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# PERFORMANCE OF CANDIDATE HTGR FUELS IN FUEL ROD IRRADIATIONS IN HFIR

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METALS AND CERAMICS DIVISION

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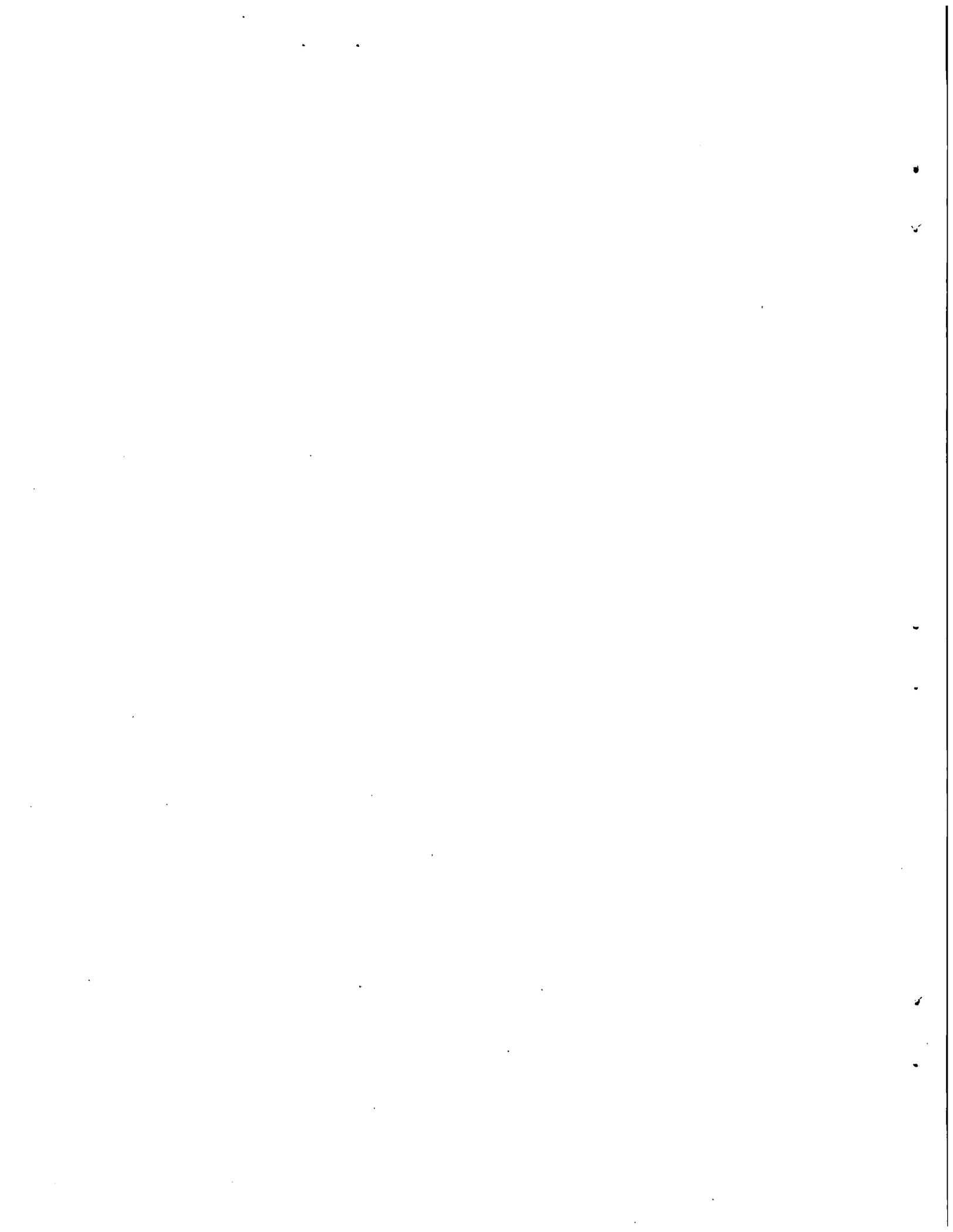
OCTOBER 1974

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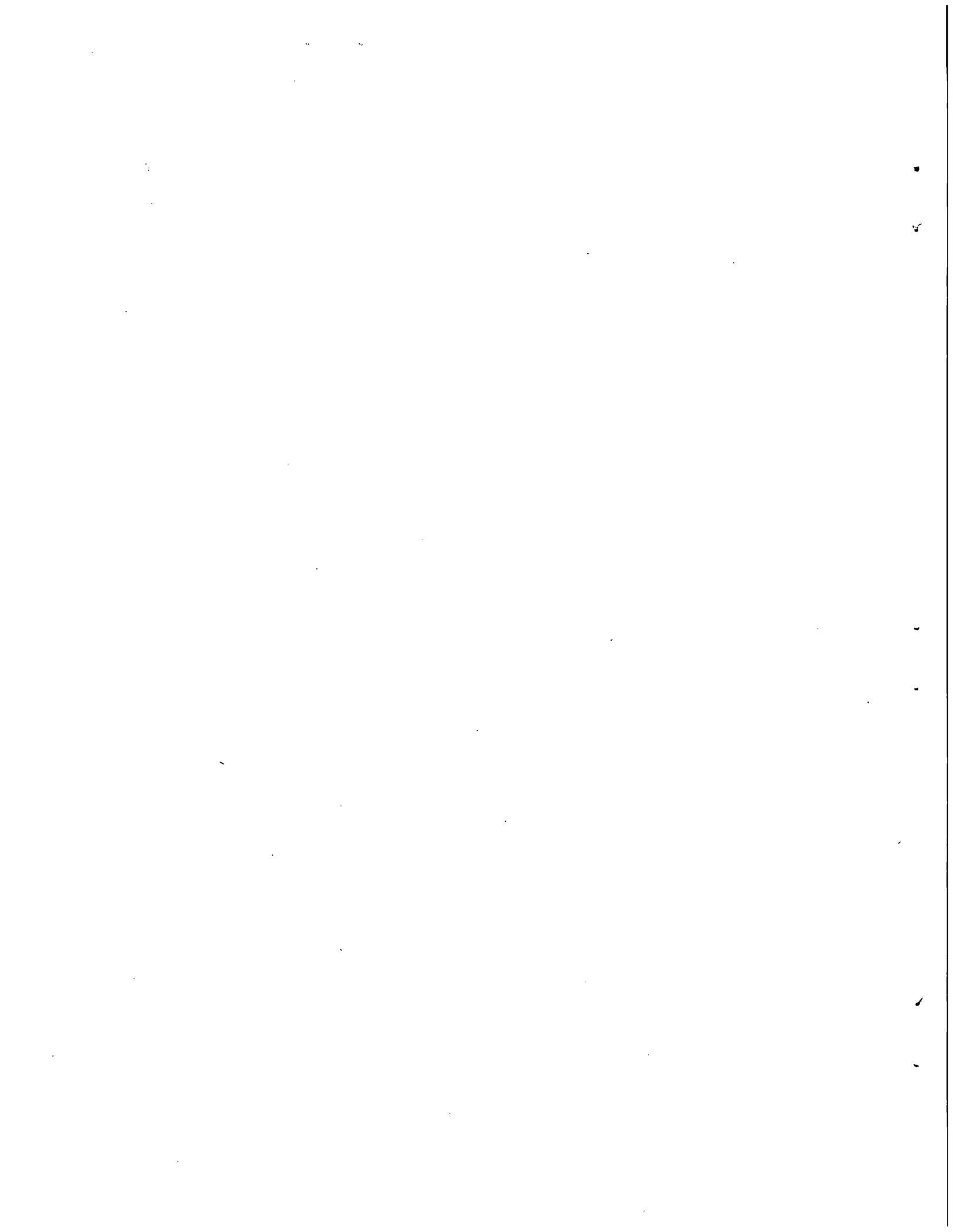


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## CONTENTS

	<u>Page</u>
Abstract . . . . .	1
Introduction . . . . .	1
Description of HRB Irradiation Tests . . . . .	4
Results . . . . .	5
Discussion . . . . .	19
Conclusions . . . . .	19
Acknowledgments . . . . .	21
References . . . . .	21



PERFORMANCE OF CANDIDATE HTGR FUELS IN FUEL ROD  
IRRADIATIONS IN HFIR

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ABSTRACT

Experience has shown that the most valid test for HTGR fuels is one in which the fuel particles are bonded into a matrix and tested with temperatures and temperature gradients simulating those which will exist in the real reactor. A series of tests was conducted in the removable beryllium positions of the High Flux Isotope Reactor (HFIR) in which the above criteria were met. Although the original purposes of the tests varied, some insight was gained on the performance of various fissile and fertile particles under HTGR conditions. The comparative performance of several different bonding matrices was also determined.

Results showed that Bisco-coated ThO<sub>2</sub> continues to be promising as a fertile particle for the HTGR, but it does exhibit amoeba migration after a burnup exceeding 7% FIMA. Bisco-coated (4Th,U)O<sub>2</sub> fissile particles containing either <sup>233</sup>U or highly enriched <sup>235</sup>U showed amoeba migration under conditions where ThO<sub>2</sub> showed none, indicating that the threshold conditions of burnup and temperature had been exceeded by the fissile particles, but not by the fertile particles. Both <sup>235</sup>U- and <sup>233</sup>U-bearing particles showed about the same migration rates.

A comparison of rods made by extrusion and slug-injection with approximately identical fuel loadings, neutron fluxes, and surface temperatures showed that extruded rods had a significantly better fuel performance than slug-injected rods, presumably because of a higher thermal conductivity.

