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QUARTERLY PROGRESS REPORT
ROVER GRAPHITE STUDIES
JULY, AUGUST, SEPTEMBER, 1966

By

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of
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BORE COATING INTERFACE STUDIES

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Previous microradiography on sections of NbC-coated Rover fuel elements revealed a rooting network of the coating at the NbC-graphite interface.[1] This network was more extensive than expected from optical microscopy studies and is being characterized as a function of location in fueled and unfueled elements. Three slices were cut from each of the elements in the current test series, which includes four fueled and four unfueled elements, untested and hot tested for varying lengths of time. The slices, cut from each end, and at 20 in. from the reactor inlet end of the elements, were thinned to 0.006 in., radiographed, and photographed at 250X to facilitate comparison with optical micrographs. Examination of the resulting microradiographs revealed many details of the root network at the NbC-graphite interface.

The roots were solid extensions of the NbC coating below the NbC-graphite interface. They were an average of 10 μ in width and extended about 20 μ below the rest of the coating. In an extreme case, a root extended 300 μ below the NbC-graphite interface. The root system was originally believed to be more extensive in the unfueled than in the fueled material. However, the present study showed the same root system development in both materials. A distinctive difference was that in the fueled material the root system penetrated into delaminated PyC fuel-bead coatings and filled empty fuel-bead cavities on

the inner bore surface. In the fueled specimens where a gap existed between coating and graphite, the 20-μ roots often did not span the gap and thus did not anchor on the graphite.

Many cases showed better root development on the end coating on the outer (machined) surfaces than on the bore (reamed) surface. Surface texture and available cracks probably have much to do with the extent of the root system. There was no systematic variation of the root system as a function of location along the length of the elements, and the roots did not change in appearance as a function of test duration.

In addition to the above observations, we discovered small amounts of heavy metal at the NbC-graphite interface in the fueled elements at the same location where optical micrographs showed pitted graphite. This metal was either uranium or niobium present as a carbide. Positive identification of the material was then attempted. The use of various X-ray tubes to utilize X-ray absorption wavelength dependence and thereby to discriminate between fuel from NbC were not successful. A photomicrograph-microradiograph pair showing the same area was produced as seen in Figures 1 and 2. The pair of photographs confirmed the location of the heavy metal on the graphite surface immediately under the coating. The same pair served as a guide for electron microprobe scans in the same area. The microprobe work was mostly unsuccessful in identifying the metal. In a few isolated locations there were indications of uranium, but the metal was too sparsely distributed for positive identification. Because these methods were unsuccessful, work was started on an alternative method for element identification.

FIGURE 1. *Photomicrograph (250X) of Station 20 Section from Element 287-14164 (Fueled, coated, tested 20 min at 2250 °C, flowing H_2)*

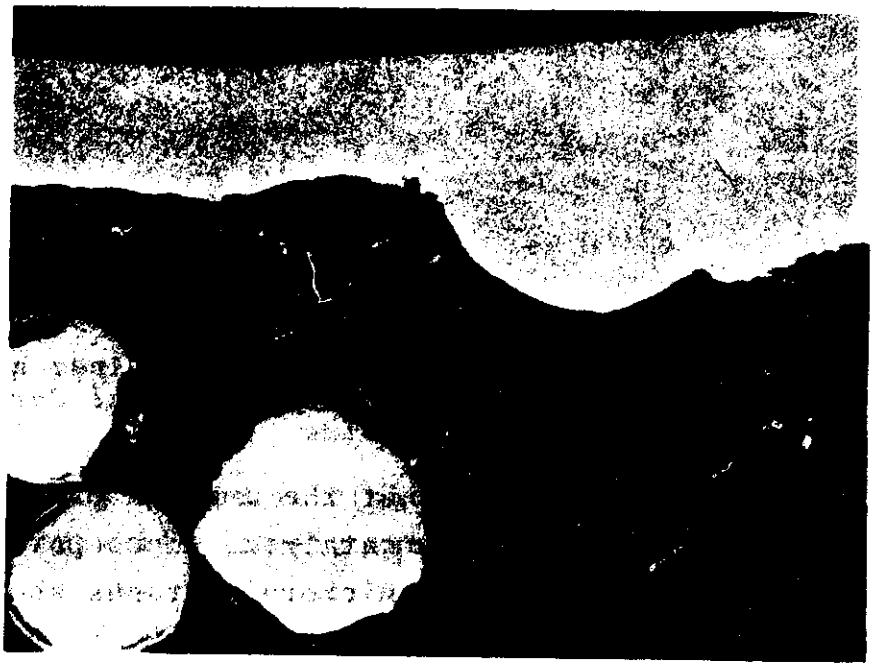


FIGURE 2. *Microradiograph (250X) of Same Area as Figure 1, Showing Location of Heavy Metal Carbide on the Graphite Immediately Under the NbC Coating*

Earlier work[2] produced a method for microautoradiography with simultaneous replication, and use of this method produced the microautoradiograph of Figure 3, which shows the same area as in Figures 1 and 2. The alpha tracks in the region of the graphite directly under the coatings substantiate the presence of uranium in this area. Note that the uranium is apparently present on both the graphite side of the coating and the porous graphite immediately under the coating.

