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IRRADIATION PERFORMANCE OF ADVANCED FUELS FOR HTGR's*

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ABSTRACT

Fuel for large HTGR power stations in the United States consists of coated particles of ThO_2 as fertile material mixed with smaller coated particles containing fissile material, either ^{233}U from recycle of bred fuel or ^{235}U as makeup fuel. Recycle fuel particles containing ^{233}U mixed with thorium in sol-gel oxide microspheres have been prepared and experiments in progress will test a fuel composition consisting of Th/U = 4 to full exposure and burnup. The use of weak-acid ion exchange resin particles as precursors for either type of fissile fuel kernel offers several advantages in processing and properties. Pilot-scale preparation and testing of resin-base fuels demonstrated that their performance is adequate and indicate that such fuels may be capable of operating at temperatures well above 1300°C. Such high-performance fuels are desirable for process heat and direct-cycle applications.

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INTRODUCTION

Fuel for large high-temperature gas-cooled reactor (HTGR) power stations in the United States consists of coated particles containing thorium as fertile material mixed with small coated fissile particles containing either ^{235}U as makeup fuel or ^{233}U derived from recycle of the fertile material. In recent studies we have concentrated on developing high-performance particle designs for these two functions. The excellent experience with coated ThO_2 as fertile particles in irradiation tests in HFIR (ref. 1) led us to further development of this particle design. For fissile particle designs, on the other hand, the results from initial tests on fuel kernels derived from uranium-loaded ion exchange resin beads indicated that advantages in processing and enhanced radiation stability might be realized by further development.

TESTING OF BISO-COATED ThO_2 PARTICLES

The fertile particle makes up 80% or more of the coated particle volume in current fuel rod designs for HTGR's. The minimal requirements in these particles thus dominates the fuel rod fabrication requirements. We designed an experiment consisting of several capsules to perform stringent tests on such particles. For the purpose of the experiment we selected the fertile

particle currently specified for initial and recycle fuel.[2] This particle has a 500-μm-diam ThO_2 kernel and a Biso coating consisting of an 85-μm-thick buffer layer and a 75-μm-thick outer isotropic carbon layer. The problem outlined was to develop information that would define the minimal requirements placed on the Biso coating in terms of thickness, thickness ratios, and physical properties. Variations on this reference design were selected for testing on the basis of performance predicted by the STRETCH code;[3] the creep coefficients and ultimate strength were presumed to be the significant variables.

Experiment Design

The experiment evolved around four HFIR target capsules, each to contain two nominal temperature regimes. The samples, 50 to 75 coated particles, are supported in small graphite bottles with annular cavities for the particles. Several particle holders are in turn supported in a graphite tube which forms a magazine. Two magazines in each capsule were designed to develop a holder temperature of 1250°C and the other two a particle holder temperature of 900°C. Detailed thermal analysis of the design indicated that maximum particle temperatures could exceed the nominal holder temperature by 200 to 300°C due to the high heat generation rate. The set of four capsules was designed to achieve a range of fast neutron exposures from 2 to 16 × 10^{21} neutrons/cm^2 (> 0.18 MeV),

from 25 to about 200% of design HTGR maximum exposure. Burnup in the ThO_2 would range from 2 to about 20%.

Preparation of Test Samples

The ThO_2 kernels for the experiment were screened from a large batch of sol-gel microspheres so that the diameter distribution of separate batches had a standard deviation of ≤ 7 μm. We used both 400- and 500-μm-diam kernels in order to increase sample size, since geometric scaling factors on the coatings are quite certain.

A recently developed technique for the formation of sol droplets during preparation of ThO_2 microspheres by the sol-gel process has vastly improved the uniformity of the product. With this technique the breakup of sol streams from capillaries is made uniform and regular by imposing on the streams a vibration at the natural frequency of drop formation.[4] Use of this technique eliminates problems of size distribution in the batches and enhances control of the coating operations.

The separate batches were coated with carbon in a 1-in.-diam laboratory-scale coating furnace. The dense outer coatings were applied at very high rates (approx 20 μm/min as compared to about 5 μm/min in large coaters) using propylene to ensure that their structures were nearly isotropic. The properties of the

nine batches are described in Table 1. The thickness distribution of the individual coated batches were carefully controlled to avoid any overlap of dimensions between batches.

