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MICROAUTORADIOGRAPHIC CHARACTERIZATION OF ROVER BORE COATING INTERFACES

L. R. BUNNELL

AUGUST 1968

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MICROAUTORADIOGRAPHIC CHARACTERIZATION OF ROVER BORE COATING INTERFACES

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August 1968

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ABSTRACT

In an effort to more completely understand the anomolous non-adherence of the NbC bore coatings on fueled ROVER elements, a modified microautoradiographic method was used to reveal the uranium distribution at the coating-graphite interface. The method was used on elements manufactured with a reduced uranium concentration at the interface. Correlation between alpha tracks and the surrounding microstructure was excellent. Observations are consistent with the concept that uranium is responsible for an accelerated attack on the graphite during coating, although this is not explicitly proven. The presence of uranium in amounts below the detection limit of the method used is associated with tightly adherent NbC coatings.

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INTRODUCTION

The niobium carbide (NbC) bore coating on ROVER fuel elements does not adhere as well to fueled elements as it does to their unfueled counterparts. In search for the reason for nonadherence, extensive microstructural examinations have been performed at the Pacific Northwest Laboratory and elsewhere. Examination of fueled, as-coated ROVER elements generally reveals a gap between the graphite and the NbC. This gap was not evident in the unfueled, as-coated elements. Furthermore, the gap was one of the few obvious differences between the fueled and unfueled as-coated elements.

There was some indication that the gap might be associated with the presence of uranium at the critical NbC-graphite interface and, therefore, a method for revealing uranium at this interface was required. Since it was obvious from the micrographs that any microstructural effect due to uranium would be small, a close correlation with the surrounding microstructure was imperative.

Microautoradiography provides such a close correlation. This report describes the development of the method currently in use and presents the latest results obtained.

SUMMARY AND CONCLUSIONS

The purpose of the experiment was to develop a means for detecting small amounts of uranium at the NbC-graphite bore-coating interface of ROVER fuel elements, and to do so in a way that provides easy correlation with microstructural details near the interface. Conventional autoradiography was adapted to the requirements of high resolution and good correlation so that the bore-coating interface could be well evaluated with respect to relative amounts of uranium contamination. This method has recently been used on elements manufactured or coated so that there was less uranium concentration at the NbC-graphite interface.

The effect of decreased uranium concentration on the tightness of the NbC bore-coating was examined. Whenever there was little or no uranium contamination, there was no gap between the graphite and coating. The concept of a direct effect of uranium contamination on coating adherence is not conclusively proven, but the method shown here will facilitate proof or disproof of this notion after it has been applied to a larger variety of samples.

EXPERIMENTAL

The protective bore coating for ROVER elements is composed of niobium carbide resulting from the deposition of niobium pentachloride on a graphite developed for ROVER. The difference in the bulk thermal expansion coefficient of these two materials is about $3 \times 10^{-6}/°$(0 to 1600 °C).* Since the coating is a brittle carbide and is usually deposited at a temperature of about 1600 °C, and since the NbC expands more than the graphite, it is to be expected that, after cooling to room temperature, the coating would either contain radial cracks or be separated from the graphite. The cracks do appear; however, most of them close when the elements are reheated above the coating temperature.(3)

A less expected phenomenon is a complete separation: i.e., a large gap at the coating-graphite interface. This gap is far wider than can be accounted for on the basis of a thermal expansion mismatch. Furthermore, as can be seen in Figure 1, there are pits (see arrow) on the graphite surface of a fueled element in even the untested state. These pits suggest an exaggerated chemical attack. Since there is usually a small amount of uranium on these surfaces, it seems logical that the uranium might cause or assist in the chemical attack. In the absence of any direct evidence in the literature that uranium contamination could exaggerate chemical attack under the coating conditions, it was desirable to at least detect the uranium at the interface and to correlate the incidence of uranium with the condition of the NbC-graphite interface.

The first method tried was fairly basic.(4) It consisted of using cellulose nitrate as a solid-state track detector with the alpha particles creating damage areas leachable in hot concentrated NaOH. The tracks were distinct at magnifications up to 900X but the required correlation

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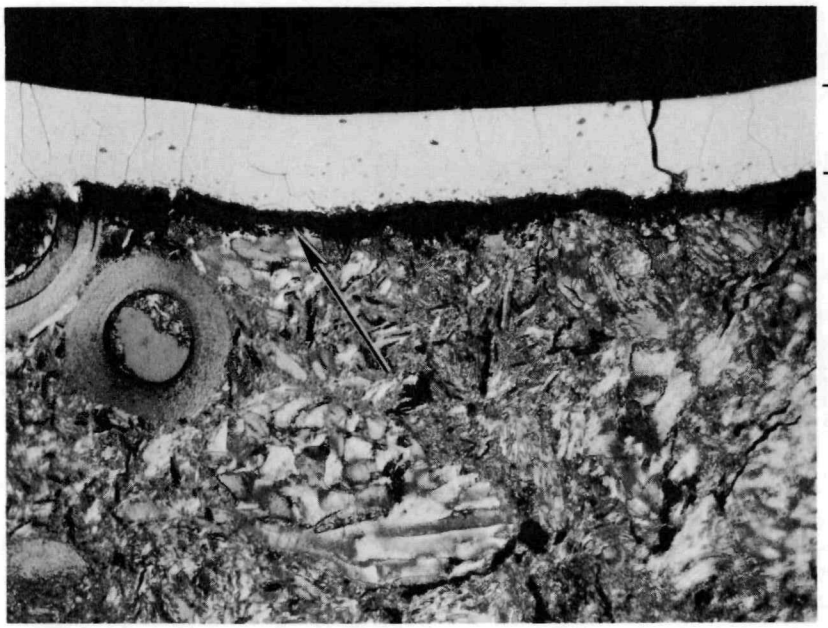
* Thermal expansion coefficient of $7.1 \times 10^{-6}/°C$ (0 to 1600 °C) for NbC;(1) thermal expansion coefficient of $4.1 \times 10^{-6}/°C$) is a typical transverse value for loaded graphite.(2)

