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IRRADIATION TEST OF-2: HIGH-TEMPERATURE IRRADIATION BEHAVIOR OF LASL-MADE FUEL RODS AND LASL-MADE COATED PARTICLES

by

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ABSTRACT

Three LASL-made, substoichiometric ZrC-coated particles with inert kernels, and two high-density molded graphite fuel rods that contained LASL-made, ZrC-coated fissile particles were irradiated in the Oak Ridge Research Reactor test OF-2. The severest test conditions were 8.36 x 10^{21} nvt (E > 0.18 MeV) at 1350°C. The graphite matrix showed no effect of the irradiation. There was no interaction between the matrix and any of the particle coats. The loose ZrC coated particles with inert kernels showed no irradiation effects. The graded ZrC-C coats on the fissile particles were cracked. It is postulated that the cracking is associated with the low LTI deposition rate and is not related to the ZrC.

I. INTRODUCTION

Coated particles and fuel rods made by Los Alamos Scientific Laboratory (LASL) have been tested in the Oak Ridge Research Reactor high-temperature irradiation experiment OF-2. This is a summary of the rationale, the fabrication history, and the high-temperature irradiation behavior of these materials.

The High Temperature Fuels Technology for Nuclear Process Heat Program at LASL had as its goals the identification, fabrication, and proof testing of nuclear fuels with higher temperature capabilities than those now being used or considered for use in gas cooled reactors. This higher temperature capability could be utilized for higher processing temperatures of the graphite-base fuels and for higher reactor fuel operating temperatures. Details of the rationale for this program and descriptions of the research, development, and technology developed during the program have been described in a series of publications.[1-5]

The objectives of the LASL part of the OF-2 experiment were:

a. To test the high-temperature irradiation performance of coated particles with substoichiometric ZrC_x coats where one of the primary variables was the carbon-to-zirconium ratio (i. e., x) in ZrC_x. The ZrC_x coats that were tested had been deposited from different coating gas compositions[6] to produce coats with different x. The original concept was that the rate and extent of grain growth in the carbide coats was determined by the value of x; the higher x yielding the smaller grains.

b. To test LASL fissile fuel particles with ZrC coats that were incorporated into a high-density graphite matrix. The fuel rods were made up using a mixture of LASL fissile particles and General Atomic Company fissile and fertile particles. This was done to allow us to compare the behavior of the different types of fuel particles under identical high-temperature and irradiation conditions. The results of these tests would allow us to identify critical problem areas in the use of ZrC as a particle coat and also to test further the behavior of the high-density graphite (matrix $\rho \sim 1.6$ g cm^{-3}) fuel rods made by compacting a combination of coated particles, graphite flour, and polyfurfural alcohol binder.[7] Past work[5,8] has indicated that this formulation has an excellent high-temperature irradiation behavior.

The OF-2 experiment is of considerable importance to the High Temperature Fuels effort since it not only operated at high temperature, but the radiation flux more nearly approximated that expected in an HTGR design than those experiments performed under greatly accelerated irradiation conditions.

II. MATERIAL AND FABRICATION DESCRIPTION

The ZrC coats on the three sets of coated particles made with carbon kernels were prepared by varying the concentration ratios of the carbon- and zirconium-containing species in the coating reaction[9,10]

$$xCH_4 + ZrCl_4 + 2(1-x)H_2 = ZrC_x + 4HCl, \quad x < 1$$

in order to vary the value of C/Zr in the coats of the particles. These particles were tested to determine the effect of the stoichiometry in the ZrC coat insofar as the irradiation performance was concerned. Should there have been an effect, our past experience has indicated that it would have been important to recognize it as early as possible in the course of the development of the ZrC-coated fuels.

The fuel test elements were made by incorporating

carbon particles

ThO_2 BISO particles (made by General Atomic Company)

$^{235}UC_2$ TRISO particles (made by General Atomic Company)

$^{235}UC_2$ ZrC-coated particles (made at LASL)

in the amount of 41 volume percent into artificial graphite of density 1.66 g cm^{-3}. This combination allowed us to investigate not only the performance of the LASL fissile particles and the LASL-made graphite fuel matrix, but simultaneously allowed us to compare the behavior of the LASL ZrC-coated particles with the GAC standard TRISO fissile and BISO fertile particles under identical irradiation and environmental conditions. To aid in the postirradiation identification of the LASL particles, the LASL ZrC-coated particles were not made in the TRISO configuration, but instead, they were made with graded C-ZrC coats. This was done by preparing the buffer-coated kernels with a low-temperature isotropic pyrolytic carbon (LTI) seal, then in place of the inner LTI, a coat which started out as an iLTI was modified by adding ever increasing amounts of ZrC until a layer of pure ZrC was deposited. After 27 µm of the pure ZrC had been deposited, the process was reversed until the outermost material on the coated particle was pure LTI. Electron microprobe analyses of the ZrC_x and ZrC-C coats made were:

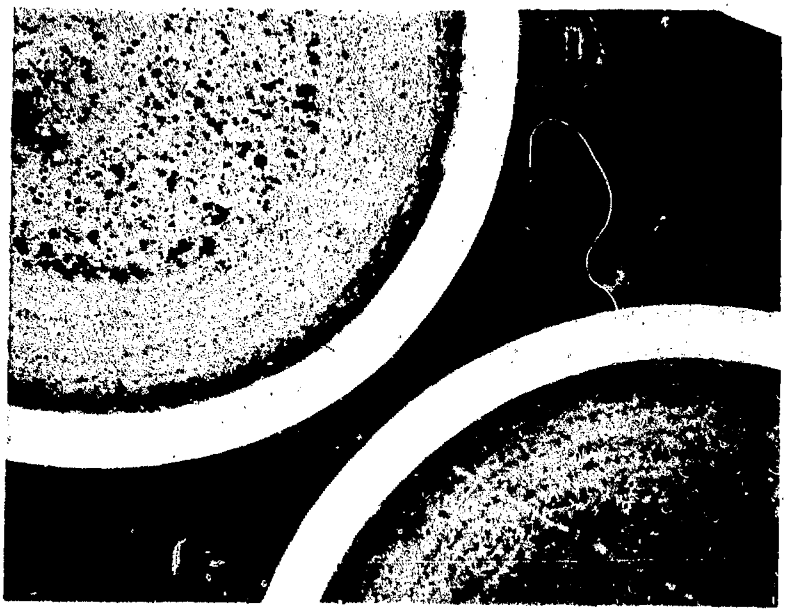
Run 1536HT: $ZrC_{.71}$

Run 1538HT: $ZrC_{.70}$

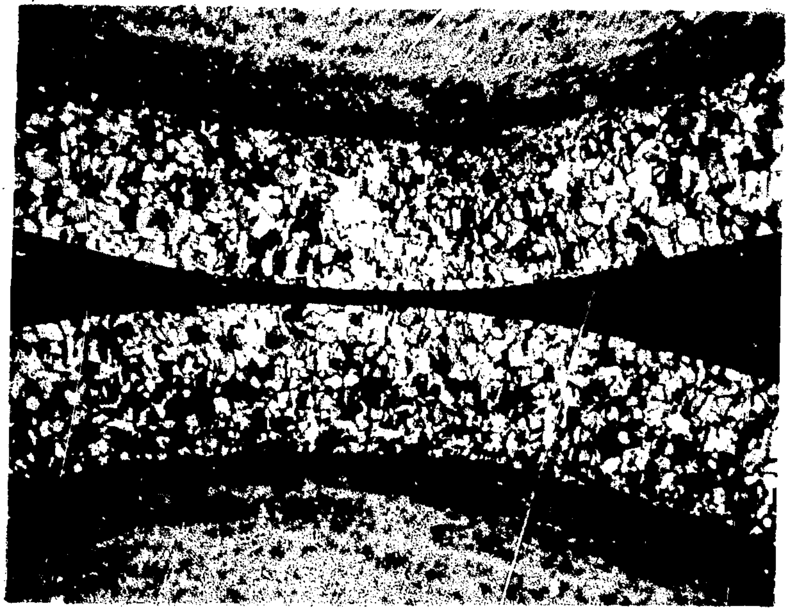
Run 1539HT: $ZrC_{1.05}$

Run 1524HT: Graded coat of average composition $ZrC_{.94}$.

Photomicrographs of these particles are shown in Fig. 1-3. The crack in the ZrC coat of Fig. 3 proved to be associated with the excess chlorine in the ZrC and is included to illustrate that some of the particles had flaws before the irradiation test.

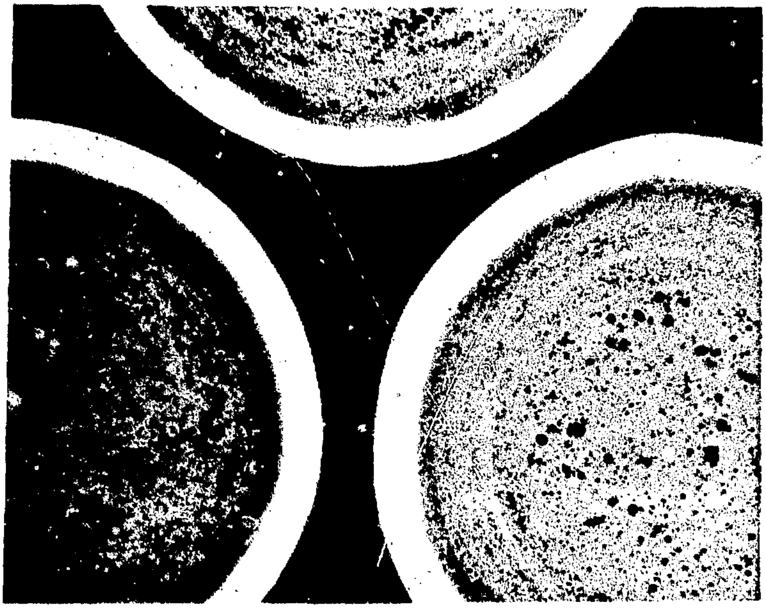


(a). 1536HT. 150X.

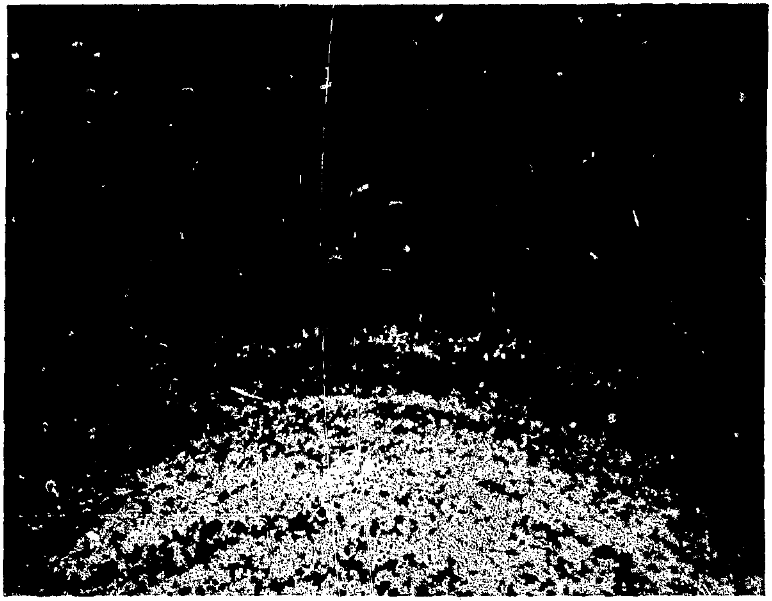


(b). 1536HT, etched. 500X.

Fig. 1. LASL Coated Particles.

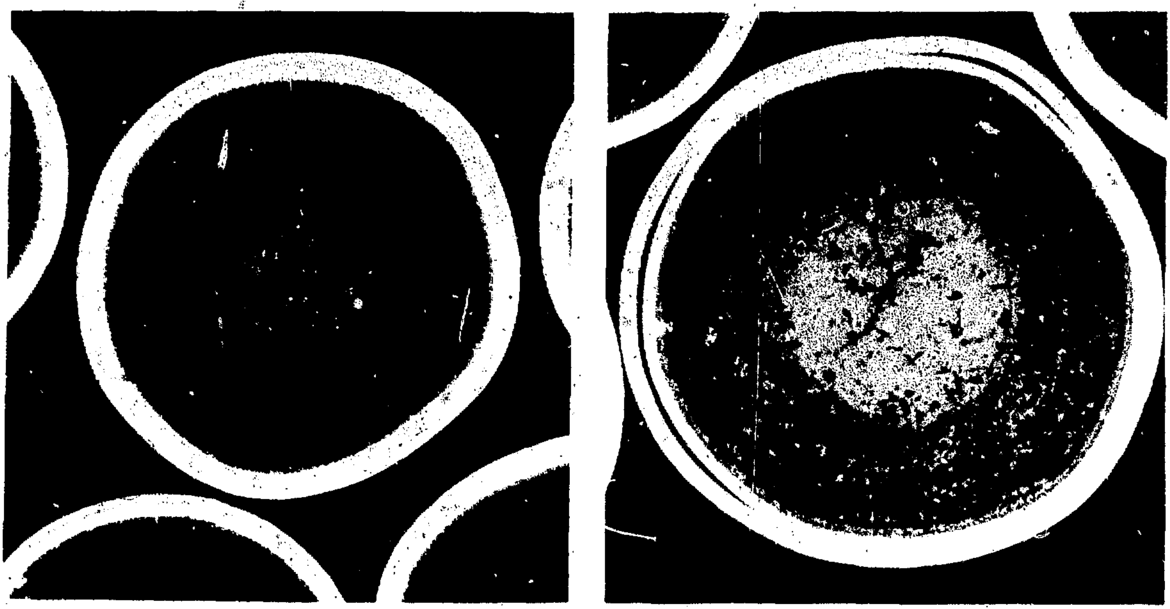


(a). 1538HT. 150X.