Operation and Results

The capsules were irradiated in the outer target positions of HFIR, and they have been removed and unloaded for examination. The first sample listed in Table 1 failed at the lowest exposure, as predicted by the code, while some specimens failed at intermediate exposures. Analyses and correlation of the results with predictions by the STRETCH code are providing a means for additional development of the input parameters and mechanisms of the code.

The performance of certain particle coating designs in the experiment is quite noteworthy, on the other hand, as shown in Table 2. The reference design particle, OR-1849, and two batches that had 400-μm-diam kernels, batches OR-1840 and OR-1838, survived irradiation to fast neutron fluence of approximately 1.4×10^{21} neutrons/cm^2 (> 0.18 MeV) and a burnup of approximately 15% FIMA. A photograph of the intact sample from batch OR-1849 after irradiation is shown in Fig. 1. This exposure is nearly equivalent to 200% of the design burnup and fluence for large HTGR's.

Table 1. Characteristics of Biso-Coated ThO_2 Particles for Irradiation in Capsules HT-12 to HT-15

Batch Number	Mean Kernel Diameter (μm)	Mean Buffer Layer Thickness (μm)	Outer Coating Layer	
			Mean Thickness (μm)	Density (g/cm^3)
OR-1837	402	1	24	2.02
OR-1830	402	1	38	2.01
OR-1846	402	20	21	1.99
OR-1826	402	21	31	2.01
OR-1840	402	25	50	2.01
OR-1749	402	33	36	1.92
OR-1838	402	32	64	1.96
OR-1850	508	45	48	1.99
OR-1849	508	79	75	1.99

Table 2. Performance of Biso-Coated ThO_2 Particles at 1450 to 1550°C in Capsules HT-12 through HT-15

Particle Design (μm)	Survival Rate, %			
	HT-12[a]	HT-13[a]	HT-14[a]	HT-15[a]
402-1-24	45[b]	0		
402-1-38	100	0		
402-20-21	100	0		
402-21-31	100	23	11	44
402-33-36	100	100	7[c]	100[c]
402-25-50	100	100	100[c]	7[c]
402-32-64	100	100	97	100
508-45-48	100	3	0	
508-79-75	100	100	100	97

[a]Maximum fast (> 0.18 MeV) neutron fluences: HT-12, 4×10^{21}; HT-13, 6.6×10^{21}; HT-14, 14×10^{21}; and HT-15, 16×10^{21} neutrons/cm^2.

[b]Values underlined indicate predicted coating failure.

[c]Possible accidental interchange of samples; postirradiation examination is not yet complete.

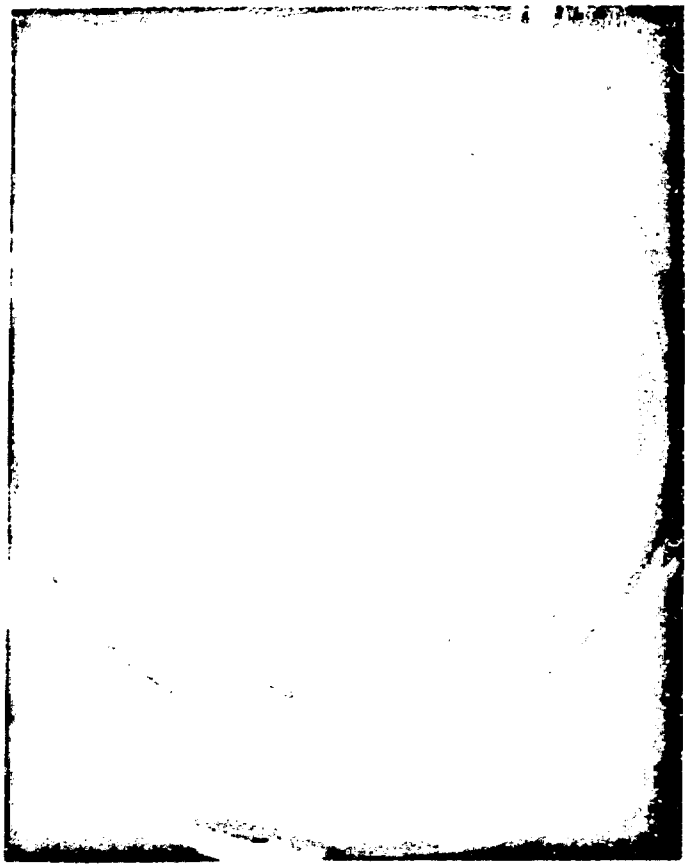

Fig. 1. Sample of Batch OR-1849 After Irradiation in Capsule HT-14 to Fast Fluence of 1.4×10^{22} neutrons/cm^2.