was absent. A replica was produced simultaneously with track production by moistening the cellulose nitrate with acetone before application, but the replicas were not of sufficient quality to allow correlation with the microstructure. The microautoradiographs showed tracks in annular rings around the bore coating even in untested elements.



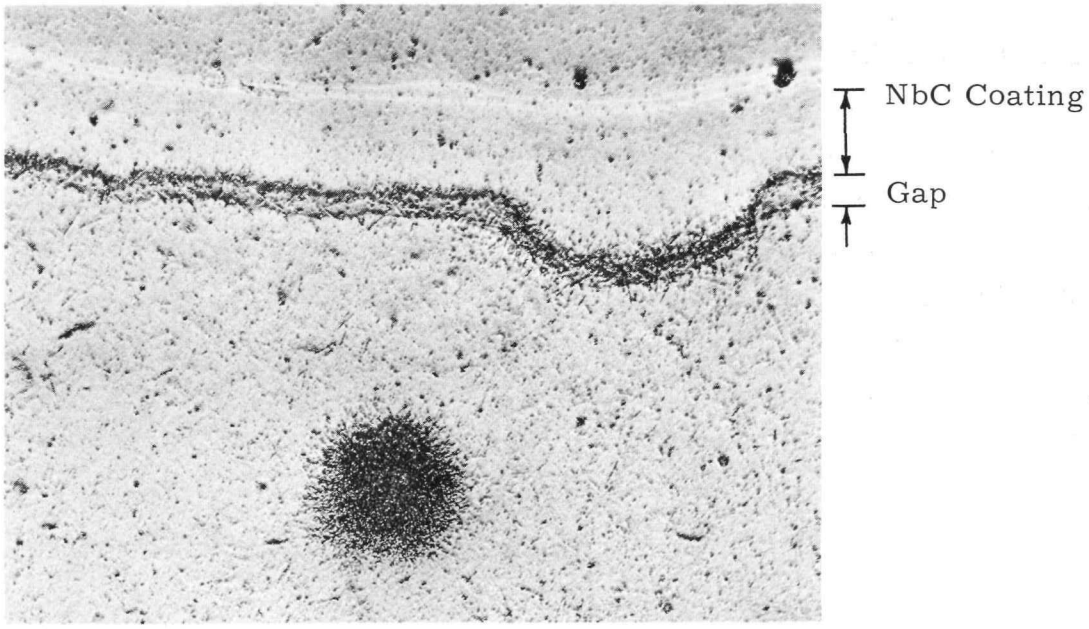
Neg 466-348 250X

FIGURE 1. Interface Between Graphite and NbC Bore Coating at Station 20, Element 287-14181, Which Was a Coated, Untested Element. [Note roughened, pitted graphite along interface (arrow).]

In an effort to provide better alpha track-microstructure correlation, another microautoradiographic method involving a fine-grained strippable emulsion* was used.[5] A partial replica was produced in the soft, thin emulsion which was applied wet and removed after exposure and processing. A thin layer of aluminum, vacuum-evaporated onto the surface of the glass-mounted replica, rendered it reflective enough for conventional photomicrography. However, the quality of these replicas

* AR-10 High Resolution Stripping Emulsion, Eastman Kodak, Rochester, New York.

was still low. Figure 2 is an example of a microautoradiograph made by this method. In cases where a gap existed between the coating and graphite, the gap was evident; except for obvious features like this, the correlation was still unsatisfactory.



Neg 461-1A 250X

FIGURE 2. Microautoradiograph Made at Station 10 of Element 287-14181. (Although tracks are difficult to see, they are clustered on the graphite near the gap.)

Workers at Low Alamos[6] used a more straightforward method. AR-10 stripping film was used but left on the samples during photography. This had been attempted at Battelle-Northwest; however, difficulty in reflecting enough light from the dark complex graphite surface for high-magnification photomicrography led to the attempt at replication described above. The absolute registry of tracks and microstructure noted in the Los Alamos work prompted a small modification. The modification consisted of merely evaporating a thin (5% optical transmission) layer of chromium on the surface of a metallographically prepared sample. Application of the stripping film, exposure in a light-tight container, and

processing followed. The chromium was not affected by the photographic solutions and provided an excellent background for photography of alpha tracks. Magnifications of 500X were used with tracks still quite distinct at 1000X.

