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AEC RESEARCH AND DEVELOPMENT REPORT

HW-83980

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MASTER

**PROGRESS REPORT:
FUELED GRAPHITE STUDIES,
April, May, June, 1964**

HANFORD LABORATORIES

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C-91, Nuclear Reactors
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TABLE OF CONTENTS

INTRODUCTION	1
SUMMARY AND CONCLUSIONS	2
DISCUSSION OF TESTS AND RESULTS: MATERIAL CHARACTERIZATION	3
DISCUSSION OF TESTS AND RESULTS: JOINING	5
DISCUSSION OF TESTS AND RESULTS: COATING ADHERENCE	13
DISCUSSION OF TESTS AND RESULTS: FUEL MIGRATION	30
ACKNOWLEDGEMENTS	36
APPENDIXES: SAMPLE PREPARATION	37
A. MATERIAL CHARACTERIZATION	37
B. COATING ADHERENCE	38
C. FUEL MIGRATION	39
DISTRIBUTION	40

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Rover Graphite Fuel	1
2	Photomosaic of One-Third Cross Section of Unfueled Element No. 1686-AA-25-3	4
3	Photomosaic of One-Third Cross Section of Fueled Element No. M1410EA-3	5
4	Weld Joint Design Dimensions	6
5	Experimental Graphite Weld Cross Section	8
6	Graphite Weld Cross Section, Sensitive-Tint Photomicrograph	9
7	Graphite Weld Cross Section	10
8	Graphite Weld Cross Section, Sensitive-Tint Photomicrograph	11
9	Rover Graphite Materials	15
10	Polished and Cathodically Etched Surface of Unfueled Sample No. 1686-AA-25-3	16
11	Matrix-PyC Coating Interface of Fueled Sample No. M1410EA-3	17
12	PyC-UC ₂ Interface of Fueled Sample No. M1410EA-3	19
13	PyC-UC ₂ Interface of Fueled Sample No. M1410EA-3	20
14	As-Machined Outer Surface of Unfueled Sample No. 1686-AA-25-3	21
15	As-Reamed Coolant Channel Surface of Unfueled Sample No. 1686-AA-25-3	22
16	Leached-Uncoated Fueled Sample No. 45-4868	23
17	Uncoated Area of Unfueled Sample No. 01-1684-105	24
18	Area of Poor Coating Adherence: Fueled Sample No. 45-2181	25
19	PyC Particle Coating from Leached-Uncoated Fueled Sample No. 45-4868	27
20	PyC Particle Coating from Poorly Coated Fueled Sample No. 45-2181	28
21	Photomicrographs of Rover Graphite Surfaces	29
22	Photomicrographs of Coated Fuel Particles	32
23	Photomicrographs of Coated Fuel Particles in Various Stages of Migration	33
24	Hot Stage Reflection Sample Holder	34

PROGRESS REPORT:
FUELED GRAPHITE STUDIES,
April, May, June, 1964

INTRODUCTION

Research on graphite matrix-coated particle fuels in support of the Rover Project was initiated at Hanford during the fourth quarter of FY 1964. The purposes of this program on Rover fuel (Figure 1) are:

- (1) Establish the feasibility of joining fueled graphite to unfueled graphite by magnetic force welding
- (2) Study the problem of uranium migration through the pyrolytic carbon (PyC) coatings on the UC_2 particles
- (3) Investigate why the NbC coating does not adhere well to fueled graphite.

This report covers progress through June 30, 1964.

FIGURE 1
Rover Graphite Fuel

SUMMARY AND CONCLUSIONS

Joining

Development work to date has shown that at least partial bonding can be accomplished between Rover graphite sections by magnetic force welding. Evaluation of most joints produced has been by metallographic techniques. Some physical testing of welded joints was accomplished.

Examination of welded joints shows some deformation of fuel particles occurred in the joint area. In general, the PyC coatings appeared to have deformed plastically in the immediate weld area. PyC coatings in an area 0.5 to 2.0 mm away from the joint were fractured radially but were not significantly deformed. The UC₂ underwent brittle fracture in the immediate joint area and is found in clusters of small fragments. There is little evidence of UC₂ fracturing in the joint area where the PyC coatings were not deformed.