Results from Instrumented HFIR Capsule HRB-3

Excellent performance of Biso-coated ThO_2 was also observed recently in an instrumented experiment operated in the reflector positions of HFIR. In this experiment, HRB-3, particles performed well during irradiation for 257 days to a burnup of 15% FIMA and a fast fluence of 10×10^{21} neutrons/cm^2. The polished section shown in Fig. 2 illustrates the appearance of a particle exposed near the center of a slug-injection bonded fuel rod. The calculated temperature at this position was 1460°C, as derived from surface temperatures, heat generation rate, and measured central temperature in adjacent specimens. Note the evidence of slight directional migration of the kernel within its coating, indicating the initiation of the amoeba effect observed in many irradiations of coated carbide or UO_2 particles. Other examples of slight migration of ThO_2 were observed in this fuel rod specimen at positions where the thermal gradient was much higher, but no case of migration through the buffer layer of the coating was detected in several polished sections.

DEVELOPMENT OF FISSILE PARTICLES FROM ION EXCHANGE RESINS

Fuel particles formed from cation exchange resins are attractive because of simplicity of fabrication and easier quality control in remote operations with

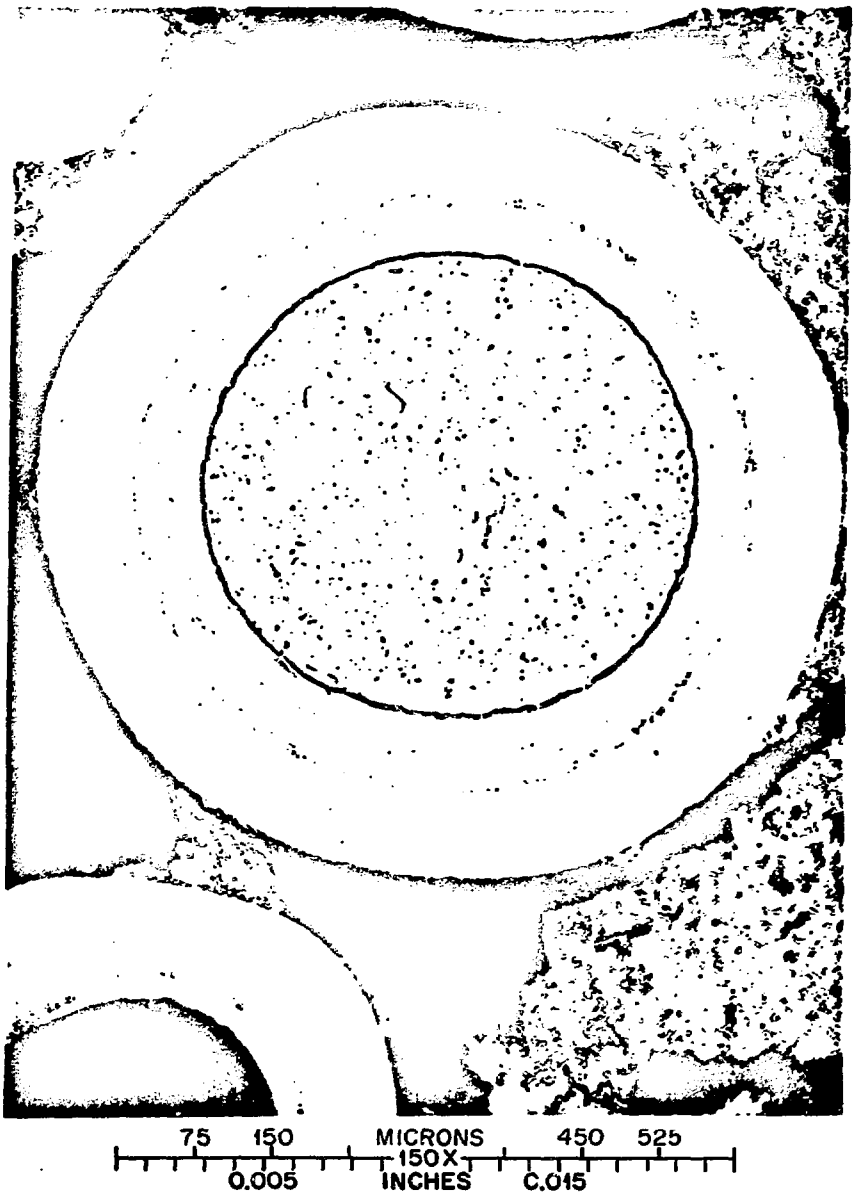

Fig. 2. Polished Section of Biso-Coated ThO_2 Particle After Irradiation in Capsule HRB-3 for 257 days to Burnup of 15% FIMA at 1460°C. As polished. 200×. Note slight migration of kernel up temperature gradient.

recycle fuel. A process was recently developed for loading uranium in high concentrations on weak-acid ion exchange resin beads.[5] The preferred grades of resin, IRC-72 (Rohm & Haas) and Relite CC (Ionac), contain no sulfur and are prepared commercially by polymerizing acrylic or methyl acrylic acid with divinyl benzene.

Carbonization Studies

We conducted a series of carbonization experiments on the loaded and dried resin beads to determine the temperature range in which the resins decomposed and emitted gaseous components. Three different types of instruments were employed: the differential thermal analyzer (DTA); the thermogravimetric analyzer (TGA); and the gas chromatograph. Typical DTA and TGA curves for uranium-loaded IRC-72 heated at 3°C/min in helium are shown in Fig. 3. From these and the associated gas chromatography data we concluded that the first broad endotherm, where about a 15% weight loss occurs, is associated with the release of most of the chemically bound water. Small amounts of water that are probably trapped along with water formed by decomposition are not removed completely until about 400°C is attained. The second endotherm and its associated 5% weight loss are probably due to the breakup of the polymer yielding allyl radicals, which give rise to the light unsaturated hydrocarbons, ethylene,