The samples involved in the present study are partially described in Table I. The first two samples contained a 2.5 vol% NbC addition, partially to act as a "getter" for UC_2 migrating to the bore-coating interface. The third element had been coated by the low-temperature bromide process in which $NbBr_5$ is used instead of $NbCl_5$, and which would be expected to have less fuel migration during coating. All three elements had been hot-gas tested, so the only indication of their as-coated condition was from samples taken from low station numbers which were essentially unaffected by the test. The experimental method used was that outlined above with a 225 hr exposure used to detect small amounts of uranium.

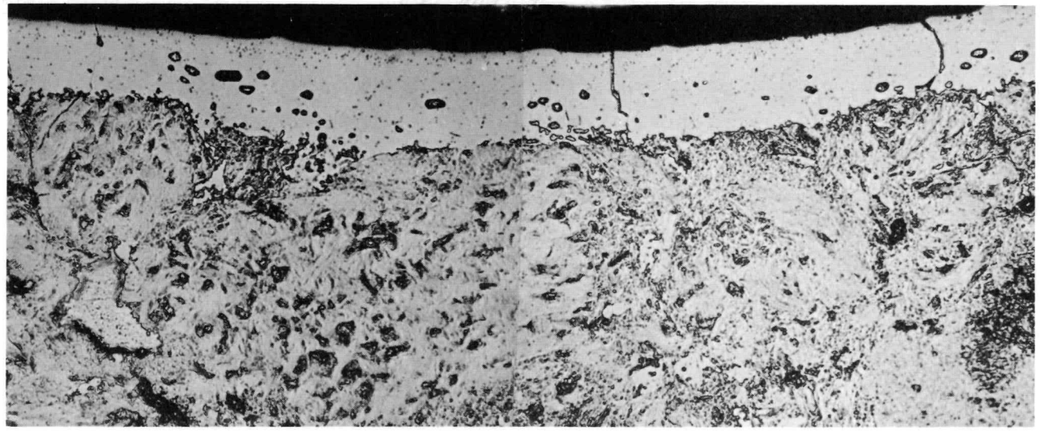
TABLE I. Element Characterization

Element Number	Distinguishing Feature	Hot-Gas Test Condition	Weight Loss During Hot-Gas Testing, g
39-80629 WANL	2.5 vol%, -325 mesh NbC addition	29.8 min at 2350 °C(a)	18.4
39-80639 WANL	2.5 vol% 300 Å NbC addition	28.8 min at 2350 °C(a)	22.5
99-78589 ORNL	1000 to 1400 °C NbC coating by bromide process TaC overcoat	53.7 min at 2350 °C(a)	21.6

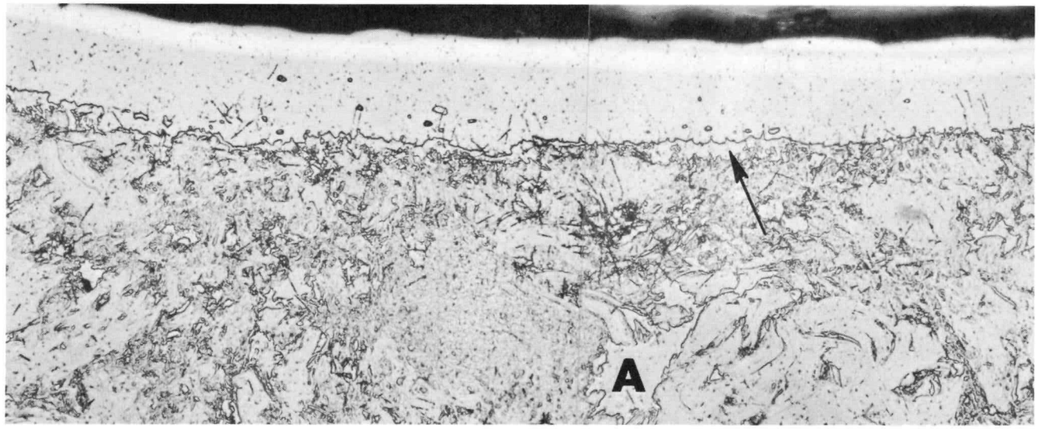
(a) Exit gas temperature.

RESULTS

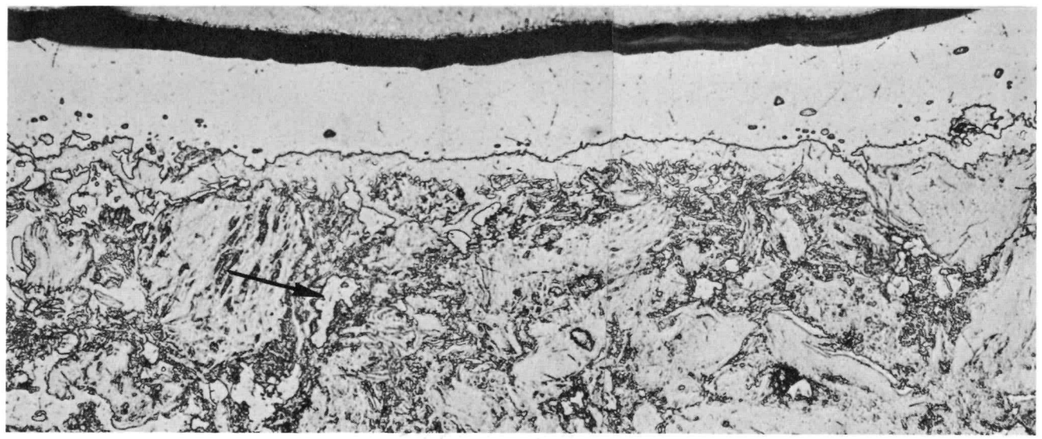
Figure 3, a through e, is a group of microautoradiographs which shows the relative uranium concentration as a function of station in Element 89-80629, which contained -325 mesh NbC. Figure 3a shows