Fissile particles made from ion exchange resins showed no amoeba migration, but moderate to severe fission product-SiC interactions were observed in the Triso coatings. Both palladium (arising primarily from plutonium fissions) and rare earths were identified in different reaction zones. Indications of a liquid phase were found where palladium reacted with SiC and in some of the kernels. More work is required to explain these observations.

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INTRODUCTION

There are three kinds of fuel in the large HTGR: (1) makeup (or initial) fuel containing 93%-enriched <sup>235</sup>U and virgin thorium; (2) recycle fuel containing <sup>233</sup>U and virgin thorium; and (3) recycle fuel

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\*Reactor Division.

containing recycle  $^{235}\text{U}$  plus  $^{236}\text{U}$  and virgin thorium. For a 1160-MWe HTGR operating with a four-year fuel life<sup>1</sup> the number of fuel elements to be loaded annually totals 986, consisting of 568 makeup elements, 388 recycle elements containing  $^{233}\text{U}$ , and 30 elements containing recycle  $^{235}\text{U}$  (plus  $^{236}\text{U}$ ). Since the use of type (3) fuel may be uneconomical and the number of elements is small, the concept is given a low priority in the ORNL program.

The reference fuels for makeup and  $^{233}\text{U}$  recycle types are listed in Table 1 together with the major alternatives.<sup>2,3</sup> Consider first the

Table 1. Reference and Alternate HTGR Fuels

	Makeup Fuel Particles		Recycle Fuel Particles	
	Fissile	Fertile	Fissile	Fertile
Reference	UC <sub>2</sub> Triso	ThO <sub>2</sub> Biso	(4.25Th,U)O <sub>2</sub> Biso	ThO <sub>2</sub> Biso
Alternates	UO <sub>2</sub> Triso	ThO <sub>2</sub> Triso	(4.25Th,U)O <sub>2</sub> Triso	ThO <sub>2</sub> Triso
			(8Th,U)O <sub>2</sub> Biso	
	WAR <sup>a</sup> UC <sub>2</sub> Triso		(8Th,U)O <sub>2</sub> Triso	
	WAR <sup>a</sup> UCO Triso		WAR <sup>a</sup> UC <sub>2</sub> Triso	
		WAR <sup>a</sup> UCO Triso		

<sup>a</sup>WAR: derived from weak-acid resins.

fertile particle. Experience has shown that from the standpoint of both fabrication costs and irradiation performance ThO<sub>2</sub> is superior to ThC<sub>2</sub>. Thus a 500- $\mu\text{m}$ -diam ThO<sub>2</sub> kernel has been selected as the reference. The only serious question concerns the adequacy of the Biso coating. Since the reactor has secondary containment, the main problem is the cleanliness of the primary coolant circuit and maintenance costs. The Biso coating will release Ba, Cs, and Sr from the hotter regions of the core unless these elements are retained by the kernel. Another consideration with the Biso coating is the higher shrinkage in comparison to a Triso coating. Because of this effect fuel rods containing Biso-coated particles experience higher temperatures with a given heating rate than do corresponding rods with Triso-coated particles. Further data are required to resolve these issues.

Turning now to the fissile particles for the makeup fuel elements, it is highly desirable to keep the  $^{235}\text{U}$  and its unwanted parasitic progeny  $^{236}\text{U}$  completely separate from bred  $^{233}\text{U}$ . For this reason the reference fissile particle contains only enriched uranium in the form of UC<sub>2</sub>. Two years ago UO<sub>2</sub> was considered to be preferable to UC<sub>2</sub> because of lower

fabrication costs, but  $\text{UO}_2$  appears to migrate up a temperature gradient (amoeba) more rapidly than  $\text{UC}_2$  below  $1400^\circ\text{C}$ .<sup>4</sup> Tests now in progress should confirm these preliminary indications.

Since comparative tests with  $\text{UO}_2$  and  $\text{ThO}_2$  have shown that  $\text{ThO}_2$  is more resistant against amoeba migration,<sup>4,5</sup> the  $(8\text{Th},\text{U})\text{O}_2$  kernel is being considered as an alternative. This kernel has the advantages of relatively economical fabrication and it eliminates any problem in blending of fissile and fertile particles in fuel rod fabrication. It might also be usable with a Biso coating since the fraction of metallic fission products released from the fuel at the maximum burnup (14% FIMA) would be relatively low. Its principal disadvantage is that the  $^{236}\text{U}$  cannot be separated from  $^{233}\text{U}$  so that the concentration of  $^{236}\text{U}$  in the fuel builds up to an equilibrium value as the fuel is recycled. Added  $^{235}\text{U}$  is required to overcome the effects of the additional poison.

One other candidate for the makeup fissile particle is being considered by ORNL. This is a particle derived from weak-acid resins. Spherical weak-acid resin (WAR) particles consisting of methacrylic acid cross linked with divinyl benzene are loaded with uranyl ions by an ion exchange process.<sup>6</sup> The loaded resins are then dried, carbonized in argon to  $1200^\circ\text{C}$  or higher, and coated with Triso coatings. The advantages of the process are simplicity and low costs. In addition, the kernel can be deoxidized to the form  $\text{UC}_2$  plus carbon prior to coating or it can be made in the form  $\text{UO}_2$  plus carbon or a mixture of  $\text{UO}_2$  and  $\text{UC}_2$  plus carbon. At the moment both the carbide and the partially deoxidized forms are being considered and tested. In earlier work at ORNL fissile particles were made from strong-acid resin (SAR) particles, but unanswered questions about possible sulfur release from exposed kernels led to a change in emphasis toward weak-acid resins.

Perhaps the most difficult choice of all will be the recycle fissile particle. The reference recycle particle consists of  $(4.25\text{Th},\text{U})\text{O}_2$  with a Biso coating. Here the uranium consists primarily of the isotope  $^{233}\text{U}$ , but it contains enough  $^{232}\text{U}$  that remote refabrication is required. On the other hand, no physics penalty is associated with blending  $^{233}\text{U}$  with thorium. The blending of thorium and uranium reduces the FIMA to about 20% and the presence of thorium gives added stability against amoeba migration. The major disadvantage with this reference recycle fissile particle is the amount of heavy metal that must be coated remotely. The minimum amount of remote coating would be achieved by use of sol-gel  $\text{UO}_2$  or particles derived from weak-acid resins. If the rate of migration of  $^{233}\text{UO}_2$  is comparable to  $^{235}\text{UO}_2$ , sol-gel kernels of  $\text{UO}_2$  probably cannot be used. Since the fission-product spectrum of  $^{233}\text{U}$  is somewhat different from that of  $^{235}\text{U}$ , one cannot predict the relative performance, and experimental testing is required. The use of resin-derived fissile particles has the advantages that the carbide or oxide-carbide can be easily achieved and many of the inspection steps can be done before the resin particles are introduced into the remote facility. Another class of materials being considered is sol-gel oxides with thorium-to-uranium ratios other than 4.25. Tests are in progress to establish the optimum Th:U ratio.

## DESCRIPTION OF HRB IRRADIATION TESTS

There are at least four types of failure mechanisms for coated particles: (1) mechanical failure; (2) amoeba migration; (3) fission-product attack of SiC coatings; and (4) matrix-coating interactions. Mechanical failure can be studied in loose particle tests, but the other mechanisms are evaluated best in a matrix configuration with a realistic heat flux. Important criteria for a good test are accurate temperatures and heat fluxes, high fast fluence, and high burnup. These criteria have been met fairly well in a series of instrumented capsules irradiated in the removable beryllium (RB) facilities of the High Flux Isotope Reactor (HFIR). Each HRB capsule contains a 16-in.-long column of 0.490-in.-diam fuel rods. The Poco graphite sleeve that supports the fuel rods is instrumented with several chromel-alumel thermocouples. In some tests, a central temperature monitor has also been inserted into annular fuel rods. The capsule is swept with helium-neon mixtures to help control temperatures and to provide information on fission-gas release.<sup>7</sup> The peak fast flux is  $5 \times 10^{14}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  ( $>0.18$  MeV) and the peak perturbed thermal flux is  $1.18 \times 10^{15}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  ( $>0.414$  eV). In the large HTGR the peak fast flux is about  $8 \times 10^{13}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  ( $>0.18$  MeV) and the peak thermal flux is about  $1.5 \times 10^{14}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  ( $>0.414$  eV). Comparing these fluxes, one finds that the full fluence of the HTGR over a four-year period at 80% load factor can be achieved in the HRB facility in eight 23-day cycles. The major drawback to the facility is the high thermal flux (eight times the HTGR peak) which leads to the restriction that a given fuel rod can contain only one-eighth as much fissile material as a real fuel rod. We normally dilute fuel rods with coated inert carbon kernels.

Another problem with the high thermal flux is that the  $^{235}\text{U}$  is depleted more rapidly (50% in about 16 days at the reactor midplane) than the  $^{233}\text{U}$  can be bred into the thorium. The fertile particle reaches its steady-state power at the end of the fourth 23-day cycle. As a consequence the fuel rods would run cold between the first and fourth cycles if we did not add  $^{238}\text{U}$ . The  $^{238}\text{U}$ - $^{239}\text{Pu}$  equilibrium is established between the first and second cycles. Because of these considerations, the fissile particles have normally been 7 to 10% enriched in  $^{235}\text{U}$  instead of fully enriched. With this concentration the power generation rate and temperatures simulate the actual HTGR well. The only drawback is that the fissile particles that contain only the partially enriched uranium experience about 25% FIMA instead of the desired 75%. If amoeba migration and fission-product attack on the silicon carbide are burnup dependent, some tests are required to full burnup.