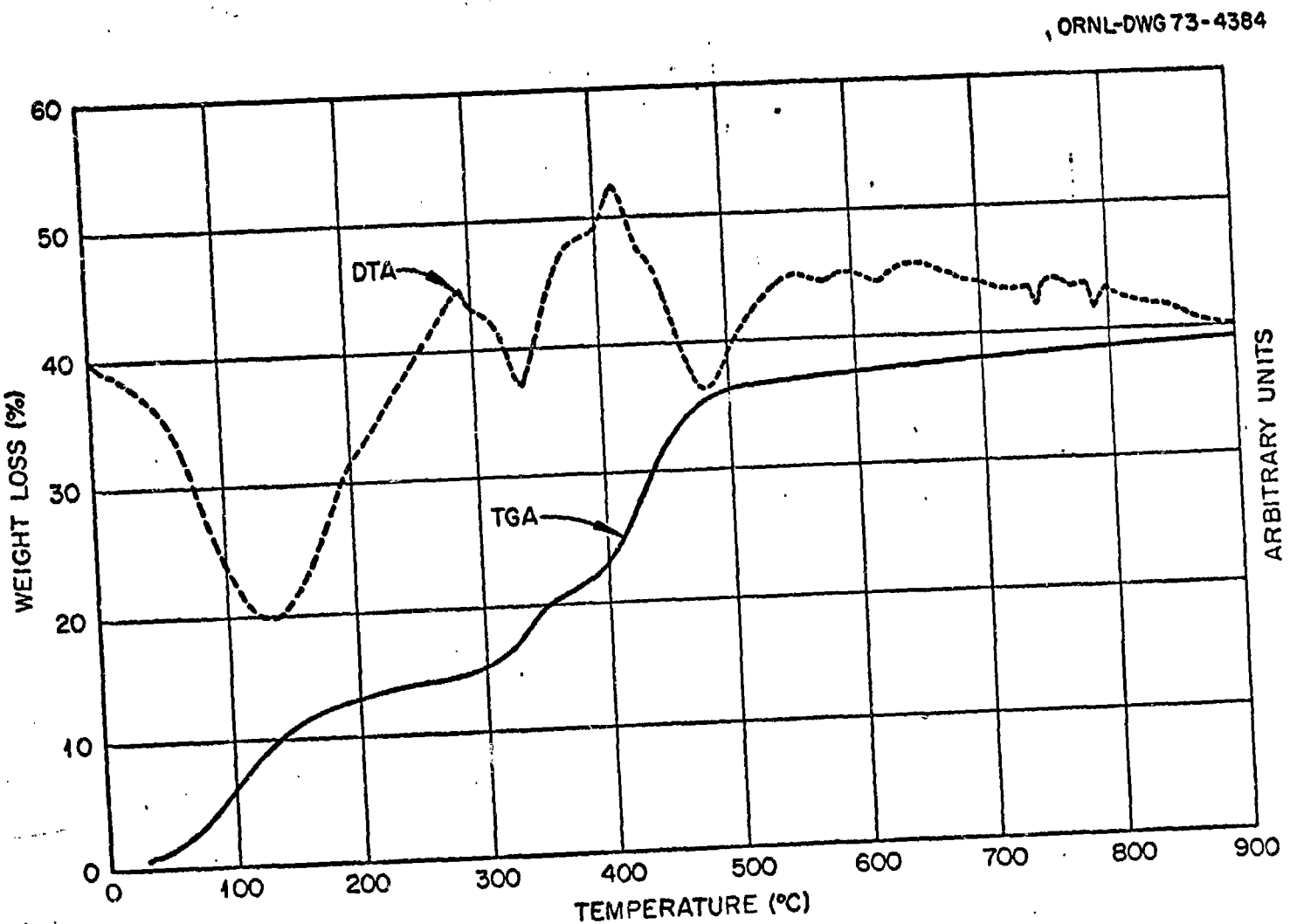

Fig. 3. Carbonization of Uranium-Loaded Weak Acid Resin (IRC-72)

acetylene, and propylene. The broad exotherm and 15% weight loss in the 550 to 750°C range probably indicate that carbonization is occurring, along with decarboxylation. Carbon monoxide and carbon dioxide are both formed in appreciable amounts. The small endotherm in the 475 to 525°C range may be due to the depolymerization of heavy organic fractions. Carbonization is largely completed by 600°C, so that the heating rate may be very high above this temperature without damage to the particles.

Compatibility of Carbonized Resins with Air

Particles carbonized to temperatures in the range 750 to 1100°C were found to be mildly reactive with moist air. Typically, a 100-g batch would heat up and gain about 4% in weight, but no damage to the particles was observed. The reaction thought to be occurring is the oxidation of UO_{2+x} to form U_3O_8. X-ray analysis is of little value because of the extremely small size of the fuel crystallites. In a study to alleviate the problem, heating to 1200°C or higher stabilized the fueled resins, and no heating or weight gain was observed over a 24-hr period. The stabilization is attributed to fuel-crystallite growth and corresponding reduction in surface area. The overall composition after stabilizing at 1200°C is approximately UO_{2+x} + 5C.

Adjustment of Oxygen-to-Metal Ratio

Kernel migration up the temperature gradient has been observed in irradiated fuel rods with both dense carbide and dense oxide fuel particles. A model for the "amoeba effect" involving UO_2 kernels, discussed by Lindemer,[6] is based on the $2CO \rightleftarrows CO_2 + C$ equilibrium, which provides a mechanism for carbon transport from the hot to the cold side of the fuel kernel. Lindemer suggested that the addition of about 1% carbide per 10% FIMA would be sufficient to fix the CO pressure at all burnups by the UC_2-UO_2-C equilibrium value.

Fuel particles derived from weak-acid resins are particularly amenable to the desired oxygen-to-heavy metal (O/M) reduction. We heated stabilized resin for various time intervals at temperatures in the range 1200 to 1800°C in flowing helium. The reaction $UO_2 + 3.86C \rightarrow UC_{1.86} + 2CO$ occurs above 1300°C, the amount increasing with increasing time and helium flow rate. At 1600°C in 1 hr about half conversion to $UC_{1.86}$:UO_2 is found by x-ray analysis; in 3 hr the reaction is essentially complete. At 1700 and 1800°C the reaction proceeds to completion rapidly. Thus, the O/M may be adjusted to any desired value.