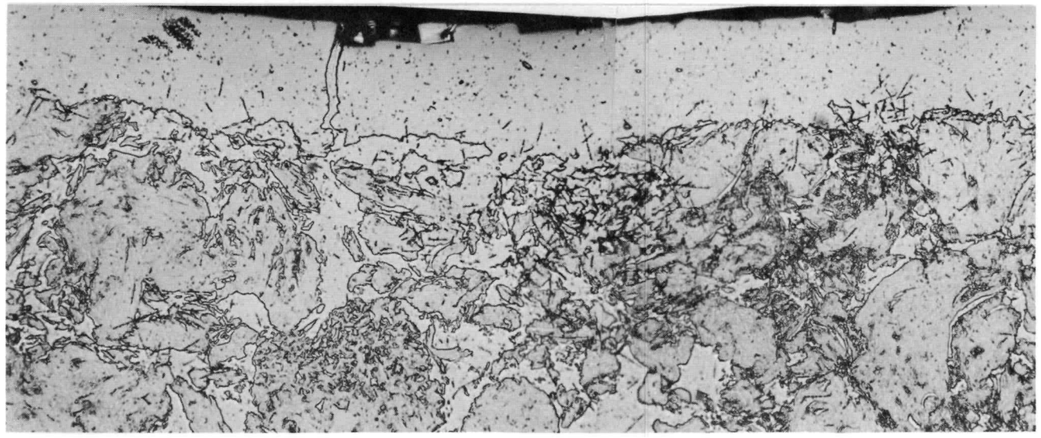
3a. Station 2



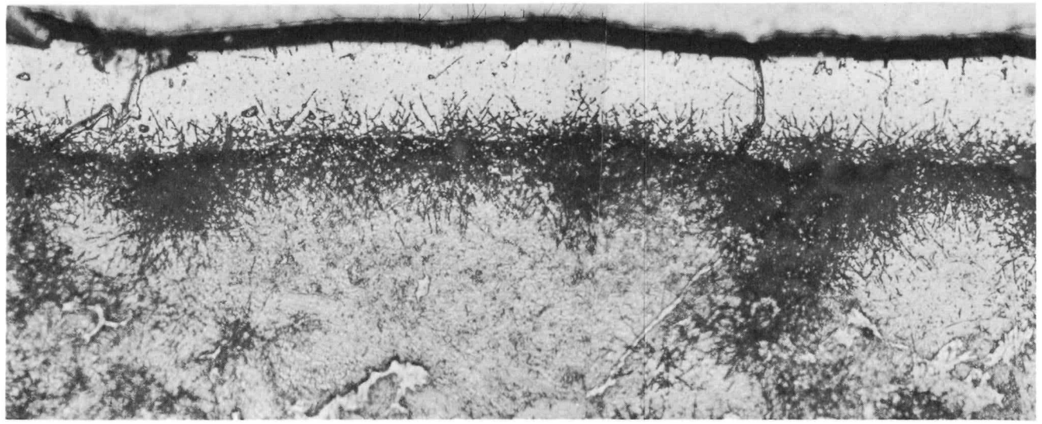
3b. Station 19



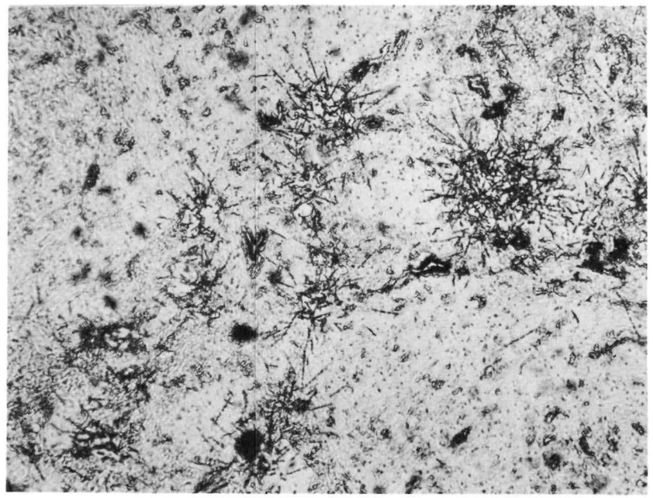
3c. Station 29



3d. Station 39



3e. Station 49



3f. Station 39

FIGURE 3. (a-e) 500X Microautoradiographs Showing the α-Track Density at the Indicated Stations of the NbC-Graphite Interface, and (f) in the Matrix at Station 39, of Element 39-80629, Containing -325 Mesh NbC.

the bore coating-graphite interface at Station 2. The coating is tight, and there are no alpha tracks at the interface or in the matrix graphite. Figure 3b was taken at Station 19. There are some tracks at the bore-coating interface and some in the matrix graphite. There is also a gap (arrow) between the bore coating and graphite and corrosion deep in the matrix graphite, as area "A" in the micrograph. Both of these regions are filled with plastic mounting resin. Figure 3c, from Station 29, shows little tracking at the bore-coating interface or in the graphite and contains a gap between the bore coating and graphite as well as deeper corrosion. The arrow shows an NbC particle. There are no noticeable tracks associated with these particles at this station. Figure 3d, from Station 29, has the same general appearance except that a noticeable number of tracks appear at the interface and in the graphite. Figure 3f, a microautoradiograph of the matrix at Station 39, shows particles of NbC surrounded by alpha tracks. Figure 3e shows Station 49, where migrated fuel has concentrated at the bore-coating interface, probably during hot-gas testing.