Improvement of the control and measurement of welding variables directed toward optimizing the uniformity of joint temperature and forging pressures is required for producing satisfactory joints on a reproducible basis.

Coating Adherence

Optical and replica electron microscopy techniques on both the polished and as-machined surfaces are capable of revealing useful information on the nature of the fueled and unfueled graphite. Boundaries between binder and filler residues and the effects of hydrochloric acid leaching and chloride vapor niobium coating of the surface are clearly evidenced. These techniques will definitely permit a systematic investigation of the relationship between the character of the graphite and coating adherence.

Fuel Migration

The primary approach used to investigate the problem of fuel migration has been to observe a cross-section sample directly in the electron microscope while heating to anticipated service temperatures. In general,

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3

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interpretation of these tests has been made difficult by the extreme roughening of the graphite surface and loss of image resolution due to carbon deposition within the microscope. However, techniques for handling the samples have advanced to the point where acceptable time-lapse motion pictures of high temperature reactions in the matrix have been obtained. Further studies of fuel migration or graphite-coating interactions by in-microscope experimentation appears promising.

DISCUSSION OF TESTS AND RESULTS: MATERIAL CHARACTERIZATION

Initially, studies were made to characterize the Rover materials on hand. Using metallographic techniques (Appendix A) developed at Hanford for graphite, 75X photomosaics of a one-third cross section of a fueled and an unfueled element were prepared (Figures 2 and 3).

Examination of the unfueled graphite (Figure 2) showed that some low density regions occur within the matrix areas away from the coolant channels. The fact that mandrel support spiders cause alignment or local densification is most evident between the upper left and middle left channels. The absence of cracking is apparent. The shape and degree of internal alignment of the graphitized Texas coke particles are typical of Cleves or Texas cokes used in nuclear graphites.

Low density areas were also examined in longitudinal sections and found to be elongated parallel to the channels. They do not, however, form a continuous crack in the regions examined.

Coke-particle alignment is not easily detected in the bright field mosaics of the transverse sections. Under sensitive-tint illumination however, a concentration of preferred alignment becomes apparent in the thinnest portions of the wall between the wall of the outer faces of the element and the first row of coolant channels. Coke-particle alignment throughout the matrix is also apparent in longitudinal sections.

The fuel particles in the fueled element (Figure 3) are well dispersed. Low-density regions are more scattered than in the unfueled material and the degree of coke-particle alignment appears to have been reduced.

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FIGURE 2

Photomosaic of One-Third Cross Section
of Unfueled Element No. 1686-AA-25-3

≈ 8X

Neg. 0641193

The UC_2 particles intersected below their center line on the prepared surface were removed during vibratory polishing leaving a shell of PyC surrounding a dark void. Within the dark void areas, cruciform light-to-dark patterns are observed at 75X although a considerable variation of intensity exists. The formation of this pattern with sensitive-tint light requires the presence of highly ordered carbon. This intensity variation could also indicate considerable bead-to-bead variation in pro-eutectic graphite at the UC_2 -PyC interface.

FIGURE 3

Photomosaic of One-Third Cross Section
of Fueled Element No. M1410EA-3

Neg. 0641232

$\approx 8X$

DISCUSSION OF TESTS AND RESULTS: JOINING

Welding Test Samples

The feasibility studies on magnetic force welding of fueled to unfueled graphite elements were limited to small sample sections machined from Rover fuel materials received from Los Alamos Scientific Laboratories (LASL). The welding test sample cross-sectional area was dictated primarily by the maximum capability of the existing magnetic force welder. The specific cross section used and the joint design

showing the most promise to date are detailed in Figure 4. The unfueled cap dimensions, with the exception of the weld joint, were established by electrode design and can be modified as required by the finished part design. These original sample dimensions did not, however, allow four-point bend testing of the joint, as proposed by LASL.