When the HRB tests were initiated, the number one problem was the development of matrix materials stable enough to bond particles together and retain integrity during test. Consequently, the fissile and fertile particles were selected for convenience. Since fissile particles made from ion exchange resins are easiest to prepare in small lots with various enrichments, these were used for capsules HRB-2 through HRB-5. In HRB-6 the fissile particles were sol-gel  $(4\text{Th,U})\text{O}_2$  with Biso coatings, the reference recycle particle; particles containing either  $^{233}\text{U}$  or  $^{235}\text{U}$  were tested. A description of the fissile and fertile particles in the various

HRB capsules is given in Table 2. The purpose of each capsule is listed in Table 3 together with test conditions. Detailed results have been reported previously on capsules HRB-1 (ref. 7) and HRB-2 (ref. 8).

## RESULTS

The principal results obtained from HRB capsules consist of three types of information: general stability of the various matrices, dimensional changes induced by fast-neutron irradiation, and performance of the fissile and fertile particles. In general the stability of all but the earliest bonding matrices was good. In a few instances extensive failure of particle coatings was observed; this resulted in general degradation of the fuel rods. The dimensional changes of densely packed rods were determined by the densification of the coatings. Rods with all Triso coatings showed diameter decreases of about 2% at full fluence. Rods with Biso coatings showed increasing shrinkage with decreasing initial coating density;<sup>9</sup> results are shown in Table 4. From the shrinkage standpoint, initial coating densities above 1.95 g/cm<sup>3</sup> are desirable. However, we have found that these coatings must be applied at coating rates above 10  $\mu$ m/min (in our research coaters). Otherwise the anisotropy of such dense coatings is unacceptable (BAF > 1.10).<sup>9</sup>

The most interesting results were obtained by metallographic examination of various rods near the peak flux positions. Figure 1 shows reference preproduction fissile and fertile particles for the Fort St. Vrain (FSV) Reactor irradiated in HRB-2. Both the (4Th,U)C<sub>2</sub> fissile and ThC<sub>2</sub> fertile particles performed well at the full HTGR fluence to burnups equal to or exceeding the HTGR peaks. These results give assurance that the FSV fuel will perform well. The performance of UO<sub>2</sub> in HRB-1 is indicated in Fig. 2. The rod containing this particle had a matrix that contained large amounts of glassy carbon derived from phenolic resins. Severe cracking and debonding produced a structure such that the thermal conductivity was essentially that of loose coated particles; however, the linear heating rate was only 3.5 kW/ft so that the maximum particle temperature was about 1250°C. Under these conditions, some slight amoeba migration of the UO<sub>2</sub> was observed (Fig. 2). The breakage of the outer low-temperature isotropic (LTI) coating was due to the character of the outer nonbonding and sacrificial coatings, which are no longer used. A fissile particle consisting of (4Th,U)O<sub>2</sub> in a companion rod to the above particle is shown in Fig. 3. The enrichments were adjusted to make the burnup of the two particles about the same. With the mixed oxide, no hint of amoeba was observed, suggesting that increasing the thorium content increases the resistance against amoeba migration.

Fissile particles derived from strong-acid resins are shown in Fig. 4 after irradiation in the HRB-2 capsule. The coatings were generally intact and undamaged. The broken coating shown on the right of the figure was caused by a matrix-coating interaction, and was one of only three failed particles found. Fissile kernels derived from strong-acid resins were tested under more severe conditions in HRB-3. Results are shown in Fig. 5. The particle design being tested consisted of a Triso coating applied directly onto the kernel without a buffer. The majority of the particles performed well, but a few particles showed failure of the inner LTI

Table 2. Description of Fissile and Fertile Particles in HRB Capsules

	HRB-1			HRB-2				HRB-3		HRB-4, -5		HRB-6			
	Fissile 1	Fissile 2	Fertile	Fissile		Fertile		Fissile	Fertile	Fissile	Fertile	Fissile 1	Fissile 2	Fissile 3	Fertile
				GGA	ORNL	GGA	ORNL								
Type	UO <sub>2</sub>	(4Th,U)O <sub>2</sub>	ThO <sub>2</sub>	(4Th,U)C <sub>2</sub>	SAR UOS <sup>a</sup>	ThC <sub>2</sub>	ThO <sub>2</sub>	SAR UCS <sup>b</sup>	ThO <sub>2</sub>	WAR UC <sub>2</sub> <sup>c</sup>	ThO <sub>2</sub>	(4Th,U)O <sub>2</sub>	(4Th,U)O <sub>2</sub>	(4Th,U)O <sub>2</sub>	ThO <sub>2</sub>
U Enrichment, %	7.1	36.0		93.1	10.2			7.3		6.0		93.1	98 <sup>233</sup> U	93.1	
Kernel Diameter, μm	195	195	380	150	252	350	201	430	400	370	490	366	351	366	504
Buffer								None							
Density, g/cm <sup>3</sup>	0.9	0.9	0.9	1.1	0.9	1.1	0.9		1.2	0.85	0.95	1.0	1.1	1.1	1.2
Thickness, μm	42	37	64	55	31	55	56		55	45	88	97	105	98	96
Inner LTI <sup>d</sup>					None		None		None		None	None	None		None
Density, g/cm <sup>3</sup>	1.85	1.85	1.85	1.85			1.85	1.8		1.94				1.95	
Thickness, μm	20	20	5	25			25	22		31				31	
SiC					None		None		None		None	None	None		None
Density, g/cm <sup>3</sup>	3.14	3.15	3.15	3.21		3.21		3.21		3.21				3.20	
Thickness, μm	19	23	17	25		25		23		32				27	
Outer LTI <sup>d</sup>															
Density, g/cm <sup>3</sup>	1.78	1.80	1.88	1.80	1.93	1.80	1.91	1.86	1.97	1.89	1.92	2.05	1.81	1.98	1.81
Thickness, μm	43	53	48	25	74	30	61	63	76	28	79	93	85	41	93

<sup>a</sup>SAR UOS - multiphase kernels prepared by carbonizing uranium-loaded strong-acid resins at 1200°C.

<sup>b</sup>SAR UCS - multiphase kernels prepared by carbonizing uranium-loaded strong-acid resins at 1800°C.

<sup>c</sup>WAR UC<sub>2</sub> - kernels prepared by carbonizing uranium-loaded weak-acid resins at 1600°C.

<sup>d</sup>LTI - low temperature isotropic PyC coating.

9

Table 3. Description of HRB Irradiation Tests

Capsule	Specimen Description	Irradiation Conditions		Maximum Fast Fluence (neutrons/cm <sup>2</sup> , > 0.18 MeV)  × 10 <sup>21</sup>	Maximum Burnup, % FIMA		Irradiation Schedule	
		Rod Surface Temperature (°C)	Maximum Linear Heating Rate (kW/ft)		Particle		Start	End
					Fissile	Fertile		
HRB-1	Initial design matrix materials; improved matrices with higher carbon contents; sacrificial layers on coatings to prevent matrix-coating interactions	1100	3.5	8	25	10	8/69	2/70
HRB-2	Effect of filler material on matrix performance; FSV production-type fuel rods	1100	3.3	11	31	15	12/70	11/71
HRB-3	Warm-molded fuel rods with matrix density of 1.45 g/cm <sup>3</sup> ; fuel rods made by slug-injection; experimental fuel rods made by GGA	1100	5.8	11	31	15	1/72	10/72
HRB-4	Extruded rods with matrix density of 1.75 g/cm <sup>3</sup> ; rods made with improved slug-injection techniques; experimental fuel rods made by GGA	1100	5.4	11	30	15	10/72	6/73
HRB-5	Extruded rods with matrix density of 1.75 g/cm <sup>3</sup> ; rods made with improved slug-injection techniques; experimental fuel rods made by GGA	1100	5.4	5	15	4.4	10/72	2/73
HRB-6	Reference recycle particles; extruded rods; slug-injected rods; experimental fuel rods made by GGA	1100	5.4	8	30	10	2/73	9/73

Table 4. Evaluation of the Density of Particle Coatings in ORNL Fuel Rods at  $8 \times 10^{21}$  neutrons/cm<sup>2</sup> Fast Fluence Exposure

Initial Outer Coating Density (g/cm <sup>3</sup> )	Range of Measured Fuel Rod Diameter Decrease (%)		Calculated Final Outer Coating Density <sup>a</sup> (g/cm <sup>3</sup> )		
	Maximum	Minimum	Maximum	Minimum	Average
1.98	3.35	2.00	2.18	2.10	2.14
1.89	4.70	4.00	2.16	2.12	2.14
1.85	6.20	5.15	2.19	2.14	2.16
1.67	7.50	5.15	2.05	1.93	2.00