Figure 4, a through e, is a group of microautoradiographs which shows the relative uranium concentration as a function of station number in Element 39-80639, which contained 300 Å NbC. Figure 4a shows the bore-coating interface at Station 2. There are tracks at the interface and the arrow shows that a small gap exists (compare with Figure 3a). There is also some tracking in the matrix. At Station 19, Figure 4b, there is some tracking and a large amount of corrosion (A). The same is true of Station 29, Figure 4c, and Station 39, Figure 4d. Figure 4e shows Station 50 where very dense tracking occurs at the bore-coating interface. Figure 4f shows the matrix graphite at Station 50 and demonstrates the preferential nature of uranium migration in the NbC-containing binder phase, since the two large objects without tracks are probably filler particles.

In these two elements with NbC additions, it appears that there is much less tracking at the bore coating-graphite interface

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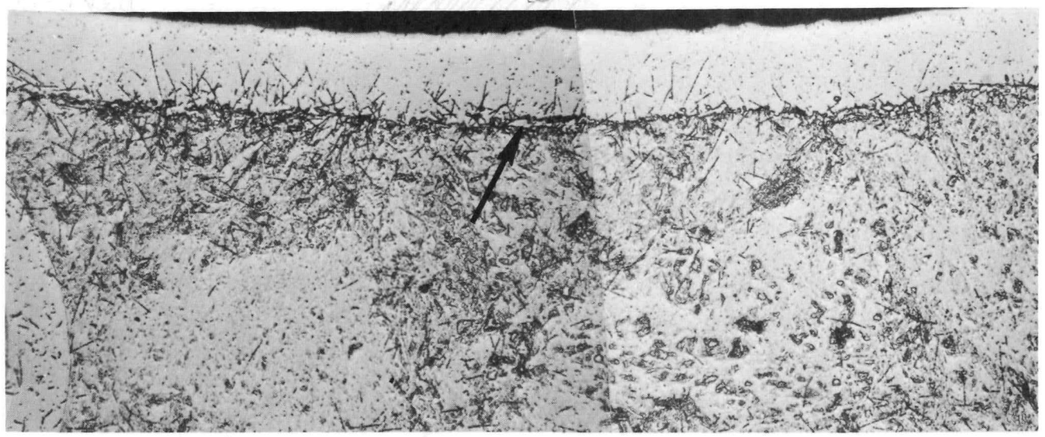
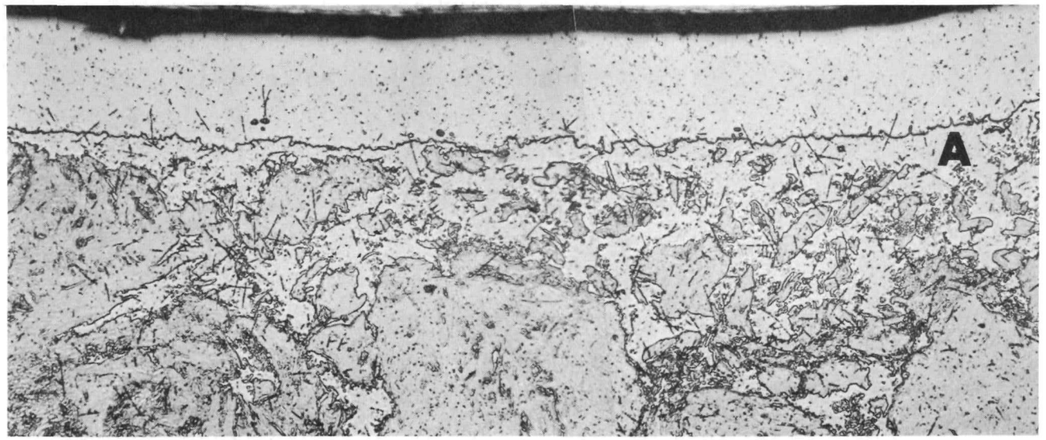
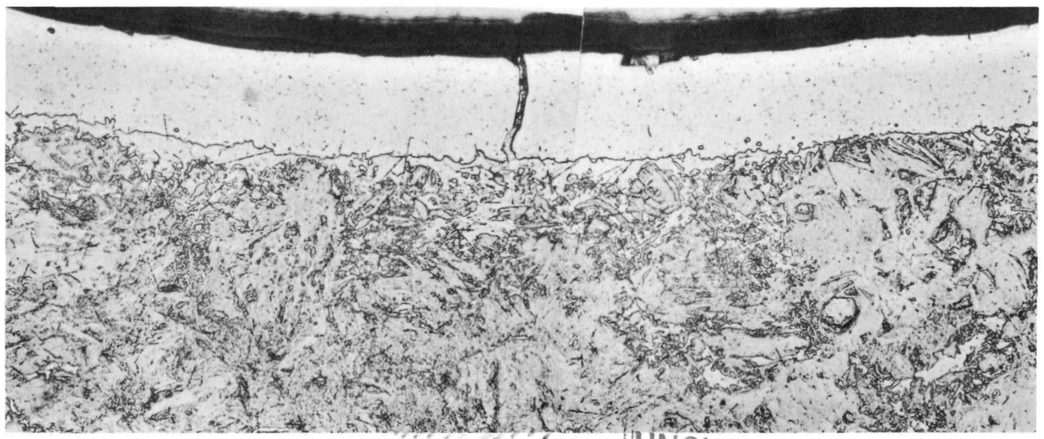


