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POSTIRRADIATION EXAMINATION OF
A MIXED-OXIDE FUEL ELEMENT
IRRADIATED TO END-OF-LIFE CONDITIONS
IN SUBASSEMBLY X106 IN EBR-II

by

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and J. R. Honekamp

EBR-II Project

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ABSTRACT

Seven elements containing UO_2 -20 wt % PuO_2 fuel 93% enriched in ^{235}U were irradiated in fail-safe subassembly X106 in EBR-II until a defect developed in the stainless steel cladding of one element that had reached a burnup of about 7 at. %. The loss of cladding integrity was detected by monitoring the fission gases released from the element plenum to the EBR-II cover gas. In postirradiation examination, the defective element was identified by gamma scans for ^{133}Xe in the gas-plenum volume, by change in weight, and by change in balance point. The fission-gas release was benign in that no damage was visually apparent on the adjacent elements. The location of the defect could not be determined by standard visual examination, but was found by internally pressurizing the element with helium while it was immersed in an alcohol bath. Detailed destructive examinations of the element and of an intact sister element were performed to determine the nature and cause of the cladding failure. Evidence gathered during the investigation suggests that the cladding degradation was caused by introduction of a chlorine-containing contaminant into the fuel element during fabrication. Therefore, the failure was atypical of those expected to be encountered in LMFBR mixed-oxide fuel elements.

I. INTRODUCTION

Subassembly X106 was one of a series of irradiation-to-end-of-life tests being conducted in EBR-II in support of the Liquid Metal Fast Breeder Reactor (LMFBR) program. These irradiations have three primary goals: (1) generating data on the failure frequency of stainless steel-clad mixed-oxide fuel elements as a function of design and operating parameters, (2) determining the consequences of cladding failure on the safety, operation, and maintenance of the reactor plant, and (3) determining the mechanisms of failure and identifying the factors related to cladding degradation in an effort to minimize the occurrence of cladding failure in LMFBR fuel elements by altering the choice of materials, processing variables, basic design, or operating conditions.

The first test in the series was irradiation of an intentionally defected element to a burnup of 0.88 at. % in subassembly X085. The braze over the cladding defect opened then, releasing the fission gas from the plenum.^{1,2} Subassembly X106 represents the first spontaneous, or uncontrived, cladding failure of an unencapsulated mixed-oxide fuel element in EBR-II. The nature of the fission-product signals produced by the failure, the response of the EBR-II cover-gas monitoring systems, and the results of nondestructive examinations performed at the Hot Fuel Examination Facility (HFEF) at EBR-II were reported in Ref. 3.

II. DESIGN AND OPERATING PARAMETERS

A. Design

The seven elements irradiated in subassembly X106 were designed and built at ANL-East (Illinois) in 1967 by personnel of the then Metallurgy and Reactor Physics Divisions⁴ and were irradiated, with 11 ANL-fabricated elements of similar design, to ~6 at. % burnup in EBR-II subassemblies X040 and X040A before the end-of-life testing in X106.

Figure 1 is a schematic diagram of the typical element construction. The element was $60\frac{7}{8}$ in. long and 0.290 in. in diameter. The portion of the element that contained the fueled region was ~18 in. long and was joined to 21-in.-long solid stainless steel rods at either end. The 0.290-in.-OD, 0.020-in.-wall cladding over the fueled region was annealed AISI Type 304L stainless steel, an austenitic 18 wt % Cr-8 wt % Ni, low-carbon grade. The fuel column was nominally 11 in. long, and its bottom end was about 0.85 in. above the bottom of the EBR-II core. The fuel was in the form of solid pellets having oxygen-to-metal (O/M) ratios of 1.98-2.005 and smear densities in the relatively low range of 78.0-82.6% of theoretical. Pellet density was nominally 84%. A depleted- UO_2 insulator pellet was located above and below the (U,Pu) O_2 fuel column, and a 0.230-in.-dia, 0.030-in.-thick tantalum disk was placed above the upper insulator pellet and below the lower pellet. After irradiation, the disks served as radioactive gamma markers for determination of changes in fuel-column length. The entire fuel section was held in place by a restrainer spring above the column, in the gas-plenum region. The as-built plenum volume was nominally 3.6 cm³, equivalent to a plenum/fuel volume ratio of 0.4.

The elements were separated from one another by Type 304L stainless steel, 0.056-in.-dia spacer wires that were wrapped on the elements with a right-hand spiral on a 6-in. pitch. Table I gives the design parameters of each element in the subassembly. Some of the parameters are slightly different from those given in Ref. 3.

A more detailed characterization of the materials used in the fabrication of the elements is presented in Sec. VI.

B. Prior Irradiation*

The seven elements in subassembly X106 received prior irradiation in subassemblies X040 and X040A, with the nominal EBR-II reactor power level at 50 MWt. Subassembly X040 was loaded into core position 5B2 on August 14, 1968, for run 30. Irradiation continued to 3 at. % burnup, reached on June 29, 1969 (end of run 35), and the subassembly then was removed for interim

*In this report, it is assumed that the reactor power and flow are the nominal values. Recent analysis, however, indicates that the reactor power is currently about 9% lower than the nominal 62.5 MWt.⁵ Nevertheless, as reactor power and flow are coupled, the combination results in nearly the same coolant temperatures reported here.