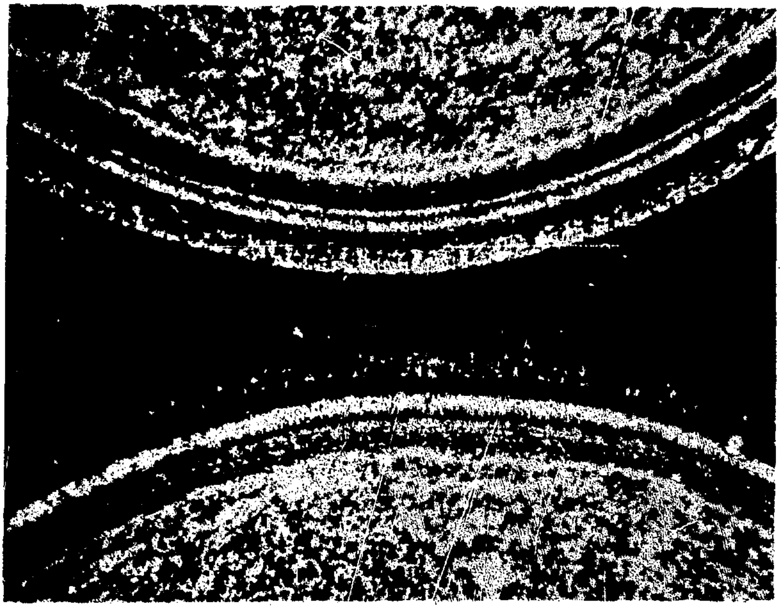


(b). 1538HT, etched. 500X.

Fig. 2. LASL Coated Particles.



(a). 1539HT. 150X.



(b). 1539HT, etched. 500X.

Fig. 3. LASL Coated Particles.

III. TEST MATERIALS

LASL materials tested in OF-2 at Oak Ridge National Laboratory (ORNL) were:

1. Coated particles from Run 1536HT; carbon kernels + buffer + ZrC(Fig.1).
2. Coated particles from Run 1538HT; carbon kernels + buffer + ZrC(Fig.2).
3. Coated particles from Run 1539HT; carbon kernels + buffer + ZrC(Fig.3).
4. Fueled specimens from batch no.006 (Figs.4,5) with nominal loadings of:

   ^{235}U - 0.175 g/cm

   Th - 3.20 g/cm
5. Fueled specimens from batch no.007 (Figs.6,7) with nominal loadings of:

   ^{235}U - 0.106 g/inch

   Th - 2.19 g/inch

Items 1, 2, and 3 were heat treated at 1800°C for one hour in vacuum as a preirradiation preparation. They were provided to test the stability of ZrC to reactor conditions. Photomicrographs of these materials are shown in Figs. 4-7.

Items 4 and 5 were molded fuel compacts consisting of GAC TRISO fissile particles, LASL graded C-ZrC-coated fissile particles (ID, 1524HT) GAC BISO fertile particles, M-3 graphite flour and Varcum[5] binder. These fuel rods were graphitized at 1800°C.

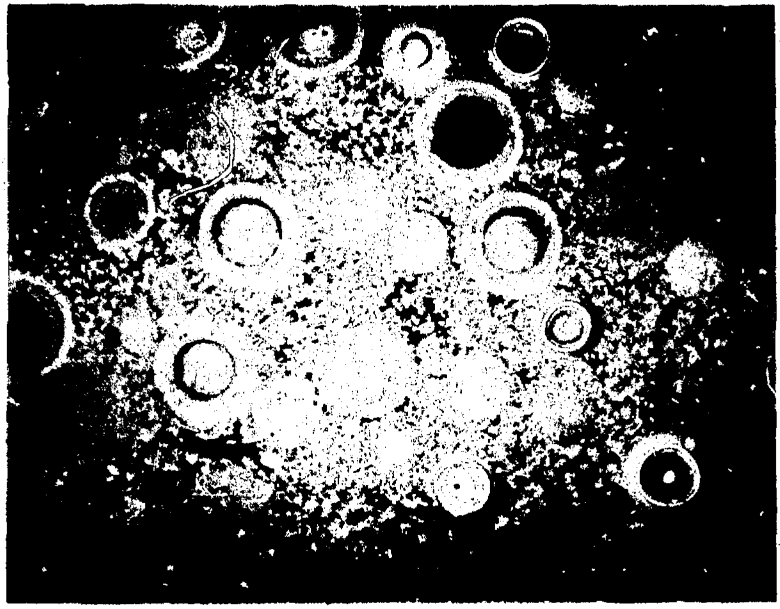
IV. IRRADIATION CONDITIONS

The OF-2 experiment was carried out in the Oak Ridge Research Reactor. Time duration for the OF-2 test was approximately fourteen months. The irradiation test conditions are summarized as follows:

Reactor Location	LASL Identification	FLUENCE (E > 0.18 MeV) ($n\ cm^{-2}$)	TEMPERATURE (°C)	AVERAGE BURNUP (%FIMA) ^{235}U	^{238}U	^{232}Th
A-4-12	007	5.58×10^{21}	1150	73.0	8.31	2.48
B-4-12	006	8.36×10^{21}	1350	79.5	13.2	4.28
B-4-12(Spine)	1536HT	8.36×10^{21}	1350	79.5	13.2	4.28
B-4-12(Spine)	1538HT	8.36×10^{21}	1350	79.5	13.2	4.28
B-4-12(Spine)	1539HT	8.36×10^{21}	1350	79.5	13.2	4.28

V. POSTIRRADIATION EXAMINATION RESULTS

The postirradiation examination results (PIE) were done at the ORNL hot cell facility. The results of the examination are summarized as follows:



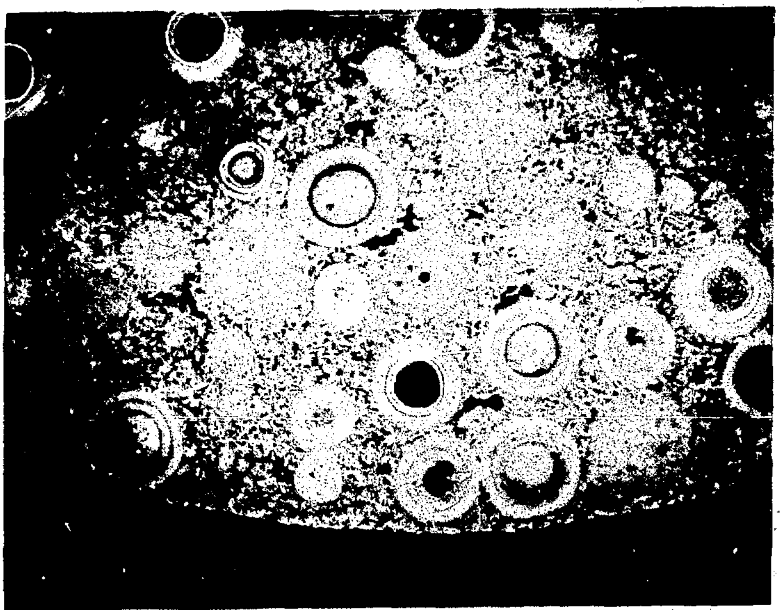


Fig. 4. LASL Fuel Element for OF-2. Lot 006; graphite matrix with carbon particles, GAC BISO fertile particles, GAC TRISO fissile particles, and LASL graded C-ZrC fissile particles. Metallographic mounts were not impregnated after initial grinding and polishing. (20X).