FIGURE 4

Experimental Weld Joint Design Dimensions

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Welding Process Development

The approach used for the preliminary welding development work was to attempt to duplicate the welding parameters (joint design, current, current density, weld time, and forging pressure) which previously produced satisfactory (metallurgical) joints on nuclear grade and isotropic raw coke graphite materials in the past. Weld processes developed for the above materials were not, however, adequate for joining Rover graphite due to the changes in test sample geometry and/or material.

A series of welding tests was then initiated to define the welding and bonding characteristics peculiar to the Rover material and test sample geometry. These tests were successful in outlining the basic welding parameters sufficiently to allow production of some small bonded areas as shown in Figures 5 and 6.

Attempts to further scope alternate weld processes within the equipment capability were discontinued when the first bonded areas were produced. Emphasis was narrowed to refining detailed welding techniques within the broad process outline established, to more thoroughly evaluate feasibility. Efforts along this line were successful in producing some joints with bonded areas, as shown in Figures 7 and 8.

Joint Evaluation

Essentially all joint evaluation has been by metallographic techniques. Those joints of particular interest were evaluated using the sensitive-tint photographic process. This process is of particular benefit in illustrating graphite because different orientations of reflecting surfaces are illustrated by a variation in color.

The most significant observation made from the sensitive-tint photographs, other than the detection of actual bonded areas, was the nature in which deformation of fuel particles occur. In general, the PyC coatings appear to have deformed plastically in the immediate weld area. The PyC coatings in an area 0.5 to 2.0 mm away from the joint were fractured radially but were not significantly deformed. The UC_2

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Magnetic Force
Butt Weld
0.240 in. OD
0.093 in. ID Tubing

Polaroid

≈ 10X

4L1019A

36X 4L1019B

36X

FIGURE 5

Graphite Weld Cross Section

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9

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4L1019A

75X

FIGURE 6

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Graphite Weld Cross Section
Sensitive-Tint Photomicrograph; Reference Figure 5

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Magnetic Force
Butt Weld

Polaroid

≈ 10X

4L1166A

36X 4L1166B

36X

FIGURE 7

Graphite Weld Cross Section

AEC-GE RICHLAND, WASH.

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4L1166B

75X

FIGURE 8

Graphite Weld Cross Section
Sensitive-Tint Photomicrograph; Reference Figure 7

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AEC-GE RICHLAND, WASH.

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underwent brittle fracture in the immediate joint area and is found in clusters of small fragments. There is little evidence of UC₂ fracturing in the joint area where the PyC coatings were not deformed.

Physical testing (tensile strength) of joints has been limited to only a few samples. The tensile tests which were performed were made by cementing the ends of weld samples to adaptors which fit an Instron tensile machine. (The four-point bend test, proposed by LASL, could not be used due to the design of the weld samples.) This method of attaching graphite to adaptors is used routinely at Hanford and experience has shown that the results obtained are comparable to those obtained by conventional means of attachment. The samples tested ranged in strength from 100 to 200 psi (based on total joint area). Metallographic examination of tensile samples after fracture, however, showed that the actual diffusion bond areas were quite small (less than 30%) or nonexistent. Representative tensile strength of joints will be difficult to obtain until a greater degree of reproducibility in the welding process can be achieved.

Work in the area of nondestructive joint quality testing has also been delayed primarily because of the lack of sufficient quantities of representative welded joints. A more comprehensive study in this area of the program will be possible with routine production of welded joints typical of those shown in Figure 7.

Proposed Development Direction

To produce fully satisfactory joints on a reproducible basis, the following areas of concern must be more fully evaluated:

- Welding equipment performance data must be developed for LASL graphite. In particular, the current-voltage relationship is desirable and the determination of magnetic force developed with various magnet gaps is essential in optimizing the overall welding process.

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- The effect of weld current peak values, time, and uniformity must be determined with the material of interest. Examination of metallographic results indicate nonuniform deformation of the joint area which could be due to temperature differentials and/or joint design.
- The joint design and forging pressure for optimum joining, without fracture of the work piece, is not considered optimum at this time. Fracture of the work pieces in the joint area must be eliminated to minimize stress riser effects on the joints.
- The effect of the time at temperature, with and without forging pressure, has not been evaluated to date. A more comprehensive investigation of welder preheat cycling on weld quality is required.