FIGURE 3. Microautoradiograph (250X) of Same Area as Figures 1 and 2, Positively Identifying Metal Carbide Undercoating as Uranium Carbide

It has been suggested[2] that the uranium present here might have a possible role as a catalyst, since porous graphite is usually found in areas where microradiographs showed the heavy-metal images as in Figure 2. More work, to better define the extent of this uranium dicarbide, is now in progress.

(1) *Quarterly Progress Report Rover Graphite Studies, October, November, December 1965, BNWL-212.*

(2) *Quarterly Progress Report Rover Graphite Studies, January, February, March 1966, BNWL-259.*

ELECTRON AND OPTICAL MICROSCOPY

E. M. Woodruff

SAMPLE PREPARATION

Impregnation of Rover fuel-element specimens with a low-melting alloy (52% Bi, 48% Sn) has been a source of some difficulty in the recovery of replicas from severely corroded samples. The impregnant supports fragile NbC and graphite structures during grinding and polishing operations in preparation for replication and examination by electron microscopy. Although satisfactory cathodic etches are obtained on graphite and NbC surfaces, the alloy etches at a higher rate leaving a surface of high relief. Replicas taken from these surfaces tend to break, particularly along the edges of NbC or adjacent graphite, which are of primary interest in this study. Impregnating samples with resin has improved the quality of replicas.

However, successful use of the resin depended on eliminating the problem of resin decomposition during cathodic etching. Both the low thermal and electrical conductivity caused overheating of the impregnant and deposition of decomposition products on NbC and graphite surfaces in early experiments. Maraglas resin was found to be less susceptible to overheating than the other resins which were tried. Thinning Maraglas-impregnated specimens to 3/16-in thick wafers and cycling the etch at 10 min intervals to allow the sample to cool eliminated overheating.

Replacing the metal with resin reduced the electrical conductivity of the specimen, but the loss of electrical conductivity was corrected by placing a 3/32 in. thick aluminum mask over the surface to be etched and connecting it to the cathode. The mask attracts ions which pass through a 1/4 in. diam hole centered over the area to be etched. Beveling the edge of the hole reduces redeposition of aluminum on specimen surfaces.

PRELIMINARY OPTICAL EXAMINATION

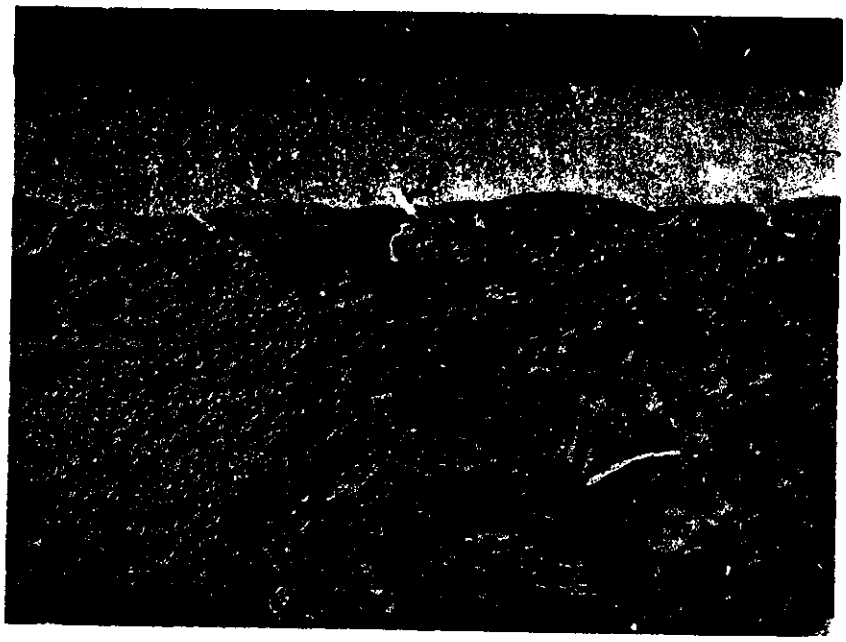
Optical examination of longitudinally sectioned specimens being prepared for electron microscopy reveals significant differences between fueled and unfueled elements in the nature of the separations at NbC-graphite interfaces. The following observations apply in general to samples taken from Stations 10 through 50. However, accompanying micrographs are from Station 20 in each element and illustrate coating thickness and gap widths for that position only.

In fueled elements, separation of the bore coating occurs during coating or cool-down as shown in Figure 1a. Separation is "clean" in the sense that no graphite particles span the gap or adhere to the coating. The graphite surface is pitted however, and does not match the contour of the NbC surface. Immediately under the surface, the graphite structure appears unaffected.