Coating and Testing of Resin-Derived Particles

The carbonized particles are composed of a fuel phase uniformly distributed in a low-density carbon matrix. The density and the void fraction of the

particle vary significantly with heat treatment. As-carbonized beads (heated to 1000°C) have a density of 3.0 to 3.4 g/cm^3 and a uranium content of 70 to 72 wt %, while particles heated to 1600°C or higher are fully converted to UC_2 and have a density of 5.0 to 5.7 g/cm^3 and a uranium content up to 89 wt %. The STRETCH code[3] and the TRISO code[7] are used to model fuel behavior during their reactor life, and these codes have been used to design coatings on resin-derived particles. The enclosed void volume in the kernel can be used to accommodate fuel swelling and gas release.

We prepared several batches of coated particles using resin-derived kernels for testing in various irradiation experiments. The batch of fissile particles prepared and tested in capsules HRB-4 and HRB-5 is a good example of the potential of resin-derived fuels. The resin beads were loaded with partially enriched uranium to avoid extremely high initial heating rates in the experiment and were then deoxidized and converted to UC_2 before coating. Triso coatings for these particles were designed with a thin (40-μm) buffer layer to take advantage of the void volume within the kernel. Coating deposition conditions for the buffer and other layers were equivalent to operations for other fissile particles. Properties of this batch, 52A, are shown in Table 3, along with the other batches of particles used in experiments HRB-4 and HRB-5. These particles

Table 3. Characterization of Coated Particles for HRB-4 and HRB-5

Batch Number:	52A		OR-1856		OR-1833		OR-1815	
Kernel								
Type material:	UC_2[a]		ThO_2[b]		Carbon[c]		Carbon[c]	
Uranium content (wt %):	23.8							
^{235}U enrichment (at. %):	5.99							
Thorium content (wt %):			56.62					
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Diameter (μm)	366	42	488	30	370	d	370	d
Density (g/cm^3)	6.2		9.72		1.4		1.4	
Buffer								
Thickness (μm)	44.6	6	88	8	20	d	30	d
Density (g/cm^3)	0.95	d	0.95	d	1.0	d	1.0	d
Inner Carbon Coating								
Thickness (μm)	30.8	4			20	d		
Density (g/cm^3)	1.94	0.01			1.90	0.06		
SiC								
Thickness (μm)	31.8	6.6			15	2		
Density (g/cm^3)	3.21	0.006			3.21	0.002		
Outer Carbon Coating								
Thickness (μm)	28.3	3.9	79	7	30	d	30	d
Density (g/cm^3)	1.89	0.007	1.92	0.023	1.98	0.004	1.92	0.022

[a] Weak-acid-resin derived.

[b] Sol-gel derived.

[c] Strong-acid-resin derived.

[d] Not determined.

were blended and formed into bonded fuel rods and were finally heat treated at 1800°C before irradiation.

Irradiation was carried out in the reflector facilities of HFIR. Monitoring of sweep-gas samples for fission gases indicated successful performance of these fissile particles.

The polished section shown in Fig. 4 illustrates the appearance of a typical particle after irradiation for 107 days at 1300°C to a burnup of 15 at. % FIMA and fast fluence of 4.5×10^{21} neutrons/cm^2 in capsule HRB-3. Note that the kernel and buffer layer have shrunk considerably and the fuel has densified, but shows some microporosity; however, the outer coating layers appear unaffected by the test.

Similar specimens from capsule HRB-4 are awaiting examination after irradiation for 244 days to a burnup of approximately 30 at. % FIMA, and other specimens with highly enriched fuel are being tested under conditions that will produce burnup of 70% or greater.