In general, the proposed development work will consist primarily of increasing background knowledge on the equipment operating characteristics during magnetic force welding of graphite materials and applying this knowledge to the optimum joining of the Rover graphite.

DISCUSSION OF TESTS AND RESULTS: COATING ADHERENCE

A NbC coating is applied to the fueled graphite by vapor deposition of NbC from a mixture of NbCl_5 , HCl , H_2 , and, recently, CH_4 . However, the coating does not adhere as well to fueled graphite as to unfueled graphite.

Electron microscope replication techniques were applied in the examination of various fuel material surfaces to investigate why the NbC coating does not adhere well to the fueled graphite. The limited results obtained and observations made indicate that these techniques should be of definite use in understanding some of the adherence problems.

Effort in this area was concentrated on the replication of as-received surfaces detailed in Table I.

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TABLE I
AS-RECEIVED ROVER MATERIALS EXAMINED

<u>Sample No.</u>	<u>Description</u>	<u>Surface Examined</u>
01-1685-105	Unfueled support-rod piece with good coating adherence.	Outer surface not undercut and not coated.
45-2181	Fueled material with poor coating.	Undercut outer surface where coating had fallen away.
45-4868	Fueled material, leached but not coated.	Undercut outer surface.

Figure 9 is a photomacrograph of these samples.

Polished Surfaces Evaluation

The polished and cathodically etched surface (Appendix B) of an unfueled sample is shown in Figure 10. Binder areas are characterized by the carbon-black inclusions forming circular projections on the surface ranging from 5,000 to 10,000 Å in diameter. The petroleum-coke filler is characterized by an aligned pattern of grooves developed during cathodic etching and a crack system parallel to the layer planes. Detailed studies of these grooves⁽¹⁾ have shown that they represent either open cracks or cracks that healed during graphitization leaving a zone of disordered carbon. Further treatment of the surface by oxidation would be required to distinguish open from closed cracks on the surface shown in Figure 10.

The binder appears to be featureless indicating the presence of disordered or nearly amorphous carbon. In general, the system is tight with good bonding between the graphitized-coke filler and the binder. The carbon-black addition is evenly dispersed and is also well bonded. Figure 11 is typical of matrix areas on the fueled sample shown in Figure 3.

(1) E. M. Woodruff. "Electron Microscopy of Structural Changes in Irradiated Graphite," HW-SA-3411. Paper presented at the Symposium on Carbon, Tokyo, July 20-23, 1964.

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15

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45-4868

45-2181

01-1658-105

0642095

~2X

FIGURE 9

Rover Graphite Materials

The interface between the matrix and the PyC fuel particle coating in this sample is shown in Figure 11. Here again good bonding is apparent. Layered structure in the PyC is fairly evident.

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2265C

4500X

FIGURE 10

Polished and Cathodically Etched Surface
of Unfueled Sample No. 1686-AA-25-3

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2263A

15,000X

FIGURE 11

Matrix-PyC Coating Interface
of Fueled Sample No. M1410EA-3

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In Figure 12, the PyC-UC₂ interface is shown. Long shadows along the edge of the PyC on the lower right and the distorted reaction zone indicate intermittent cracks are present. Larger cracks occur between the reaction zone and proeutectic graphite inside the reaction zone. A flake of proeutectic graphite within the UC₂ enters the micrograph from the upper left. A crack in the UC₂ parallels the left margin.

A better view of proeutectic graphite between the reaction zone and the UC₂ is shown in Figure 13. Large cracks on the coating side of the proeutectic are again evident. Cracks transverse to the layer planes in the proeutectic graphite are typical of those formed in petroleum cokes which are folded in the plastic state.

The preceding micrographs illustrate the structural details which can be examined by this method. Although methods for relocation of a specific area have been developed,⁽¹⁾ time has not permitted application of this technique to the coating adherence problem.