Fig. 5. LASL Fuel Element for OF-2. Lot 006; graphite matrix with carbon particles, GAC BISO fertile particles, GAC TRISO fissile particles, and LASL graded C-ZrC fissile particles. Metallographic mounts were not impregnated after initial grinding and polishing. (50X).

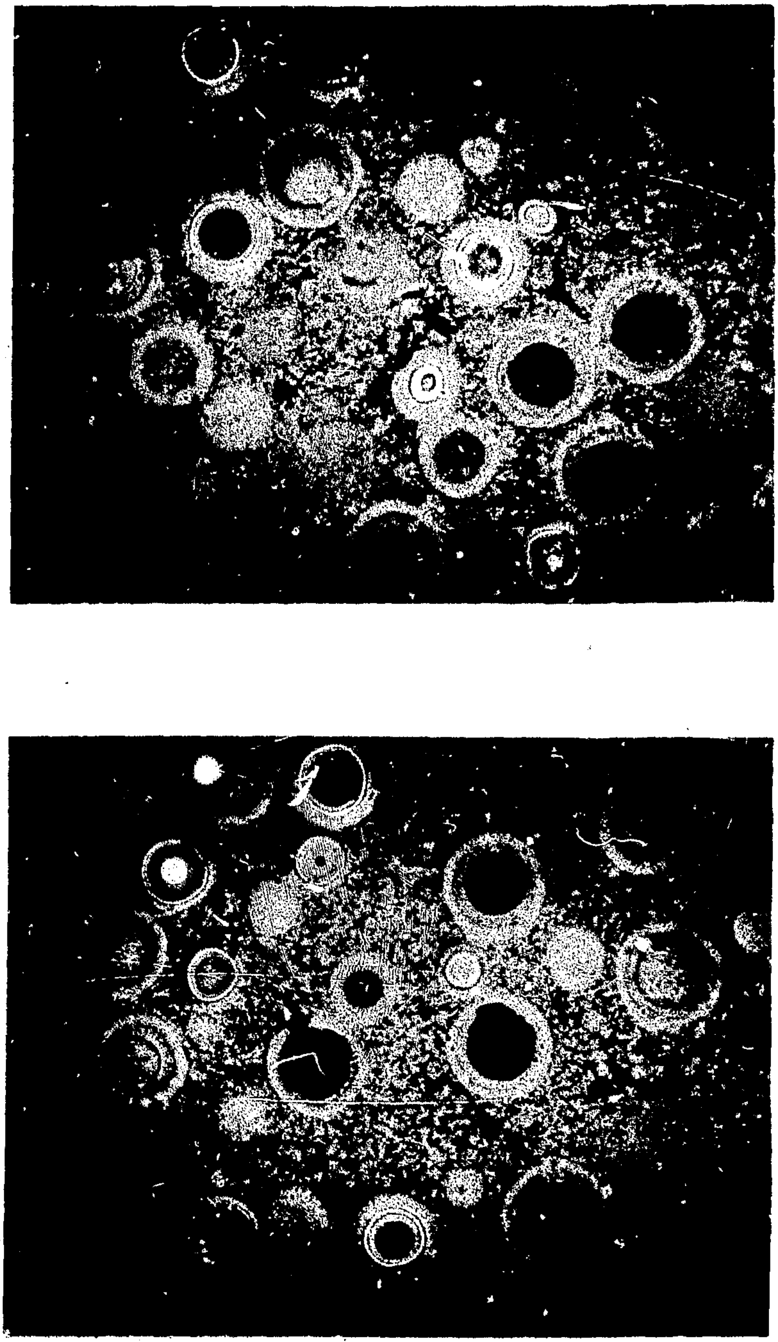


Fig. 6. LASL Fuel Element for OF-2. Lot 007; graphite matrix with carbon particles, GAC BISO fertile particles, GAC TRISO fissile particles, and LASL graded C-ZrC fissile particles. Metallographic mounts were not impregnated after initial grinding and polishing. (20X).

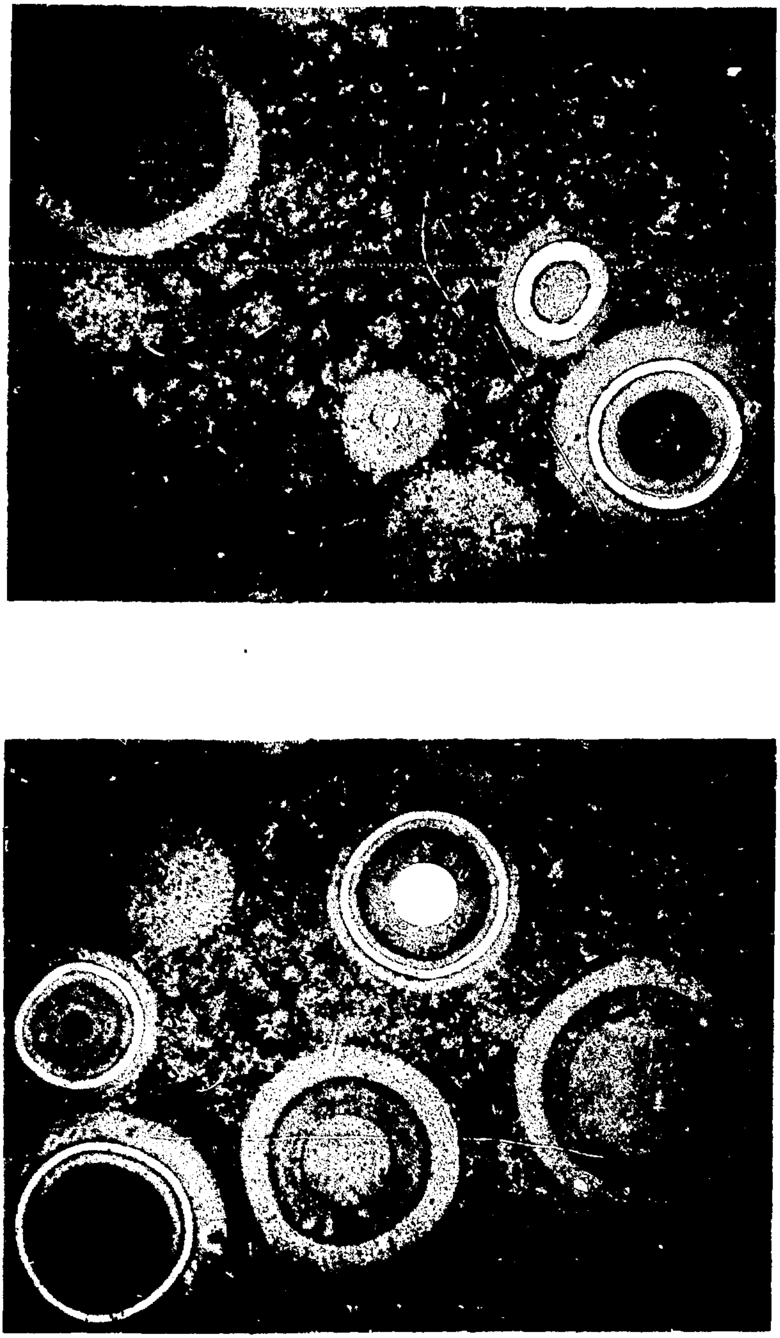
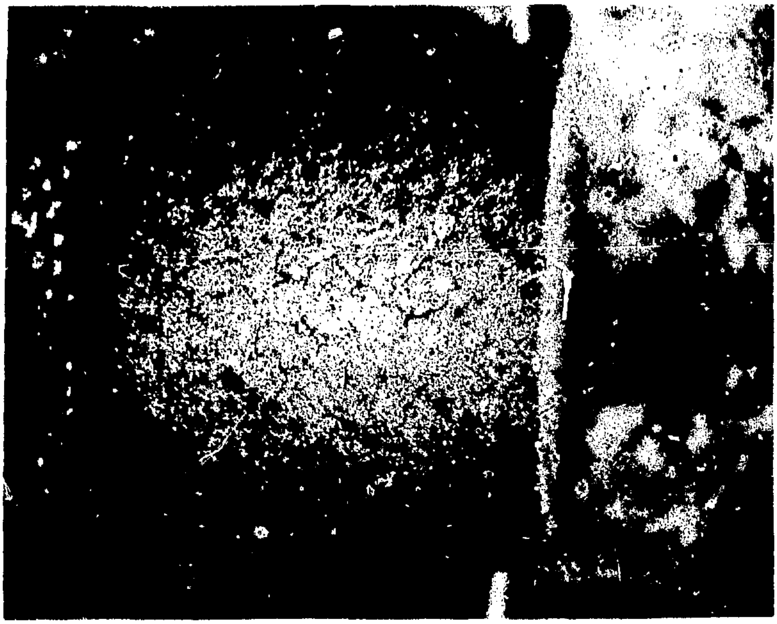