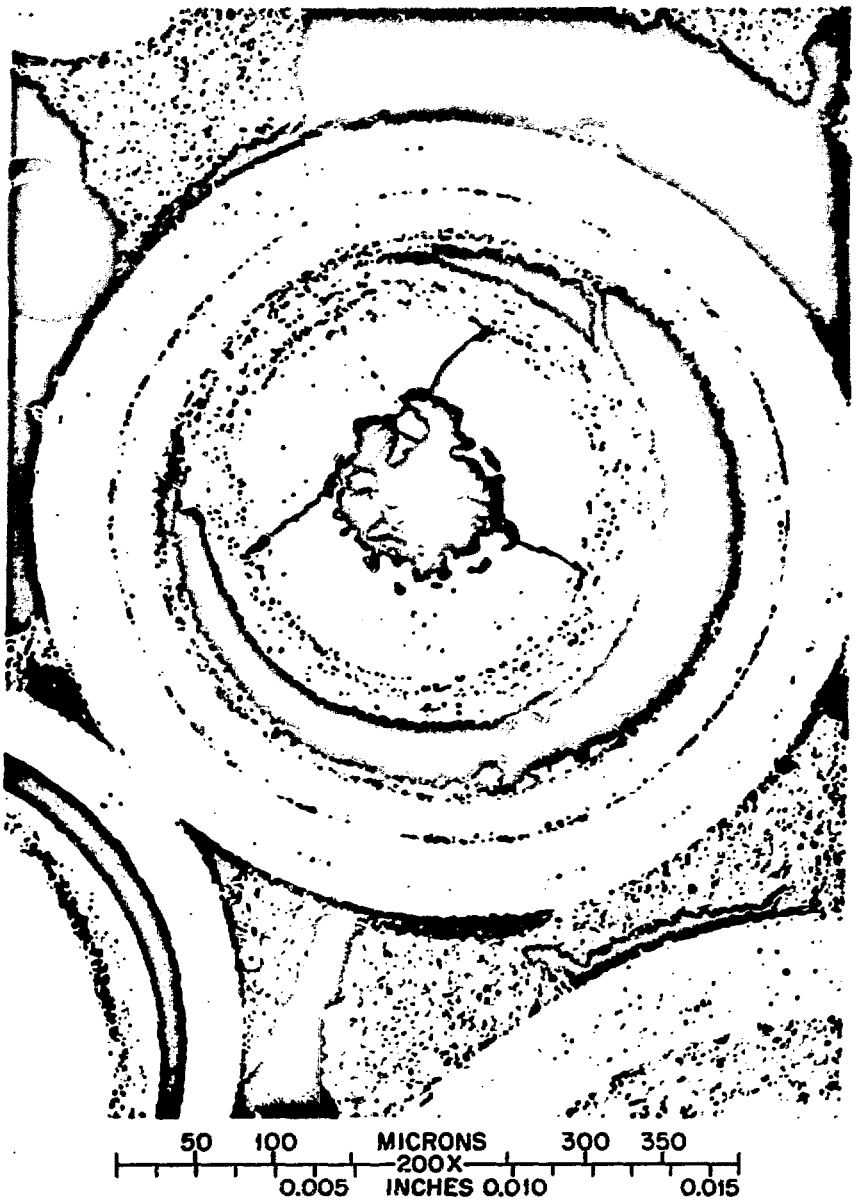

Fig. 4. Polished Section of Triso-Coated Particle Derived from Weak-Acid Resin After Irradiation in HRB-5 Capsule to 15% Burnup and Fast Fluence of 4.5×10^{21} neutrons/cm^2. As polished. 200×.

DISCUSSION AND CONCLUSIONS

1. The excellent behavior of conservatively designed batches of Biso-coated ThO_2 in capsules HT-12 through HT-15 give one a high degree of confidence in the performance of the reference Biso-coated ThO_2 fertile particles.

2. Results from this same series of capsules indicate that well designed and carefully prepared Biso-coated fertile particles have the capability of withstanding at least twice the design fluence and burnup for large HTGR's. This fact has favorable implications for fuel utilization which may be exploited by proper fuel management.

3. Conditions that induced slight directional migration, or the amoeba effect, in Biso-coated ThO_2 were produced in a fuel rod irradiation test in capsule HRB-3 at a heating rate of 5.8 kW/ft. However, other comparative irradiation tests[1] indicate that ThO_2 is clearly more stable under such conditions than is coated UO_2 or coated carbide particles.

4. Triso-coated fissile particles made from uranium-loaded weak-acid resin beads showed excellent performance at about 1300°C to 15 at. % burnup. Tests now in progress will provide information on the behavior of these particles at about 30% burnup and of similar highly enriched fissile particles after about 70% burnup.

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