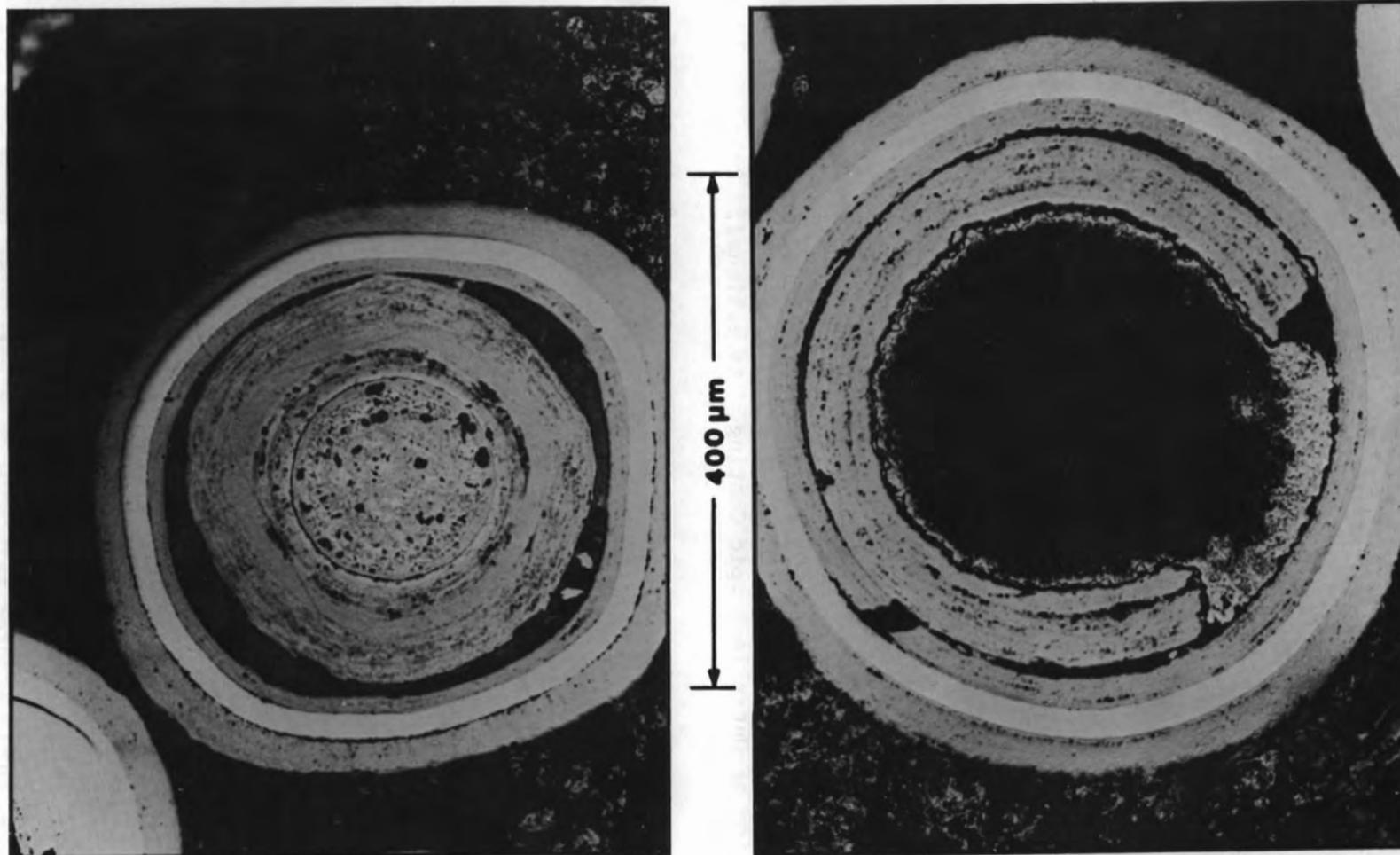
<sup>a</sup>Based on assumption that coatings shrink isotropically and that densification is not affected by internal pressure.

coating and an interaction between the fuel and the silicon carbide coating. We now believe that a thin buffer layer should have been applied to protect the inner LTI coating.

A fertile particle in the same rod is also shown in Fig. 5. Test Conditions were severe enough to cause some amoeba migration of the ThO<sub>2</sub> particle. This was not observed in earlier HRB capsules, which had lower linear heating rates. One cause for the amoeba migration observed was the low thermal conductivity of the particular bonded bed matrix (density 0.58 g/cm<sup>3</sup>). Generally, bonded beds have densities in the range 0.7 to 0.8 g/cm<sup>3</sup>. An adjoining rod to the one above, but with a much higher matrix density (1.45 g/cm<sup>3</sup>), is shown in Fig. 6. This rod, made by a slurry-blending process, had a high enough thermal conductivity that no ThO<sub>2</sub> amoeba was observed.

After a process for loading weak-acid resins was developed, emphasis shifted to this type of fissile particle because of the absence of sulfur. The performance of this type of particle in HRB-5 is shown in Fig. 7. The main effect observed was the marked shrinkage of the initially low-density kernel, so that the fissile kernel is like a pea in a pod. The fertile particle, also shown in Fig. 7, is in excellent condition.

The appearance of the same fissile particles used in slug-injection fuel rods and irradiated in HRB-4 (same conditions, but twice the burnup and fast fluence as in HRB-5) is shown in Fig. 8. A typical-appearing particle is shown on the left of this figure; the only obvious changes at this higher fluence level were additional densification of the buffer coating and the appearance of small metallic globules on the inner surface of the silicon carbide layer on the cold side of the particle. These globules have been identified as the rare earth fission products La, Ce, Pr, and Nd. The effect of the rare earths on the silicon carbide is shown in Fig. 9 along with an adjacent particle that revealed another type of attack. About one-third of the fissile particles showed random, localized



(Th,U)C<sub>2</sub> Fissile, 23% FIMA

ThC<sub>2</sub> Fertile, 11% FIMA

Fig. 1. Triso-Coated Particles Irradiated to  $7.6 \times 10^{21}$  neutrons/cm<sup>2</sup> at 1200°C.

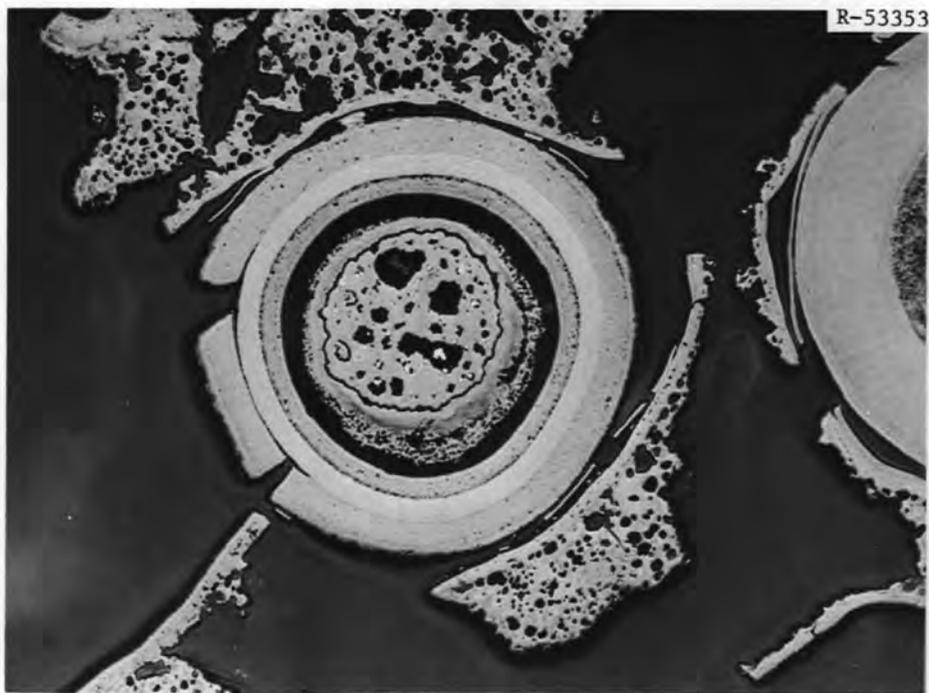


Fig. 2. Triso-Coated  $\text{UO}_2$  Fuel Particles Irradiated to a Fast Fluence of  $5.8 \times 10^{21}$  neutrons/cm<sup>2</sup> (22 at. % burnup), Showing Fracture and Deformation of Outer Isotropic Coating. As polished. 200 $\times$ . Reduced 17%.