As-Received Surfaces Evaluation

Figure 14 shows the as-machined outer surface of an unfueled sample. Coke filler particles are characterized by flat surfaces broken into steps. The steps were created by fracture of the graphite across layer planes as material was stripped away by the plucking action associated with replication. Carbon-black spheres either protrude or have left a depression where they were broken in machining. Fracture, apparently proceeds through the graphitized coke particles and around the carbon black. On the reamed surface of a channel in the same sample, Figure 15, most of the carbon black stands in relief as though the binder had been eroded away.

Detail apparent on these unpolished surfaces prompted the examination of samples which might provide information about the adherence of the NbC coating. Figures 16, 17, and 18 show a progressively increasing severity of attack on matrix material which may possibly be related to the leaching and coating history of each.

(1) R. L. Hales and E. M. Woodruff. "Technique for Microscopic Studies of Graphite," Proceedings of the Fifth Conference on Carbon, Vol. I, p. 456. Pergamon Press, 1962.

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19

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2261D

7500X

FIGURE 12
PyC-UC₂ Interface
of Fueled Sample No. M1410EA-3

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2262C

7500X

FIGURE 13
PyC-UC₂ Interface
of Fueled Sample No. M1410EA-3

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2271A

15,000X

FIGURE 14

As-Machined Outer Surface
of Unfueled Sample No. 1686-AA-25-3

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2270B

15,000X

FIGURE 15

As-Reamed Coolant Channel Surface
of Unfueled Sample No. 1686-AA-25-3

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2431A

15,000X

FIGURE 16

Leached-Uncoated Fueled Sample No. 45-4868

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2427B

15,000X

FIGURE 17

Uncoated Area of Unfueled Sample No. 01-1685-105

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2429B

15,000X

FIGURE 18

Area of Poor Coating Adherence:
Fueled Sample No. 45-2181

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The least amount of attack was found on the fueled sample in Figure 16 which had been HCl vapor leached but not coated. Comparison of Figures 16 and 14 indicates the leach may be preferentially attacking binder areas; however, the difference is only slight "texture" appearing on the binder in Figure 16.

More evidence of surface attack is seen on the unfueled sample in Figure 17. This sample had taken a sound coating, however, the area replicated was not coated. The small grains, 500 to 1000 Å in diameter, scattered over the surface are probably NbC since the area shown is near an area exposed to coating gas. Carbon black and graphitized coke particles, in addition to binder, have been attacked on this sample.

The most severe erosion is found in an area on a fueled sample from which the coating had fallen away (Figure 18). The erosion of binder and carbon blacks in this case appears to have been much more rapid than that of the graphite filler.

A difference in the erosion of PyC particle coating is also apparent in Figures 19 and 20 taken from HCl leached-uncoated fueled and poorly coated fueled samples, respectively. The results seem to indicate that the leaching process alone does not severely attack the matrix or the fuel-particle coating and that within the matrix the attack that does occur is preferentially on the binder.

The severe erosion observed on the poorly coated sample could result from the consumption of carbon in the formation of NbC or from additional leaching during the coating process. Evidence of severe attack on the fuel-particle coating prompted optical examination of these surfaces to see if fuel had been exposed. The possibility that erosion of fuel coatings during the coating operation may be even more rapid than erosion of the matrix is suggested by Figure 21(a). The fuel-particle coatings are recessed and some remaining UC_2 is exposed.

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27

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2431B

4500X

FIGURE 19

PyC Particle Coating
from Leached-Uncoated Fueled Sample No. 45-4868

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28

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2429C

4500X

FIGURE 20
PyC Particle Coating
from Poorly Coated Fueled Sample No. 45-2181

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29

45-2181

55X

45-4868

55X

01-1685-105

55X

(a) Poor Coating-Fueled

(b) Leached-Uncoated-Fueled

(c) Uncoated-Unfueled

FIGURE 21

Photomicrographs of Rover Graphite Surfaces

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Fuel particles with bright undamaged PyC coatings of a leached but uncoated sample are shown in Figure 21(b). The HCl vapor leach has possibly exposed some of the particle surface by removing the binder.