4a. Station 2



4b. Station 19



4c. Station 29

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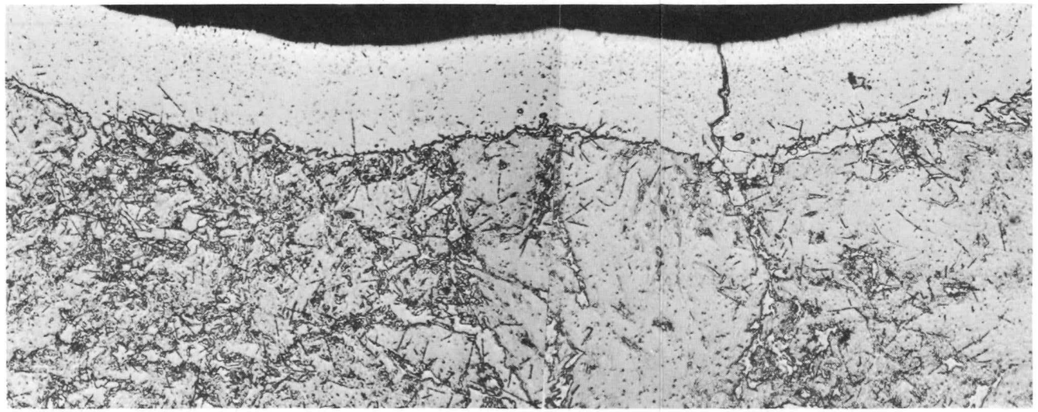
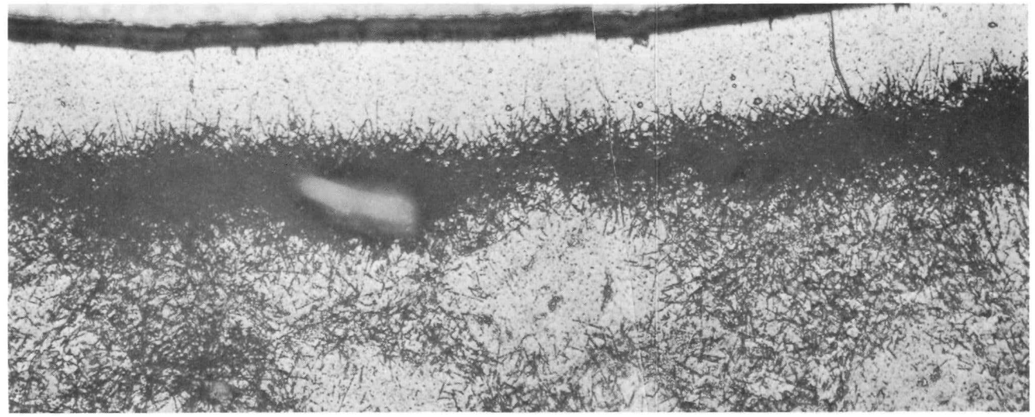
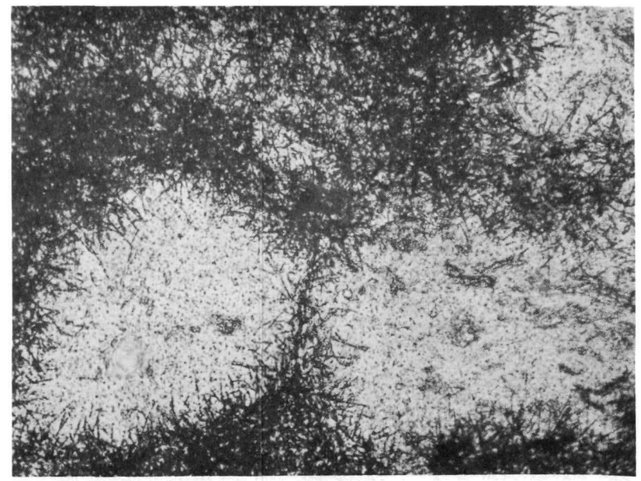


4d. Station 39



4e. Station 50



4f. Station 50

FIGURE 4. (a-e) 500X Microautoradiographs Showing the α-Track Density at the Indicated Stations of the NbC-Graphite Interface, and (f) in the Matrix at Station 50, of Element 39-80639, Containing 300 Å NbC.