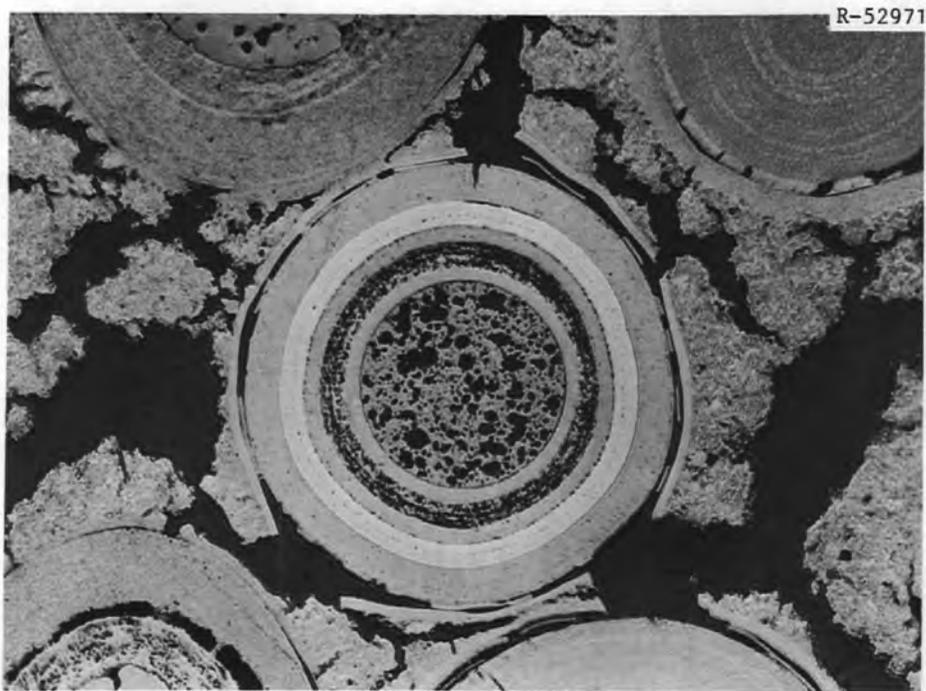
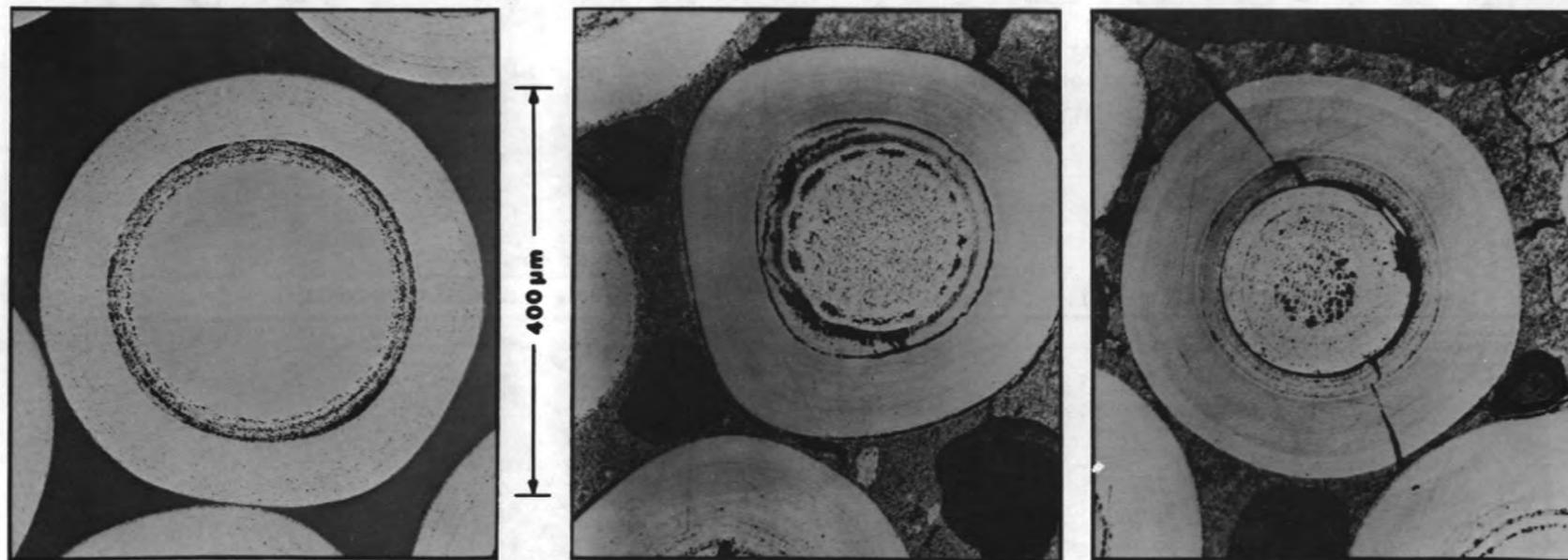


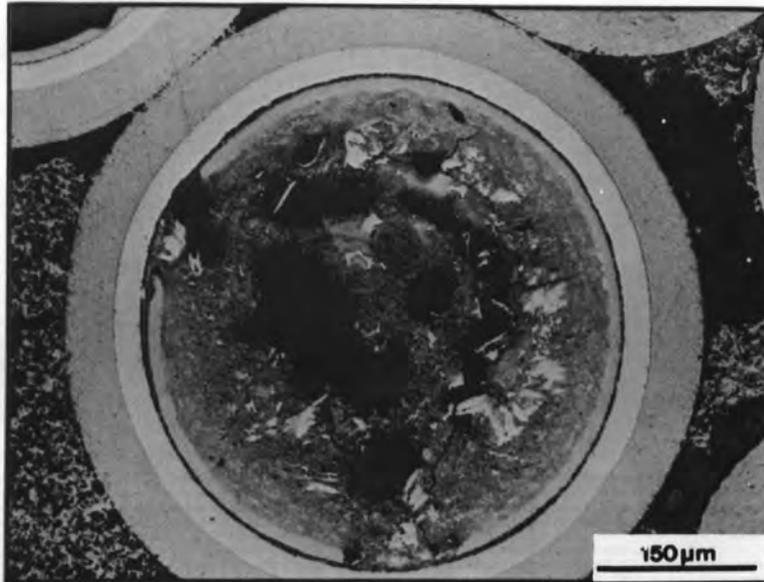
Fig. 3. Triso-Coated  $(4\text{Th,U})\text{O}_2$  Fuel Particles Irradiated to a Fast Fluence of  $5.8 \times 10^{21}$  neutrons/cm<sup>2</sup> (15 at. % burnup). As polished. 200 $\times$ . Reduced 17%.



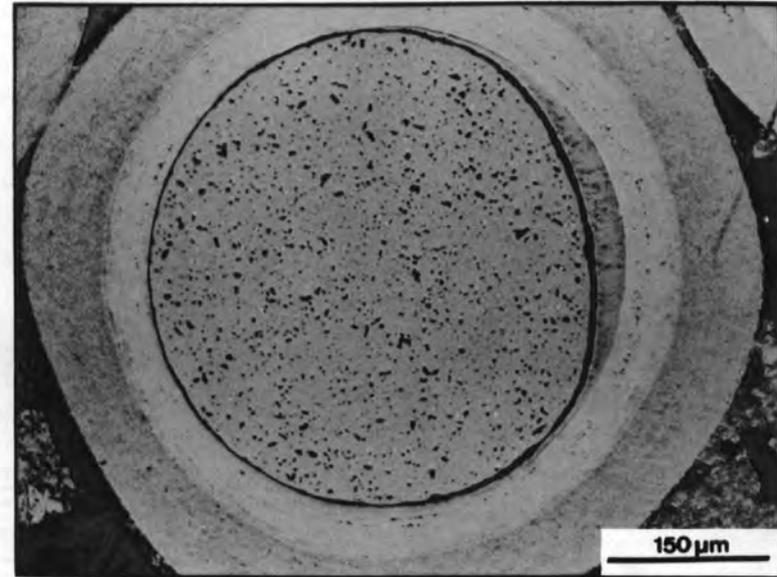
Unirradiated

 $7.9 \times 10^{21} \text{ n/cm}^2$  and 31% FIMA at 1280°C

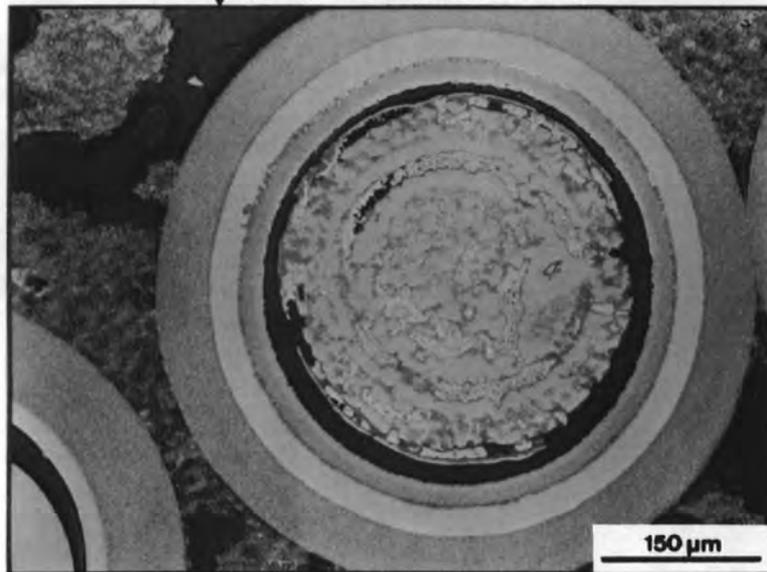
Fig. 4. Biso-Coated UOS Plus Carbon Fissile Particles Derived from Strong-Acid Resins.



↑STRONG ACID RESIN (31 % FIMA)



ThO<sub>2</sub> (14.5% FIMA)



Center-Line Temperature: 1460°C  
 Fast Fluence:  $8 \times 10^{21}$  neutrons/cm<sup>2</sup>  
 Time at Power: 254 days

Fig. 5. Relative Thermal Stability of Fissile and Fertile Kernels Irradiated in HRB-3 to a Fast Fluence of  $8 \times 10^{21}$  neutrons/cm<sup>2</sup> at a Center Line Temperature of 1460°C for 254 Days. As polished.

