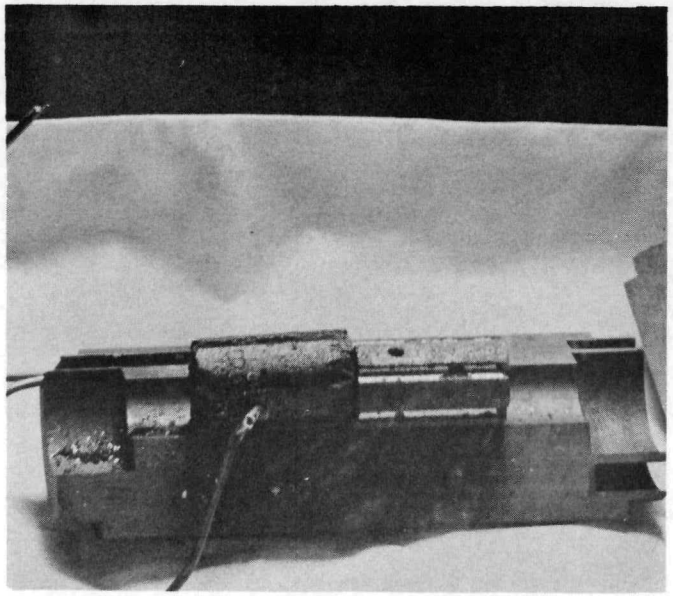
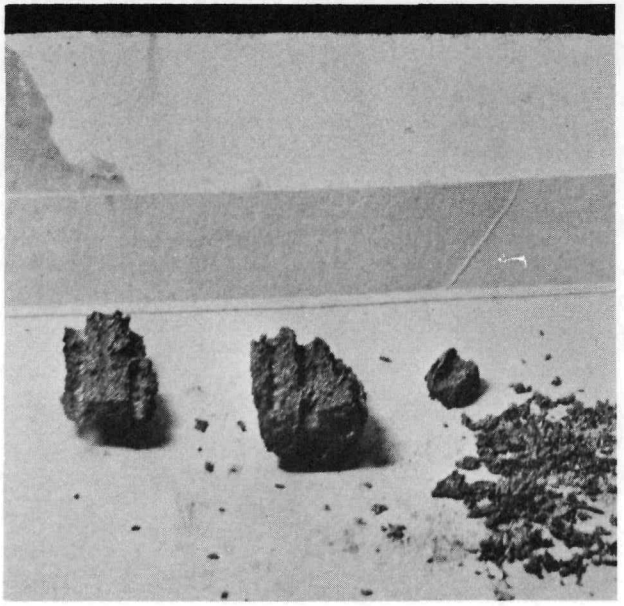


(a)



(b)

Figure 11

Pellets from capsule T-T4

(a) Left to right: (1) T-T4 T - machined from a hydrogen corroded fuel element. Irradiated at 2040°C for 100.2 minutes. Burnup: 1.1×10^{17} fiss/cm^3. (2) T-T4 M - received no pre-irradiation treatment. Irradiated at 2220°C for 100.2 minutes. Burnup: 1.3×10^{17} fiss/cm^3.

(b) T-T4 B - Hydrolized fuel. Irradiated at 2400°C for 100.2 minutes. Burnup: 1.4×10^{17} fiss/cm^3.