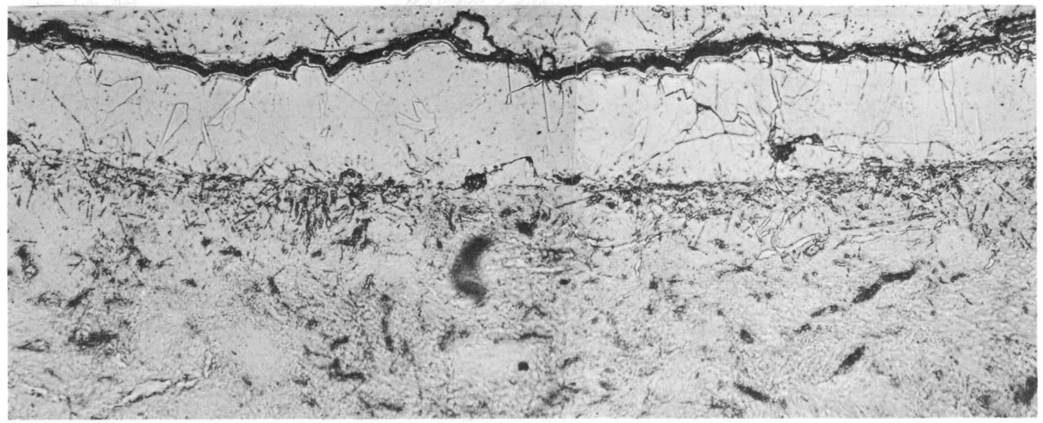
than in samples examined previously.[5] The elements observed in the past included an untested element which had much more uranium at the bore-coating interface than either of these elements. However, the present elements, which contained NbC, had a smaller bead loading than the previous elements and thus a direct comparison is difficult.

In the element with the -325 mesh NbC addition, which is the only one where individual carbide particles could be seen, the NbC does act as a getter, but whether the gettered uranium migrated during coating or during testing is not known.

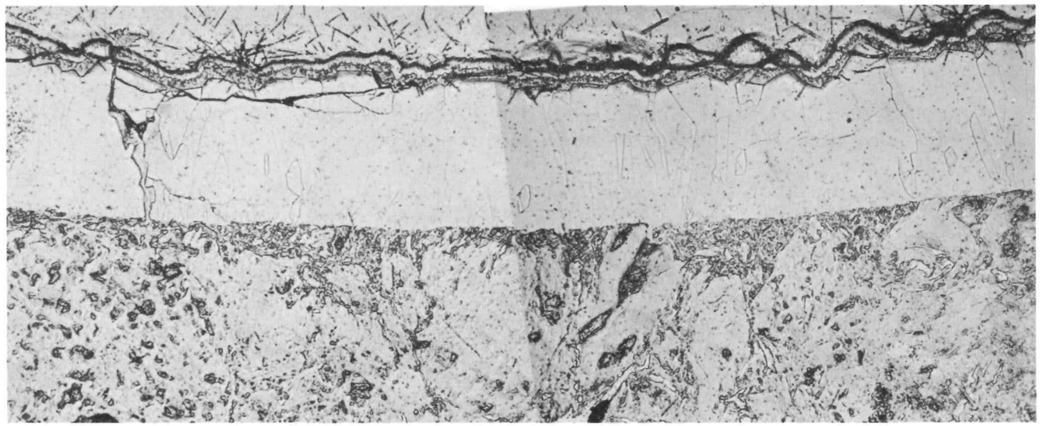
Figure 5, a through f, is a group of microautoradiographs which shows the relative uranium concentration as a function of station number in Element 99-78589, which was coated by the bromide process. For orientation in Figure 5c, (A) is mounting resin, (B) is two layers of a TaC overcoat, and (C) is the NbC bore coat. At Stations 10, 20, and 30 (Figures 5a, 5b, and 5c, respectively) there is a complete absence of tracks and a tight bond between the graphite and bore coating. At Station 40, Figure 5d, the first tracks appear and there is also a gap at the interface (see arrow). At Stations 47 and 49, Figures 5e and 5f, the tracking is at its usual high level.

It is interesting to note that high-sensitivity electron beam microprobe work done at ORNL[7] on neighboring samples from the same element did not detect any uranium at the bore coating interface until Station 39-1/2, which is in excellent agreement with the first microautoradiographic indication at Station 40.

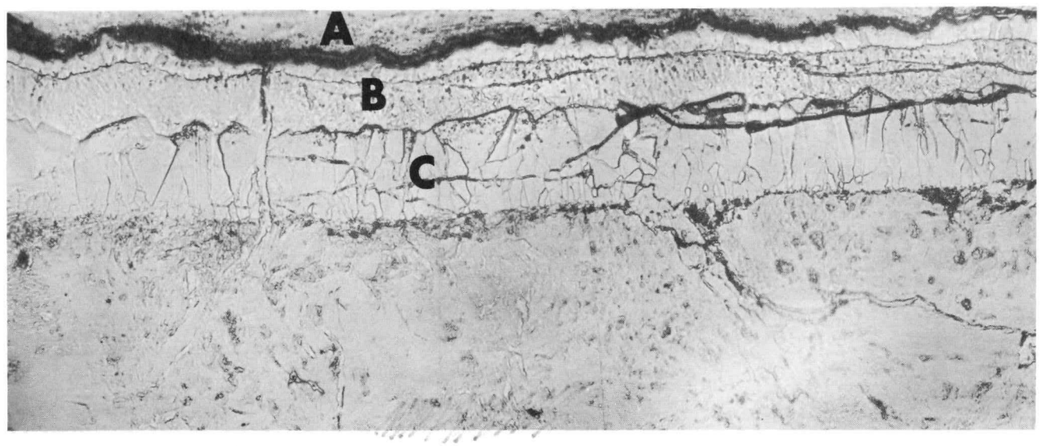
The hypothesis that uranium causes an accelerated corrosion in ROVER fuel elements remains a hypothesis. There is no evidence that refutes this concept. However, there is little that definitely supports it except the observation, in several fuel elements, that tight bore coatings are associated with a complete absence of uranium contamination.