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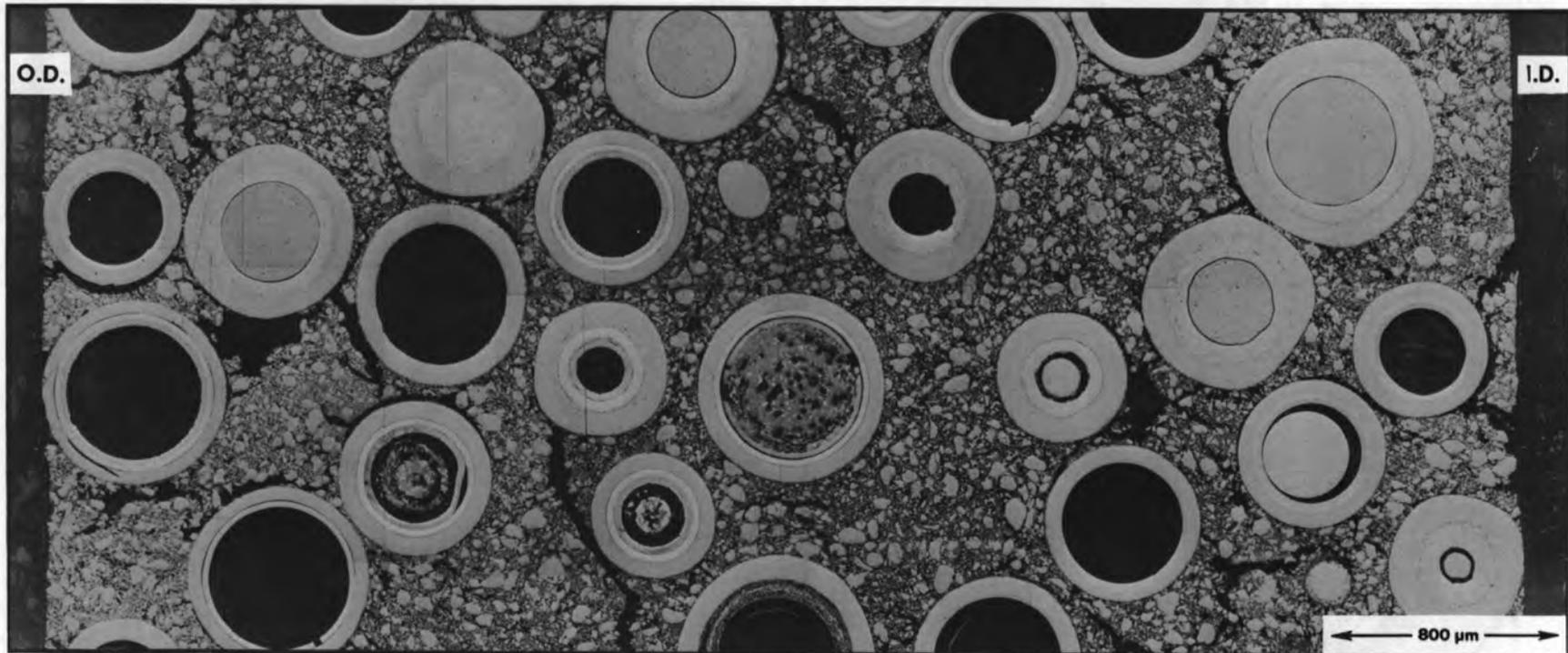


Fig. 6. Cross Section of HRB-3 Molded Specimen 1-D Containing 42 vol % Triso SA Resin, Biso  $\text{ThO}_2$ , and Inert Particles.

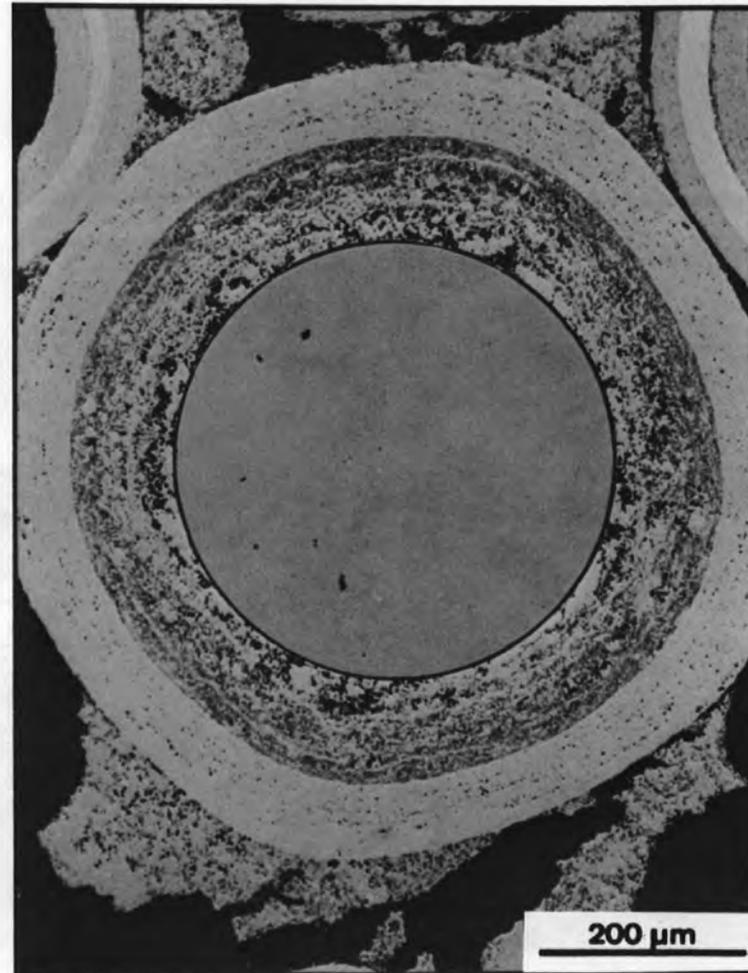
**WEAK ACID RESIN (15% FIMA)****ThO<sub>2</sub> (4.4% FIMA)**

Fig. 7. Thermal Stability of Fissile and Fertile Kernels Irradiated in HRB-5 to a Fast Fluence of  $4 \times 10^{21}$  neutrons/cm<sup>2</sup> at a Center Line Temperature of 1230°C for 107 Days. As polished.

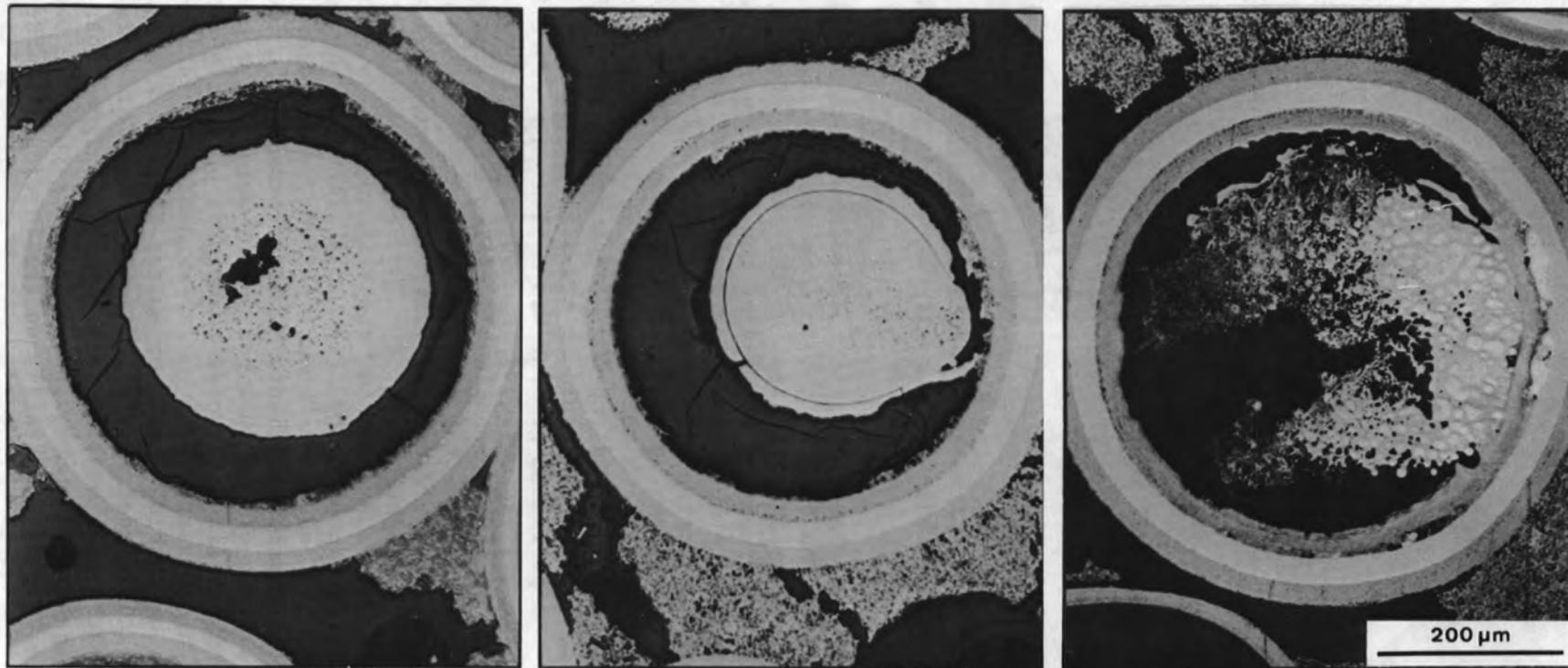


Fig. 8. Weak-Acid-Resin-Derived Fissile Coated Particles ( $\sim 95\%$   $UC_2$ ) from Irradiation Capsule HRB-4. The kernel on the left is typical in appearance; the kernel on the right was molten during irradiation.