Figure 21(c) shows the surface of an unfueled support rod which took a good coating. Coating was not applied, however, to the area shown in this photomicrograph.

In general, the foregoing observations indicate that the severity of attack is consistently dependent on the crystalline state of the carbon being attacked. If these preliminary observations are proven true, protection against fuel coating exposure during leaching would result by development of a more graphitic filler and binder. In addition, protection of the fuel, during the NbC coating process, would be improved with a more graphitic outer shell on the fuel particles.

Proposed Development Direction

It is clear from this exploratory study that microscopy techniques on both the polished and as-machined surfaces are capable of revealing useful information on the nature of various components in the fueled and unfueled material, the boundaries between these components, and the effects of leaching and coating the surface. In addition to a more systematic investigation similar to the work that has been described, several other types of studies are suggested that could not be explored in the time available. These include investigation of the sectioned NbC-C boundary and the study of the effect of HCl on matrix and PyC by the repeated replication of specific areas during a series of exposures to HCl.

DISCUSSION OF TESTS AND RESULTS: FUEL MIGRATION

Microscopy Studies

Hot stage reflection electron microscopy was used to study UC_2 migration in the Rover fuel materials.

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A number of photomicrographs were taken initially at room temperature of polished sections (Appendix C) through fuel elements to reveal the coated particles in various stages of migration. Photomicrographs of typical sections are shown in Figure 22. The distinction between the UC_2 , PyC, graphite matrix, and reaction zones is quite apparent, as is the existence of flakes of proeutectic graphite in some of the UC_2 particles. These photomicrographs were also of value in illustrating the difference in behavior of the migration process between particles.

The physical appearance of the particles was well established with 3600X photomicrographs. Time lapse motion pictures were then taken of the fuel material at 100X during self-resistance heating to 2500 C. These motion pictures were taken with an exposure cycle of 2.5 sec exposure per frame with 0.5 sec between frames. Therefore, 1 min of viewing at 20 frames per second equals 1 hr of filming on the microscope.

Samples for these in-microscope studies were prepared by cutting a 0.2-0.3 x 1.0 x 8.0 mm slice from a polished fuel element section. These samples were then evaporative coated with a transparent layer of niobium a few hundred angstroms thick. A low magnification (67X) photomicrograph (Figure 23) was then taken to serve as a map for locating particles while viewing the sample in the electron microscope. The hot stage reflection sample holder is shown in Figure 24.

The use of a niobium coating on the samples was initiated in an attempt to reduce the evaporation of carbon from the samples during heating. Earlier test results had shown that evaporation of carbon was so excessive at only 1800 C that the window in the microscope became opaque in a matter of minutes, and contamination of the microscope caused such a loss of image quality that photography was not possible. Use of the very thin niobium coating proved to be quite successful in that samples, so coated were held at temperatures above 2300 C for more than 3 hr without excessive evaporation.

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PYROLYTIC CARBON
COATING

UC₂

REACTION ZONE

18° VIEWING ANGLE
650X

Neg. 0642146-3

FIGURE 22

Photomicrographs of Coated Fuel Particles
(Typical Sections Before Heating)

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FIGURE 23

Photomicrographs of Coated Fuel Particles
in Various Stages of Migration

Neg. 0642146-1

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Neg. 0640615-5

FIGURE 24

Hot Stage Reflection Sample Holder

The most informative photography obtained was the motion pictures of the sample shown in Figure 23. In these pictures, four different particles (A, B, C, and D) were observed at various times before and during heating. A series of individual frames (Figure 23) from these motion pictures is shown of PyC coating "A" during heating. In the last frame shown, the sample was at approximately 2500 C and had been above 2000 C for over 3 hr.