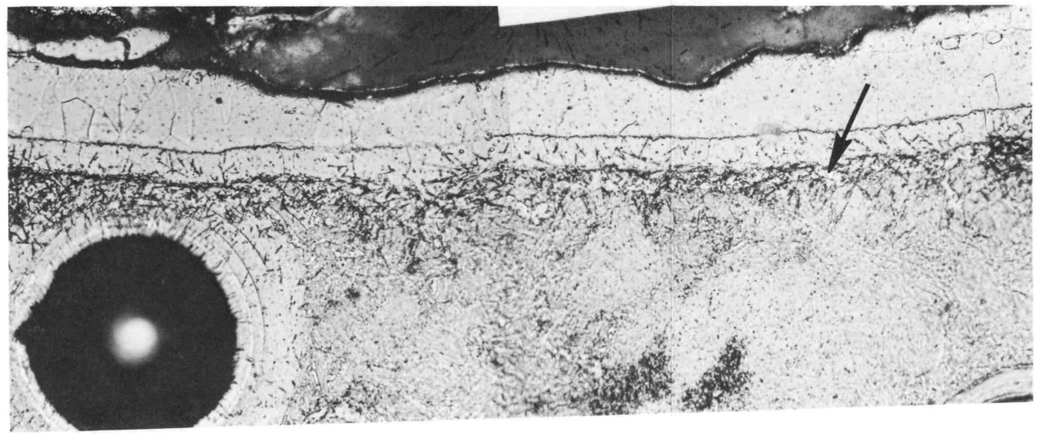
5a. Station 10



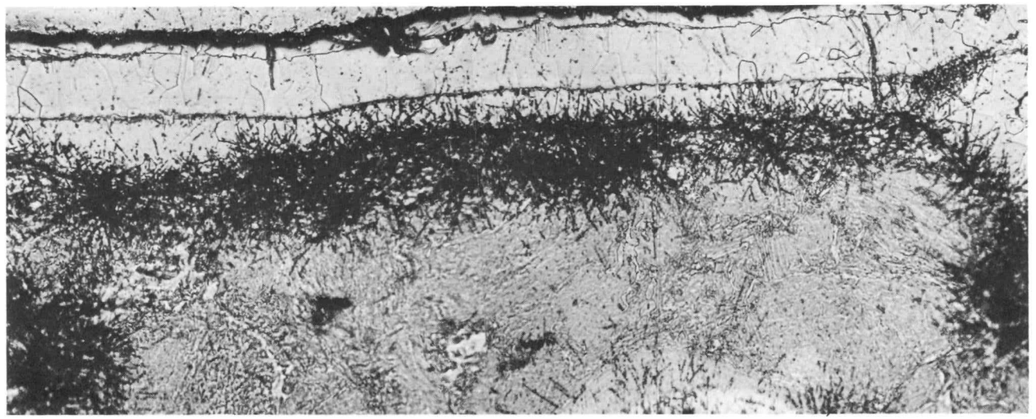
5b. Station 20



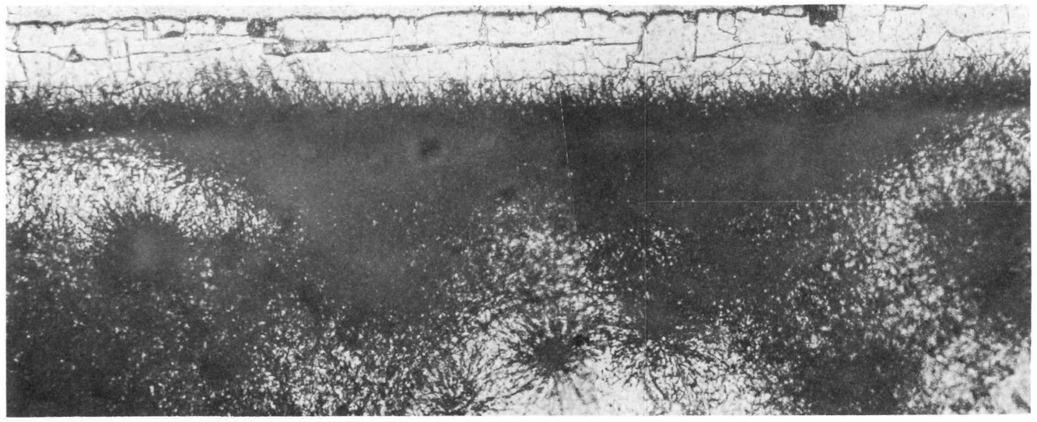
5c. Station 30



5d. Station 40



5e. Station 47



5f. Station 49

FIGURE 5. (a-f) 500X Microautoradiographs Showing the α-Track Density as a Function of Station Number in Element 99-78589, Coated by the Bromide Process.

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