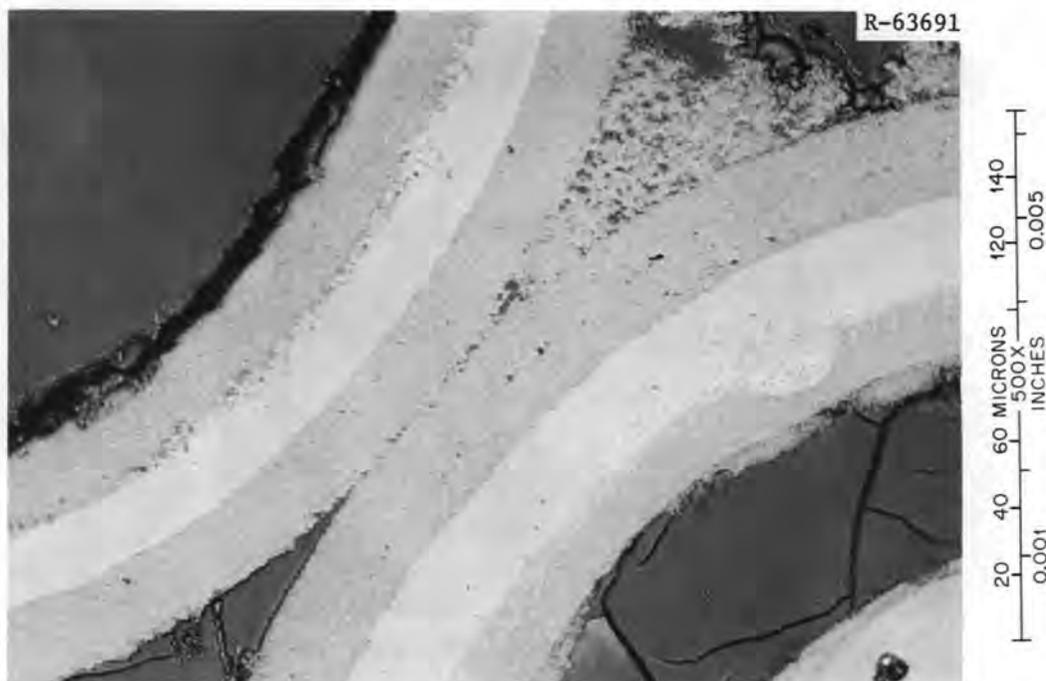


Fig. 9. Two Types of Attack on the Silicon Carbide Layer in the Fissile Particles from Irradiation Capsule HRB-4. As polished. Reduced 13%.

attack that was not temperature-gradient dependent. The attack varied in degree of severity from only slight to complete penetration of the silicon carbide. A general degradation of the inner surface of the silicon carbide is also apparent in many of the coated particles. Analysis of a region of attack with the aid of an electron microprobe revealed the fission product palladium to be involved. The attacked regions appeared to have been molten; the palladium-silicon phase diagram shows three eutectics that have melting points below the surface temperature of the fuel rods (15.5% Pd, mp 800°C; approximately 45% Pd, mp 720°C; 58% Pd, mp 850°C). This result would be atypical of HTGR conditions, since the bulk of the palladium present was a fission product from  $^{239}\text{Pu}$  and not the  $^{235}\text{U}$  (the  $\text{UC}_2$  was enriched to about 6%  $^{235}\text{U}$ ). However, this result could become significant should a decision be made to incorporate plutonium carbide in the HTGR fuel cycle.

About one-fourth of the weak-acid resin kernels appeared to have been molten, as shown in the right of Fig. 8. The light phase that dissolved a portion of the inner surface region of the silicon carbide has been identified as rare earth fission products (Fig. 10). The apparent movement of this kernel cannot be classified as an "amoeba" effect, since there was no correlation with the thermal gradient. Molten kernels were found scattered across the cross section of the fuel rod. They were always associated with severe fission product-silicon carbide reactions, but not necessarily from palladium. In contrast, there was *no* evidence of fission-product attack of the silicon carbide layers or molten kernels in the same fissile particles used in an extruded rod, also in this capsule. This extruded fuel rod operated at a peak heating rate about 20% higher than the slug-injected fuel rod described above, thus indicating that the performance of coated particles can depend heavily on the fabrication mode employed.

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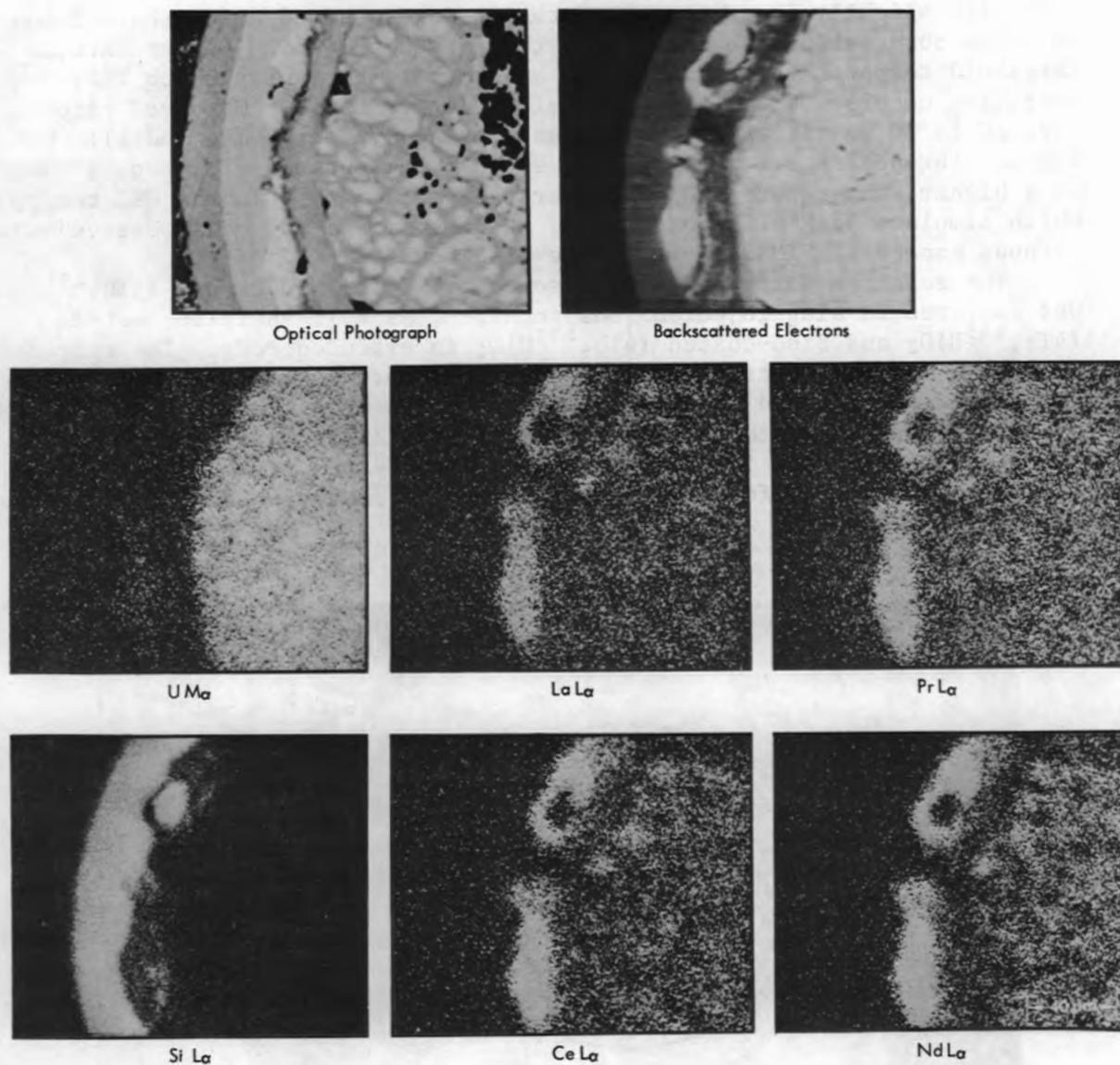


Fig. 10. Characteristic Elemental X-Ray Displays Obtained During an Electron Microprobe Analysis of the Molten Kernel Shown in Fig. 8. Reduced 20%.

The  $\text{ThO}_2$  kernels of the Biso fertile particles in HRB-4 (11 cycles) exhibited a slight "amoeba" effect in a slug-injected rod and had migrated a maximum of about  $20\ \mu\text{m}$ . No migration of the  $\text{ThO}_2$  kernels was observed in HRB-5 (five cycles) or HRB-6 (eight cycles). Thus, we believe that the migration observed in HRB-3 and HRB-4 began after the eighth cycle. As mentioned earlier, migration of the  $\text{ThO}_2$  kernels had been observed earlier in HRB-3. In both HRB-3 and HRB-4 where  $\text{ThO}_2$  amoeba was observed, adjacent rods with slightly lower power generation rates showed no amoeba. Based on these observations we think that there is a threshold temperature, a threshold temperature gradient, and a threshold burnup at which  $\text{ThO}_2$  migration occurs. Once it begins, migration is rapid. Observed rates were 20 to  $30\ \mu\text{m}$  migration in 69 days (during cycles 9, 10, and 11). The various thresholds are interrelated so that the threshold burnup is lower at a higher temperature and/or temperature gradient.<sup>6</sup> In the HRB tests, which simulate peak HTGR conditions, no  $\text{ThO}_2$  amoeba has been observed until burnups exceed 7% FIMA. None of the Biso coatings failed.

The relative performance of Biso-coated  $(4\text{Th},^{235}\text{U})\text{O}_2$  and  $(4\text{Th},^{233}\text{U})\text{O}_2$  was compared in slug-injected rods in HRB-6, as well as Triso-coated  $(4\text{Th},^{235}\text{U})\text{O}_2$  and Biso-coated  $(4\text{Th},^{235}\text{U})\text{O}_2$  in extruded rods. The extruded rods have a higher matrix density, were in about the same flux profile, and therefore operated at overall lower temperatures. There was no measurable difference in the relative thermal stability of the kernels that contained  $^{233}\text{U}$  versus  $^{235}\text{U}$  in the slug-injected rods. Both migrated up the thermal gradient for a maximum distance of about  $20\ \mu\text{m}$  (Fig. 11). No other adverse effects were noted.