Fig. 7. LASL Fuel Element for OF-2. Lot 007; graphite matrix with carbon particles, GAC BISO fertile particles, GAC TRISO fissile particles, and LASL graded C-ZrC fissile particles. Metallographic mounts were not impregnated after initial grinding and polishing. (50X).

The graphite matrix: Appearance of the high-density graphite matrix in both 006 and 007 was excellent. There was no apparent effect of the high-temperature irradiation. Figure 8 shows the fuel rods upon removal from the reactor, Fig. 9 is a photomicrograph of the irradiated graphite. The very positive irradiation test results on LASL's high-density graphite fuel rods in HT-31[8] were amply confirmed in OF-2.

Loose ZrC-coated particles with inert kernels: The ZrC coats on the loose particles (1536HT, 1538HT, 1539HT) showed no evidence of damage as a result of the irradiation. Their gross appearance is shown in Fig. 10; these are macrophotographs of the particles after removal from the reactor. Identification of the particles in Fig. 10 is by size; the largest is 1536HT (OD = 775 μm), intermediate is 1538HT (OD = 526 μm) and the smallest is 1539HT (OD = 426 μm). There was no evidence to indicate that the stoichiometry in the ZrC_x coat had any influence on the irradiation behavior of the particles. Photomicrographs of irradiated particles are shown in Fig. 11. Originally there was some concern that the prolonged high-temperature irradiation would cause excessive grain growth in the ZrC (see Fig. 1); however, laboratory work done after the OF-2 particles were prepared demonstrated that grain structure could be controlled by raising the ZrC deposition temperature. The higher temperature results in a decrease in the chlorine impurity in the ZrC and coats deposited in this manner develop a much finer (and smaller) grain structure upon prolonged heat treatment. Thus far, none of the irradiations we have done on ZrC particle coats (in HT-29[5], HT-30[5], HT-31[9] and this work) have given visible indication of radiation damage. Our concept of ZrC as a desirable candidate for a high-temperature, radiation resistant particle coat is strongly supported by this experimental evidence.

Particle matrix interaction: No evidence was seen of interactions between the matrix and the particle coats in this test or in the HT-31[8] test. The degree of intimacy and compatibility of the particle coat and the graphite matrix is seen in Fig. 12. We think that the high fraction of fully graphitized flour used in preparing LASL's fuel rods is the reason for the good particle-matrix performance. With high-temperature irradiation, the poorly graphitized binder will change dimension much more than the well-graphitized flour, but since the binder is a minor component in the system the influence of this dimensional change is not strong enough to override the stabilizing influence of the highly crystalline graphite flour.



(a). Rod 007 after 5.58×10^{21} nvt at 1150°C.

(b). Rod 006 after 8.36×10^{21} nvt at 1350°C.

Fig. 8. Irradiated LASL Fuel Rods.