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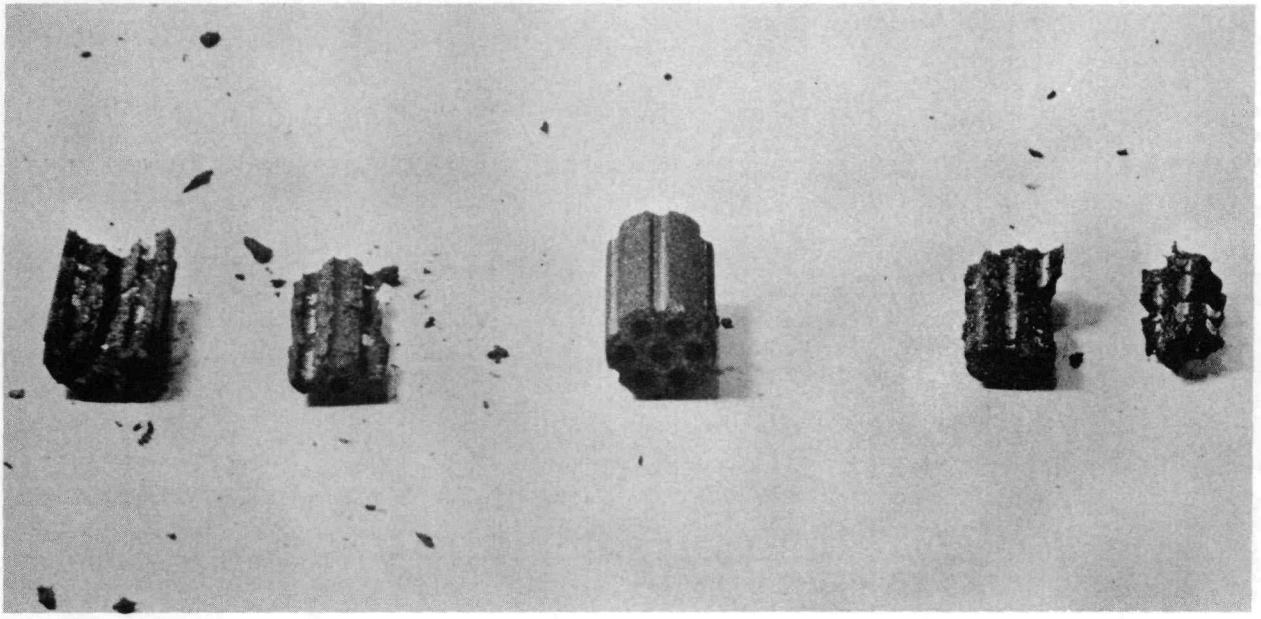

Figure 12

Pellets From Capsule T-T5. Left to Right:

(a) T-T5 T - Machined from hydrogen corroded fuel element. Irradiated at 1700°C for 130.8 minutes. Burnup: 1.1×10^{17} fiss/cm^3.

(b) T-T5 M - Received no pre-irradiation treatment. Irradiated at 1860°C for 130.8 minutes. Burnup: 1.2×10^{17} fiss/cm^3.

(c) T-T5 B - Hydrolyzed fuel. Irradiated at 2020°C for 130.8 minutes. Burnup: 1.4×10^{17} fiss/cm^3.

(a)

(b)

(c)

Figure 13

Samples which were held at 2400°C in vacuum for 0.5 hour and then stored for 1 day in 100% relative humidity at 100°C.

(a) After hydrolysis treatment (200X)

(b) After irradiation at 2400°C for 100.2 minutes.
Burnup: 1.4×10^{17} fiss/cm^3 (100X)

(c) After being held at 2400°C for 100.2 minutes.

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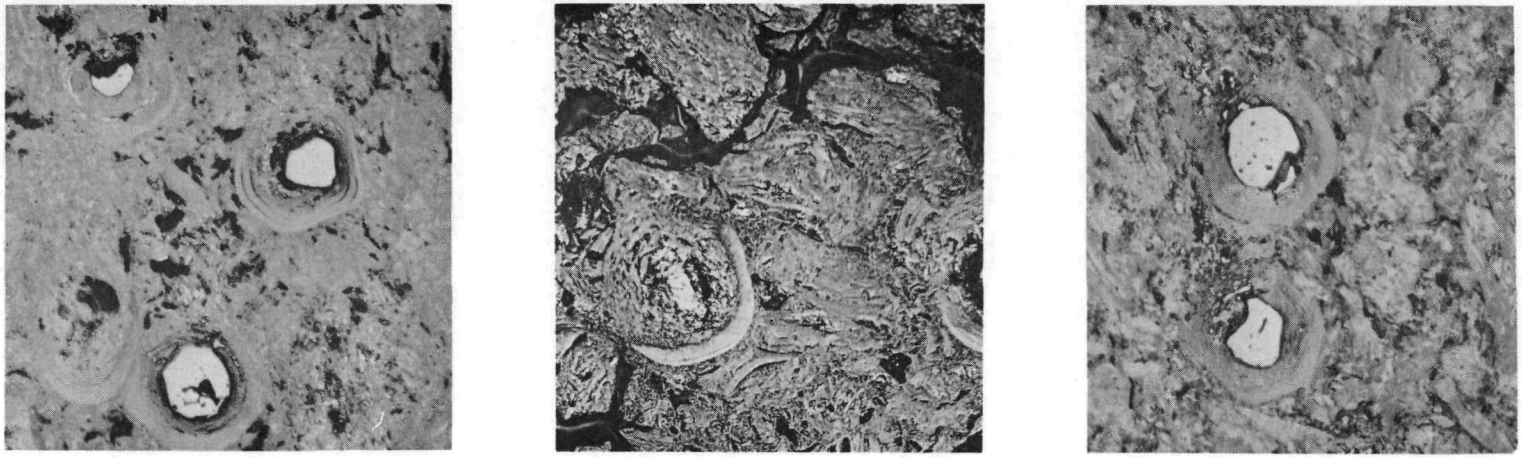

(a) (b)

Figure 14

Samples which were machined from a hydrogen corroded element.