In fueled elements, no separation occurs during the coating process (Figure 1b). After a short hot test (Figure 2a), separation appears to be the result of selective corrosion of binder. Some graphite filler particles remain attached to the NbC and the gap follows an irregular route through the weakened binder. After a 6 min test at 2400 °C (Figure 2b) some graphite particles still adhere to the NbC.

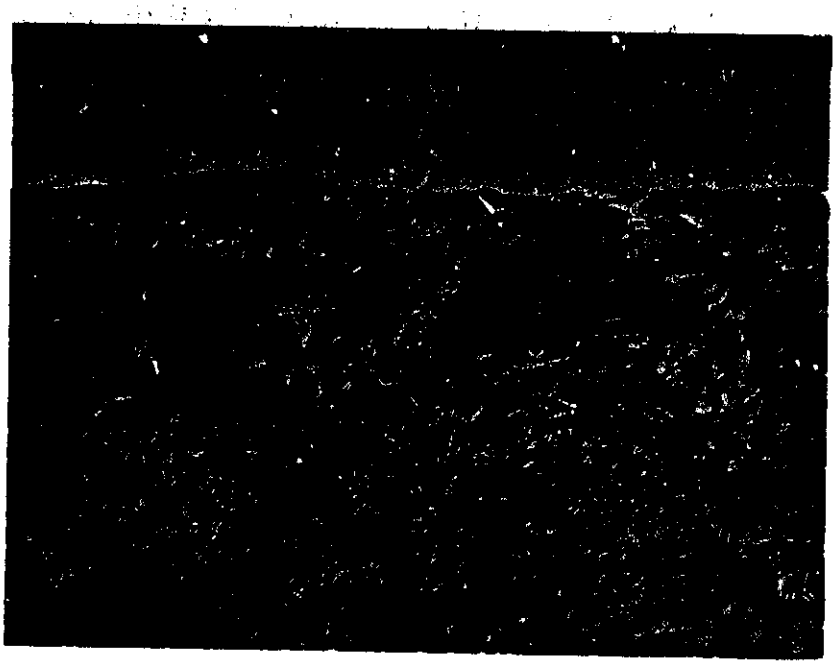
In both types of elements, graphite corrosion apparently contributes to the initial loss of coating adherence. In the fueled graphite a catalyzed surface reaction, which occurs during coating, effectively disrupts bonding. In the unfueled elements, loss of adherence is more correctly a loss of strength in the substrate caused by a diffusion reaction which selectively weakens binder carbon during hot testing.

(a)

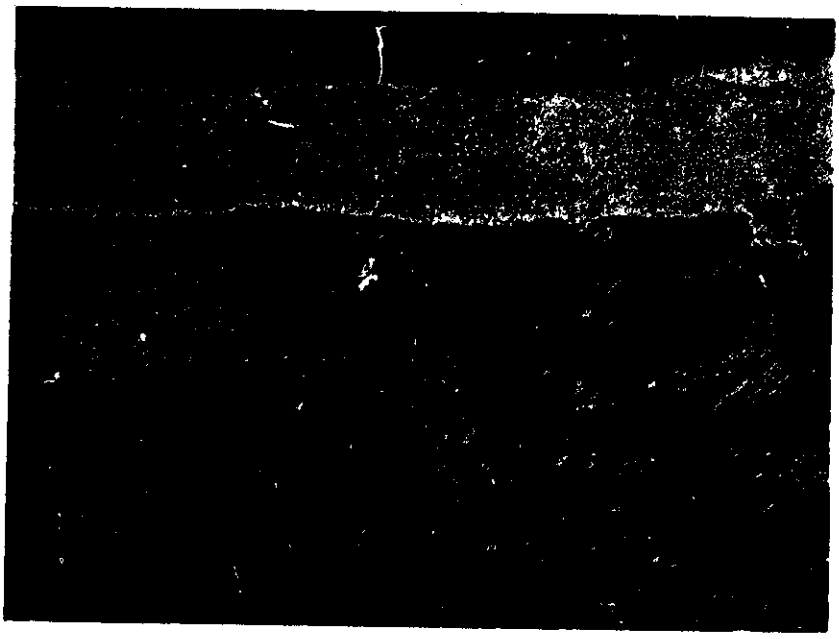


(b)

FIGURE 1. (a) *Fueled, Untested Element 287-14181. Station 20, 250X; Neg. 466-1324C*
(b) *Unfueled, Untested Element 1878-AA-264. Station 20, 250X; Neg. 466-1287C*



(a)



(b)

FIGURE 2. (a) *Fueled Element 1878-AA-220 Tested for 6 min at 2400 °C. Station 20, 250X; Neg. 466-1290C*
(b) *Unfueled Element 1878-AA-265 Tested for 30 + 30 min at 2400 °C. Station 20, 250X; Neg. 466-1296C*

Probably the most significant observation made here is the extent of surface corrosion of the fueled elements during coating. It appears this interface is open before coating gases are replaced with helium. This and other factors influencing adherence will be examined in greater detail in the electron microscope.