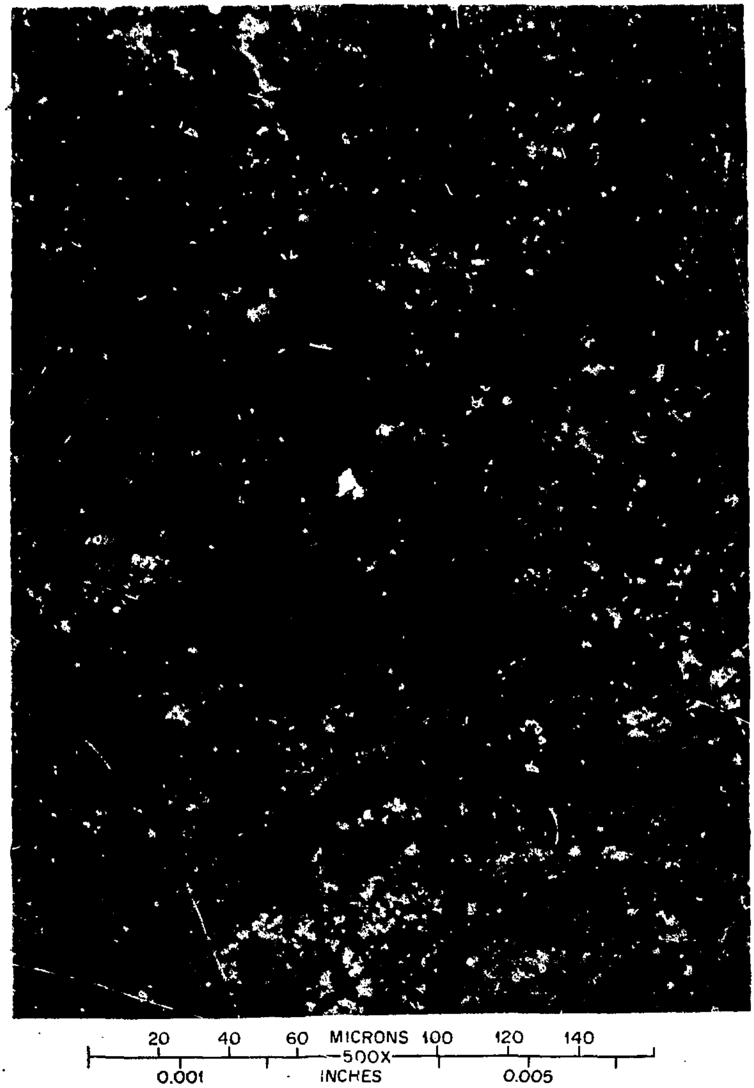
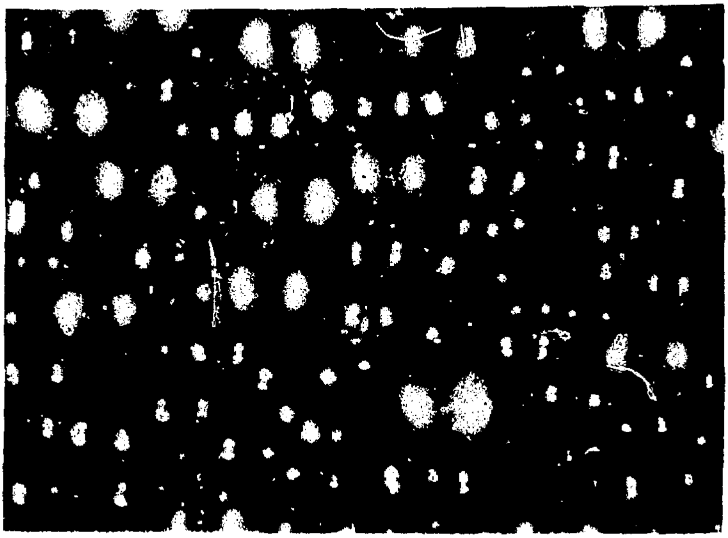
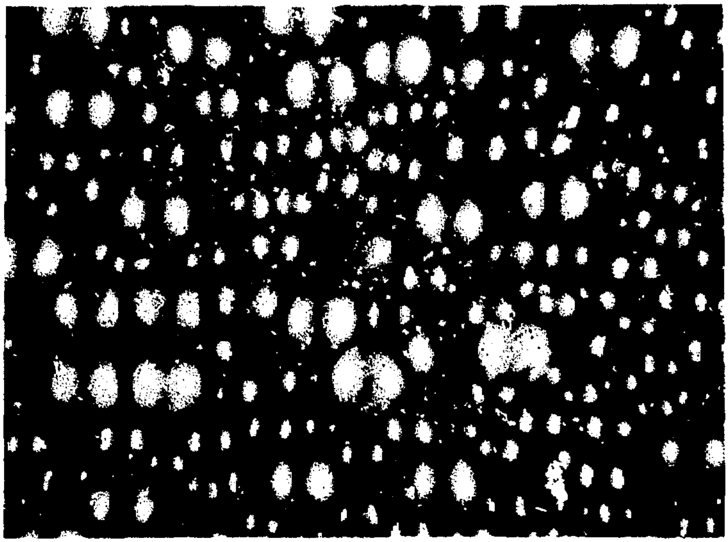


Fig. 9. Graphite matrix of fuel rod 006 after 8.36×10^{21} nvt at 1350°C. (Photomicrograph courtesy of the Oak Ridge National Laboratory).

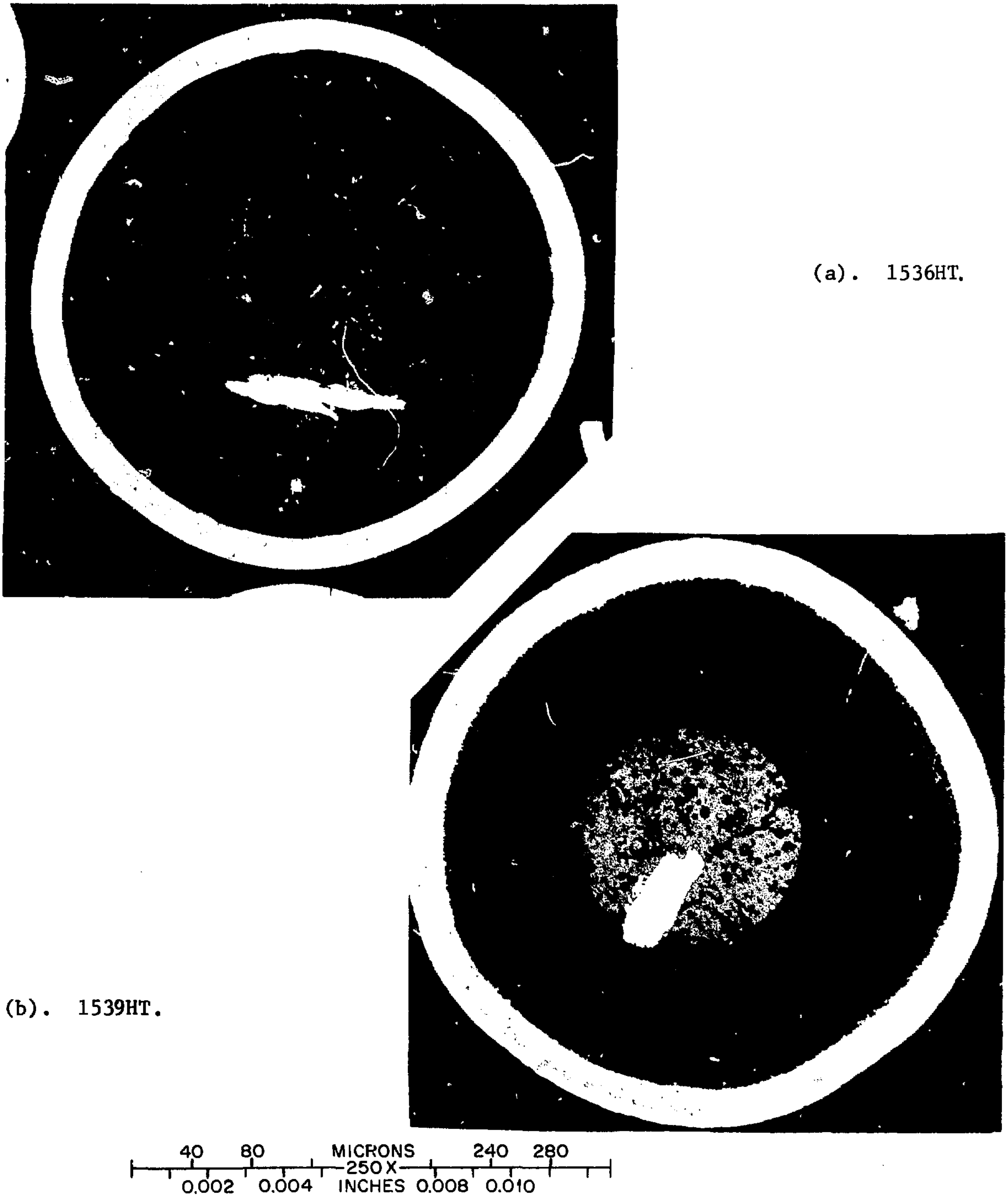


20X



15X

Fig. 10. ZrC-coated inert particles after irradiation at 1350°C and 8.36×10^{21} nvt. (Courtesy of the Oak Ridge National Laboratory).