Test Conditions: 2.75 minutes with 2500°C surface temperature

(a) After hydrogen corrosion test (200X)

(b) After irradiation at 2040°C fur 100.2 minutes.
Burnup: 1.1×10^{17} fiss/cm^3.

(c) After being held at 2040°C for 100.2 minutes.

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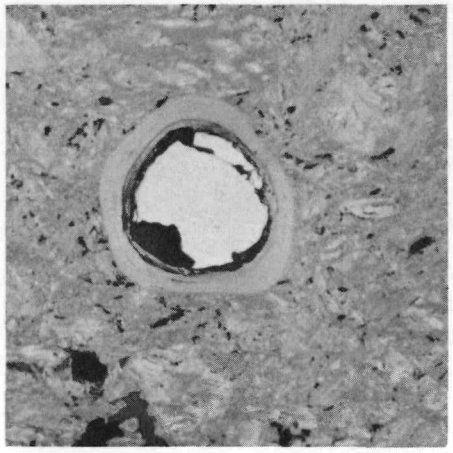

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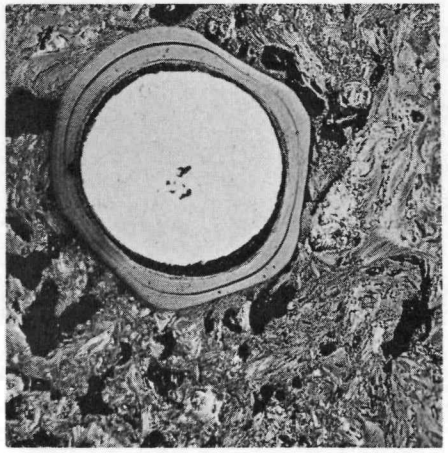

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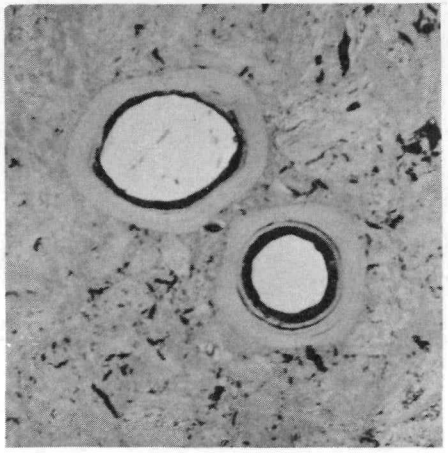

(c)

Figure 15

Samples which received no pre-treatment

(a) Unirradiated (200X)

(b) After irradiation at 2220°C for 100.2 minutes.
Burnup: 1.3×10^{17} fiss/cm^3 (250X)

(c) After being held at 2220°C for 100.2 minutes (200X)

It is believed that the hydrogen corroded samples were hydrolyzed as the result of their intermittent handling in air. However, the extent of hydrolysis in these samples should have been less than that in the intentionally hydrolyzed pellets. Note that at corresponding in-pile conditions the intentionally hydrolyzed pellets were more severely damaged than the hydrogen corroded pellets, (e.g., T-T4T and T-T5B). Clearly, the hydrolysis contributed to the observed in-pile behavior.

However, the effect of irradiation cannot be ignored. The severity of the damage increased with burnup (e.g., T-T5B, T-T6B, and T-T4B). Furthermore, it is obvious from the behavior of the control samples that the observed in-pile effects were not induced solely by the elevated temperatures or heatup rates.

It is significant that the material which received no pre-treatment prior to irradiation suffered no damage during the test. Clearly, radiation induced and/or accelerated damaging reactions take place in the NERVA fuel in which fuel migration and hydrolysis had occurred.

In future irradiations the attempt will be made to differentiate between the effects of hydrolysis and fuel migration. ~~All~~ Experiments of this nature ~~is~~ are of considerable importance since the results will ascertain the restart capability of the NERVA core during ground testing.