As the sample shown in Figure 23 was heated, it appeared that the PyC coating etched preferentially where the edges of the coating were

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exposed (along the a-axis). As heating continued and higher temperatures were reached, the coating appeared to "sink" into the graphite matrix and/or the graphite matrix "grew" over the coating. Low speed showing of the film, however, developed a very definite belief that the coating is evaporating and that condensation of the carbon is taking place on the graphite matrix surrounding the coating, leading to epitaxial growth of some graphite crystals. Actual evidence of uranium migration through the PyC coating was not observed during any part of the heating cycle despite the fact that the PyC coating was polished down to the point that the UC_2 could not have been far below the surface. It is possible that this test was compromised by use of niobium coating on the sample which could form a thin NbC layer more resistant to uranium migration than the PyC coating.

Particle "D", from the sample shown in Figure 23, did not react the same in every case as Particle "A". This particle had been polished down to the reaction zone in the center of the PyC coating. The reaction products evaporated quite readily on heating to 2000 C, leaving an irregular hole in the coating. As heating continued above 2000 C, a spherical shaped projection, approximately the size of the UC_2 particle started to raise at the coating center. This projection increased in size as the outer layers of the PyC coating evaporated at higher temperatures. Evaporation appeared less at the coating center, which is considered normal if the "c" axis of the coating was more nearly perpendicular to the surface than the "a" axis. With time, as the outer PyC evaporated, the graphite matrix "grew" until the particle was completely covered. As in Particle "A", no UC_2 -PyC reaction was observed even though a region of reaction products was exposed prior to heating by the polishing operation. The appearance of the reaction zone remained unchanged following the initial evaporation which took place at 2000 C. In this case, if the niobium layer on the sample prevented a reaction, it in fact did not prevent evaporation of the reaction products.

Samples for study of the fuel migration problem have recently been prepared from pneumatically impacted tantalum and niobium powders containing a dispersion of coated particles. Time lapse motion pictures have been taken of one tantalum matrix and one niobium matrix sample. Picture quality with these samples was considerably improved. One problem exists with metal matrix samples in that satisfactory adherence between the fuel particles and the matrix has been difficult to obtain. However, the use of metal matrix samples for in-microscope experimentation appears to be quite promising.

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37

HW-83980

APPENDIX A

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SAMPLE PREPARATION:

MATERIAL CHARACTERIZATION

To develop the fundamental characteristics of Rover graphite materials, fueled and unfueled graphite elements were sectioned and prepared for metallographic examination using the following procedure:

- (1) Mount in polyester resin (Fiberlay Clear-Cast)
- (2) 120 grit belt grinder
- (3) 2/0 - 3/0 - 4/0 emery hand polishing papers
- (4) 6 hr on Syntron using Linde "A" and Met-Cloth
- (5) 10 min on Syntron using Linde "A" and Micro-Cloth
- (6) 10 min on Syntron using Met-polish #3 and Gammal Cloth

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APPENDIX BSAMPLE PREPARATION:
COATING ADHERENCE

The preparation of polished surfaces for replication was essentially the same as that described for the material characterization work (Appendix A) with the exception that resin impregnation could not be used. Resin impregnation was omitted because volatility of the resin at low pressures and solubility in replica solvent would prevent successful cathodic vacuum etching and replication following the polishing operation. Cathodic vacuum etching followed a procedure previously reported.⁽¹⁾ Etch time varied from 1 to 3 hr, at a voltage of 3 kv and a current of 0.3 ma. The Faxfilm replicas were shadowed at an angle of 45° with UO₂.

The as-received surfaces were prepared for replication by ultrasonic cleaning. The initial replicas stripped tended to pull away loose material from the surfaces and were unsatisfactory. Replicas stripped from these surfaces thus show evidence of plucked surfaces on the petroleum-coke filler particles in which the lamellae are parallel to the surface.

(1) R. L. Hales and E. M. Woodruff. "Technique for Microscopic Studies of Graphite," Proceedings of the Fifth Conference on Carbon, Vol. I, p. 456. Pergamon Press, 1962.

APPENDIX CSAMPLE PREPARATION:
FUEL MIGRATION

The polishing procedure adopted for all samples in this work was to mount the samples in quick-mount and polish using an automet polisher with final polish being obtained with Linde "B" in water. This procedure seemed to result in the most even polish of the three or four areas of different hardness (graphite, PyC, UC_2 , and reaction zone).

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