(a). 1536HT.

(b). 1539HT.

Fig. 11. ZrC-coated inert particles after irradiation at 1350°C and 8.36×10^{21} nvt. (Courtesy of the Oak Ridge National Laboratory).

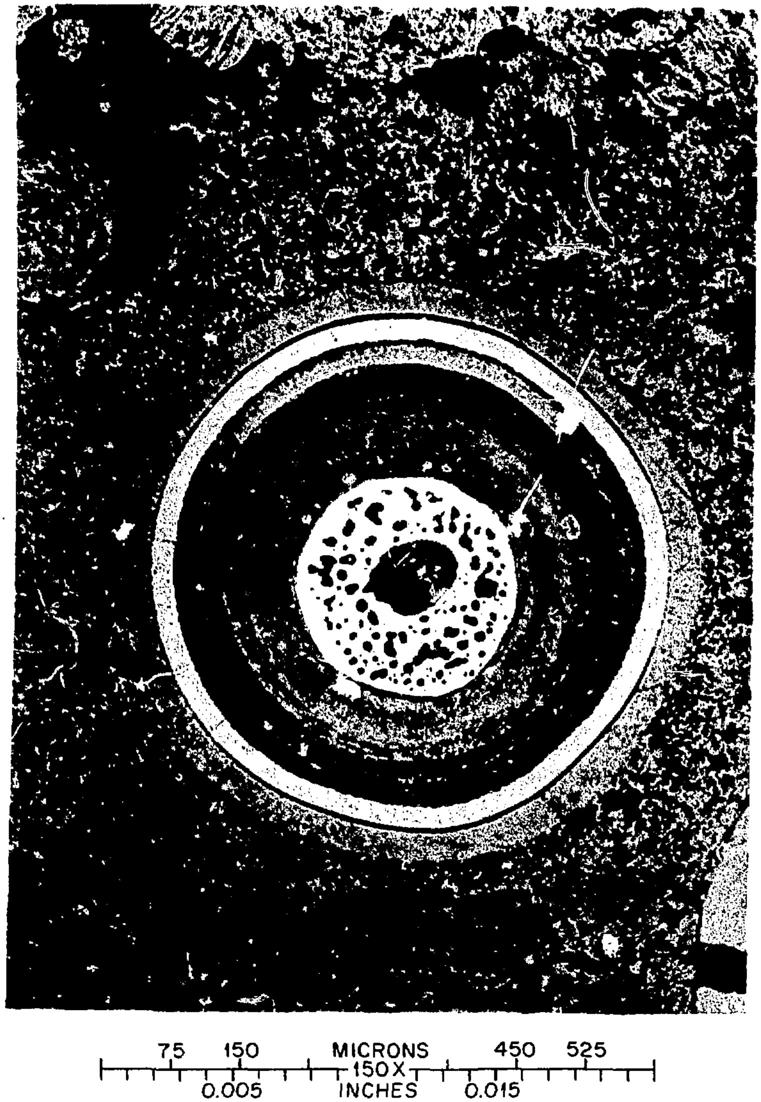
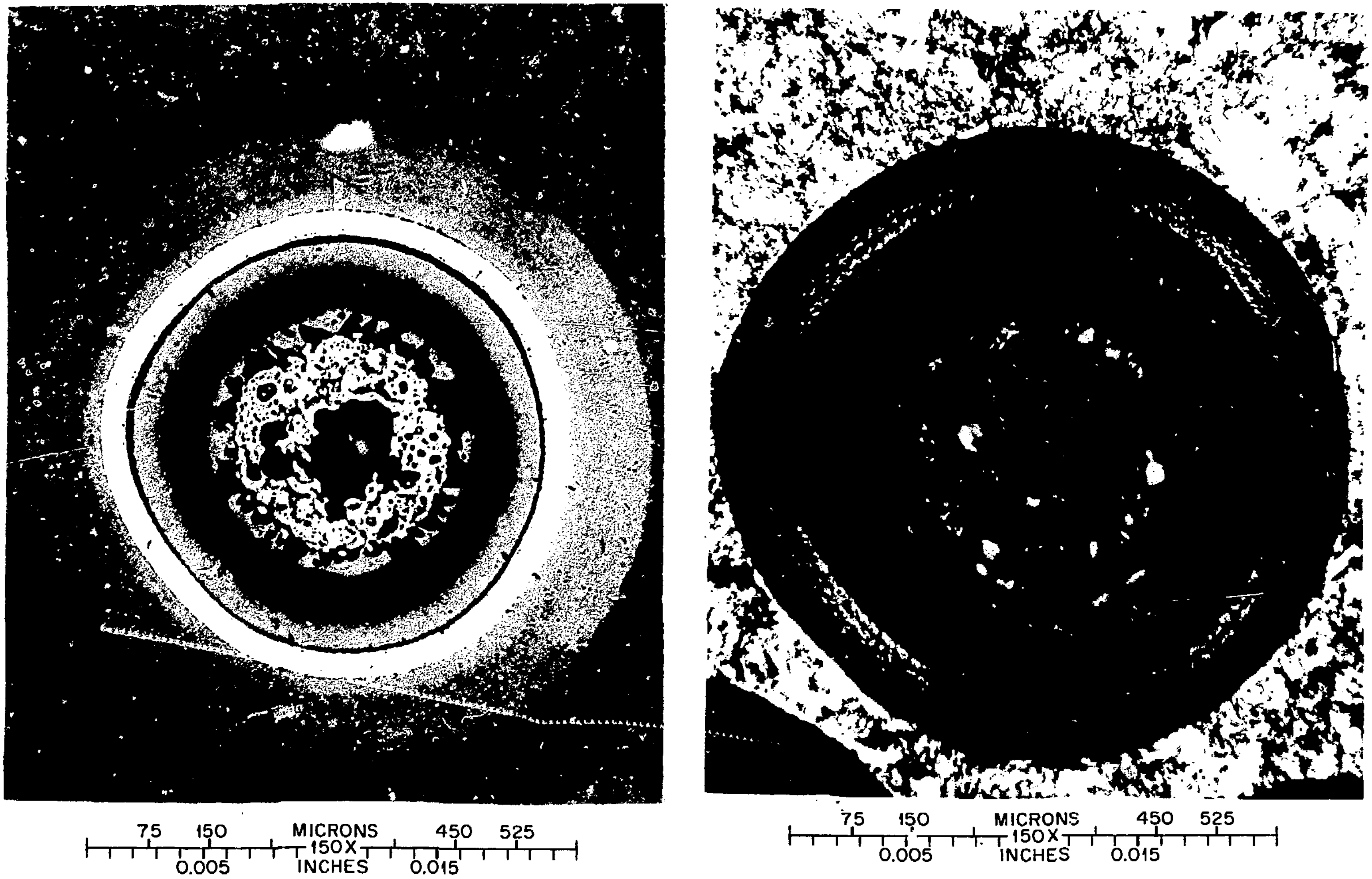


Fig. 12. Fuel rod 006 after irradiation showing compatibility of graphite matrix with fuel particle coat. (Courtesy of the Oak Ridge National Laboratory).