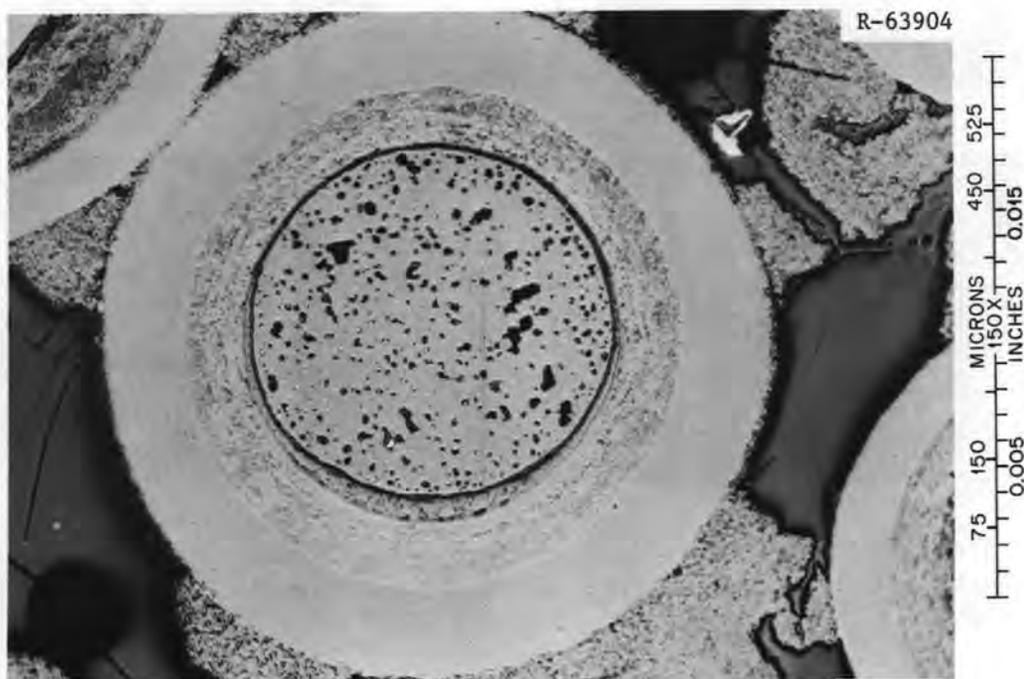


Fig. 11. Appearance of a Biso-Coated  $(4\text{Th},^{235}\text{U})\text{O}_2$  Fissile Particle in Slug-Injected Rods from Irradiation Capsule HRB-6. The kernel migrated up the thermal gradient for a distance of about  $20\ \mu\text{m}$ . As polished. Reduced 13%.

Examination of the Biso- and Triso-coated fissile particles in the extruded fuel rods from HRB-6 revealed no significant difference in their performance (Fig. 12). There was no evidence of potential failure of the Biso or Triso coatings. Intermittent plastic flow of the kernel through the fission recoil zone of the buffer coating was noted, and only slight evidence of the early stage of amoeba was noted in the Biso-coated fissile particle. Since the migration rates were much lower in extruded rods than in slug-injected rods, we conclude that the higher thermal conductivity of the extruded rods enhances their performance in comparison to slug-injected rods.

## DISCUSSION

At this time fissile particles made from weak-acid resins and sol-gel ( $4\text{Th,U})\text{O}_2$  appear to perform well under normal HTGR conditions. The total burnups achieved to date for the reference makeup fissile particle have been less than that to be experienced in the reactor, so that additional irradiation testing is required to full burnup. Examination of capsules HRB-4 and HRB-6 has helped clarify the picture for the reference recycle fissile particle, which showed evidence of slight amoeba at about half again the required burnup for HTGR in an accelerated test. The Biso  $\text{ThO}_2$  fertile particle has performed well in all tests to date, but slight amoeba migration was observed in HRB-3 and HRB-4. It should be noted that the burnup was about twice that required for thorium in the actual reactor, but the time was about one-fifth that of the large reactor. Again more testing is required.

One difficulty with testing fully enriched fissile particles in the HRB facility is the high power generation rate per particle at the beginning of the test. Some designs result in more than 1 W per particle. To get around the problem, we have initiated the irradiation of two new capsules, HRB-7 and HRB-8, which are fueled with fully enriched particles, in a new position further out in the beryllium reflector of HFIR for two to four cycles to burn out much of the fissile material before the capsules are inserted in the high-flux HRB position. Capsules HRB-7 and HRB-8 will test candidate fissile particles for makeup and recycle fuels at design center-line temperatures of 1500 and 1250°C. These tests will allow us to compare the various candidate particles listed in Table 1 in the same capsule irradiated under identical conditions. Results should allow us to eliminate some candidate fissile particles from the standpoint of performance. Additional long-term tests of the better performers will be needed to narrow the choice still further.

## CONCLUSIONS

Based on the HRB irradiation tests, we conclude that Biso-coated  $\text{ThO}_2$  continues to be promising as a fertile particle for the HTGR. Although some migration was observed (in HRB-3 and HRB-4), it did not begin (under HTGR peak temperature conditions) until the burnup exceeded 7% FIMA. Once migration started, however, it occurred rapidly, and more information is

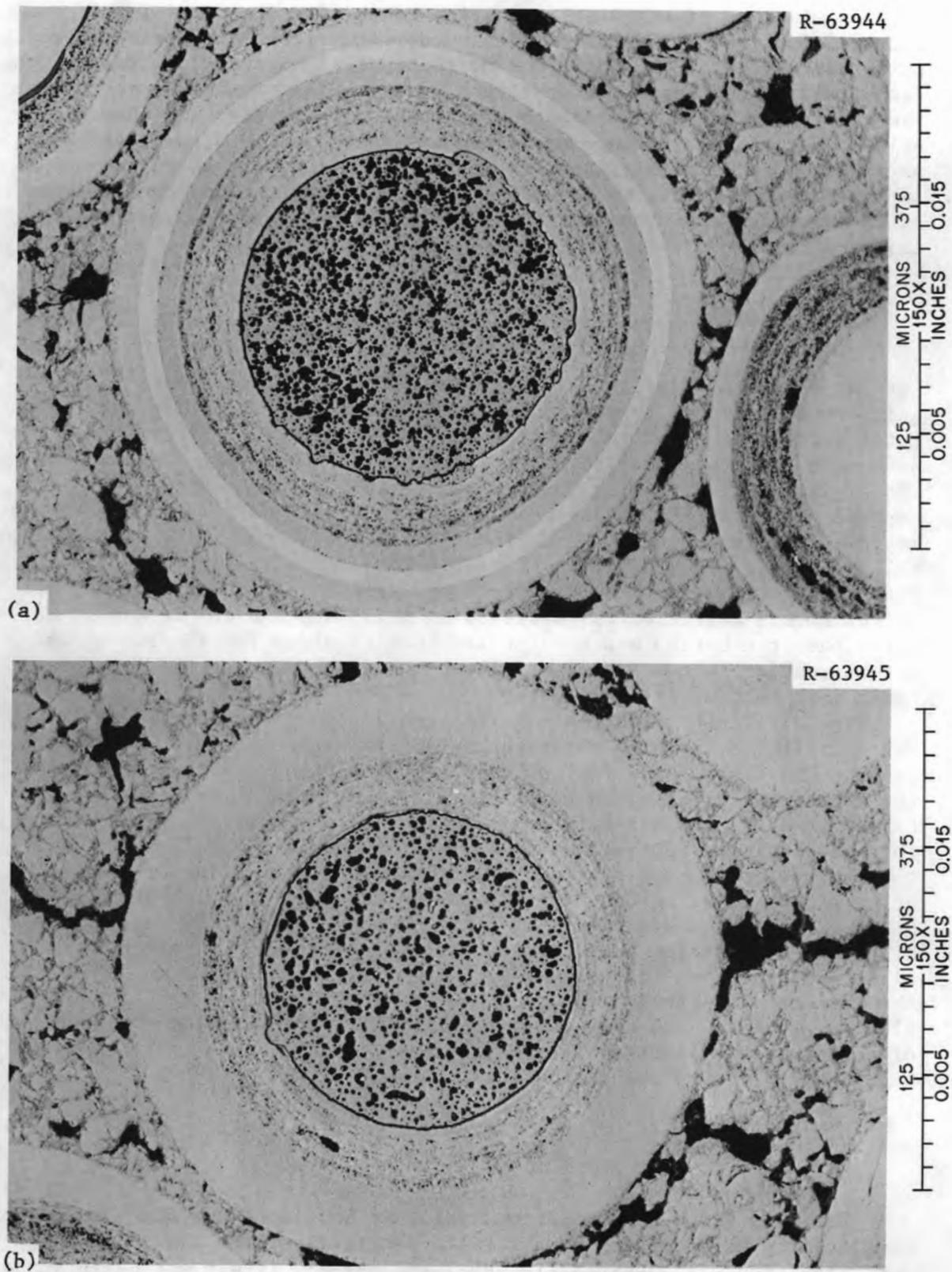


Fig. 12. Triso-Coated (a) and Bisco-Coated (b)  $(4\text{Th},^{235}\text{U})\text{O}_2$  Fissile Particles in Extruded Rods from Irradiation Capsule HRB-6.

needed on the threshold conditions which initiate migration. Migration of the Biso-coated  $(4\text{Th,U})\text{O}_2$  fissile particles was observed in HRB-6 to a distance of about 20  $\mu\text{m}$ . Adjacent  $\text{ThO}_2$  particles showed no migration, indicating that the threshold conditions of burnup and temperature had been exceeded in the fissile particles, but not in the fertile particles. Both  $^{235}\text{U}$ - and  $^{233}\text{U}$ -bearing particles showed about the same migration rates.

A comparison of rods made by extrusion and slug-injection with approximately identical fuel loadings, neutron fluxes, and surface temperatures showed that extruded rods had a significantly better fuel performance than slug-injected rods, presumably because of a higher thermal conductivity.

Fissile particles made from ion exchange resins showed no amoeba migration, but moderate to severe fission product-silicon carbide interactions were observed. Both palladium (arising primarily from plutonium fissions) and rare earths were identified in different reaction zones. Indications of a liquid phase were found where palladium reacted with silicon carbon and in some of the kernels. More work is required to explain these observations.

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