ZrC-coated fuel particles: The behavior of the ZrC-coated fissile particles in fuel rod 007 was satisfactory, their behavior in rod 006 (which operated at higher temperature and fluence) was disappointing. Photomicrographs of the LASL made fissile particles having graded ZrC-C coats are shown in Figs. 13 and 14. In general, the graded ZrC-C coats did not perform as well as we had hoped. Damage was largely in the form of radial cracks in the outermost coat that might have been caused by shrinkage of the outer LTI. The wedge-shaped form of the crack (note Fig. 14) is consistent with this hypothesis. The question of the behavior of the ZrC is more subjective. Hairline radial cracks were seen in the ZrC near the apex of shrinkage cracks in the outer LTI. Whether these cracks were an irradiation effect or whether they are artifacts associated with the metallographic mounting and polishing of the fuel rods is not clear. We (at LASL) have noted cracks in ZrC-coated particles that have been sectioned metallographically; however, we have been able to prove (by repeated fine-polishing steps) that these were artifacts caused by shrinkage of the epoxy resin used in mounting. It is our own opinion that the ZrC cracks seen in the OF-2 experiments are preparation artifacts and that the behavior of the ZrC itself in the high temperature irradiation environment is exemplary.

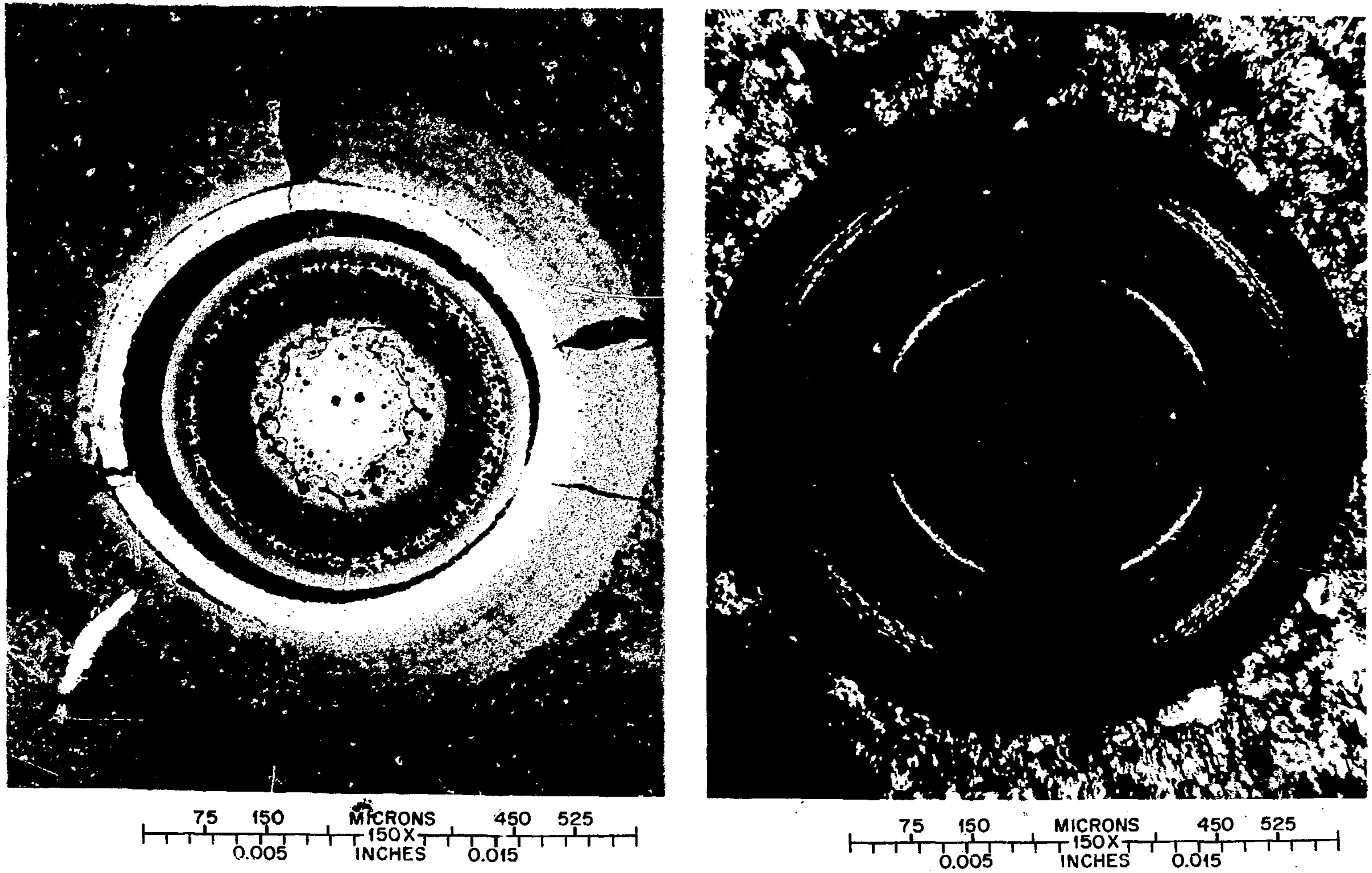
The reason for the poor behavior of the graded ZrC-C coat is reasonably clear; it was deposited at too slow a rate. It is a recognized fact, based on many irradiation tests done by GAC and ORNL, that an oLTI coat that is deposited too slowly will shrink, develop optical anisotropy and, in general, behave worse under the influence of radiation than will an oLTI coat that has been deposited at a rate of about 4 μm/minute or greater. This is an empirical observation that has also been borne out by the irradiation test results on LASL's coated particles. In the fabrication of the ZrC-C composite coats, a compromise between coating rates of the ZrC and the C had to be reached because the ZrC deposits best at a coating rate less than 1 μm/minute. The outer LTI for the fueled particles used (1524HT) was actually deposited at an average coating rate of 0.54 μm/minute - well below the desirable 4-μm/minute minimum rate for an LTI. Other irradiation test experiences with ZrC-doped oLTIs in HT-31[8] and in work reported by Kaae[11] at the 1975 Conference on Carbon have shown that when ZrC is added to the pyrolytic carbon at the proper deposition rate, the irradiation performance is actually improved. Generalizing from irradiation tests HT-28, HT-29, HT-31, and OF-2, LASL-made coated particles with oLTI coats deposited at a rate > 4 μm/minute showed no observable radiation effects, those deposited at the low rate



Bright Field.

Polarized Light.

Fig. 13. LASL fissile particle with ZrC-C graded coat after 5.5×10^{21} nvt at 1150°C (fuel rod 007). (Courtesy of the Oak Ridge National Laboratory).



Bright Field. Polarized Light.

Fig. 14. LASL fissile particle with ZrC-C graded boat after 8.36×10^{21} nvt at 1350°C (fuel rod 006). (Courtesy of the Oak Ridge National Laboratory).

(i.e., ZrC-C alloyed coats tested in OF-2, HT-28, and HT-29) all showed some effects of the irradiation.

ACKNOWLEDGMENTS

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