Fig. 1. Schematic Diagram of Typical Fuel Element in Subassembly X106

TABLE I Design Parameters of Fuel Elements in Subassembly X106

	Element Identification						
	003	004	011	014	016	018	024
<u>Fuel</u>							
Chemical composition wt %							
U	69.57	69.57	69.72	69.72	69.72	70.32	70.32
Pu	18.53	18.53	18.72	18.42	18.42	17.70	17.70
O	11.90	11.90	11.86	11.86	11.86	11.97	11.97
Isotopic composition wt %							
²³⁵ U in U	92.7	92.7	92.7	92.7	92.7	92.7	92.7
²³⁹ Pu and ²⁴⁰ Pu in Pu	92	92	92	92	92	92	92
Initial O/M	1.99	1.99	1.98	1.98	1.98	2.005	2.005
Dimensions							
Max diameter in	0.2470	0.2469	0.2469	0.2470	0.2471	0.2470	0.2471
Min diameter in	0.2457	0.2455	0.2455	0.2452	0.2459	0.2450	0.2450
Length in	11.07	10.79	10.88	10.93	10.94	10.91	11.00
Weight g	79.54	78.45	75.45	78.72	76.05	78.03	79.87
Pellet density % TD	84	84	84	84	84	84	84
Smear density % TD	81.8	82.5	78.0	81.0	78.0	80.3	81.3
<u>Insulating Pellet (UO₂)</u>							
Length in	0.47	0.47	0.47	0.47	0.47	0.47	0.47
Diameter in	0.230	0.230	0.230	0.230	0.230	0.230	0.230
<u>Tantalum Disk</u>							
Length in	0.030	0.030	0.030	0.030	0.030	0.030	0.030
Diameter in	0.230	0.230	0.230	0.230	0.230	0.230	0.230
<u>Cladding (304L SS)</u>							
Outside diameter in							
Maximum	0.2910	0.2907	0.2910	0.2910	0.2910	0.2910	0.2910
Minimum	0.2880	0.2889	0.2879	0.2885	0.2887	0.2891	0.2890
Inside diameter in							
Maximum	0.2509	0.2500	0.2503	0.2501	0.2505	0.2504	0.2509
Minimum	0.2502	0.2494	0.2498	0.2497	0.2498	0.2500	0.2503
Wire Wrap	304L SS 0.056-in-dia 6-in-pitch right hand spiral						

examination. One of the 19 original ANL-fabricated elements was destructively examined.⁶ The remaining elements were reconstituted into subassembly X040A, which was reinserted into core position 5B2 for run 38B on September 30, 1969. The subassembly was removed from the core on June 2, 1970, at the end of run 42, with a calculated peak burnup of about 6 at. %. Three elements were destructively examined after this period of irradiation.⁶ At this point, seven elements from the inside rows of the subassembly were loaded into subassembly X106 for the end-of-life irradiation. Table II summarizes the calculated burnups, peak linear powers, and maximum coolant temperatures for the seven X106 elements while they were in subassemblies X040 and X040A. (These values are from Ref. 3.)

TABLE II Conditions of Previous Irradiation of X106 Elements in Subassemblies X040 and X040A³

Element Identification	Peak Calc. Burnup (initial and final) at %	Peak Linear Power (initial and final) kW/ft	Maximum Coolant Temperature (initial and final) °F
003	0	15.4	947
	5.7	14.9	921
004	0	15.4	946
	5.8	14.8	920
011	0	15.6	946
	5.9	15.1	920
014	0	15.7	952
	5.8	15.1	925
016	0	15.3	946
	5.9	14.8	920
018	0	15.8	953
	6.0	15.2	926
024	0	16.3	962
	6.0	15.7	934

C. Irradiation in Subassembly X106

To maintain irradiation conditions of the elements in X106 as close as possible to those experienced previously, the subassembly was located in position 6D5, because the reactor was operating at nominal 62.5-MWt power by then. Irradiation of X106 began on February 23, 1971 (for run 47B), and terminated on December 15, 1971 (end of run 53A). The elements were arranged

TO REACTOR CORE CENTER

Fig. 2. Loading Diagram for Subassembly X106

in a Mark E-7B type subassembly as shown in Fig. 2. The subassembly hardware was of a fail-safe design. It contained a cylinder between the elements and hexagonal can to protect the can from pressure pulses associated with rapid discharge of plenum gas from a defected element. Potential fuel-washout problems were minimized by providing a screen above the elements to retain any fuel particles greater than 0.040 in. in diameter and by locating a catch basket below the elements to catch any particles that might fall out of an element.

Koenig³ used the HECTIC code to calculate the thermal performance of the elements in X106. Table III lists the results Koenig reported for coolant, cladding, and fuel temperatures for the seven elements, as calculated on the basis of the average power-to-flow ratio for the test during its irradiation period. When minimum and maximum power-to-flow ratios were considered for element 018 (the one that had the cladding failure), the calculated coolant temperature varied -6 and +10°F, respectively, from the average, and the calculated temperature of the inner surface of the cladding varied -11 and +16°F.

TABLE III. Calculated Peak Temperatures for Elements in Subassembly X106, Based on Average Power-to-Flow Ratios

Element	Peak Calculated Burnup, at. %	Peak Linear Power, kW/ft	Temperature, °F				
			Coolant	Cladding Outside Surface	Cladding Inside Surface	Fuel Surface ^a	Fuel Centerline ^a
003	7.6	15.5	851	889	969	1600	4440
004	7.7	15.0	849	886	964	1570	4360
011	7.9	15.1	848	884	962	1580	4370
014	7.7	14.9	848	885	962	1570	4340
016	7.8	14.2	844	878	952	1530	4230
018	7.8	14.3	844	878	953	1540	4240
024	7.9	15.0	973	1000	1080	1650	4410

^aHeat-transfer coefficient of fuel-cladding gap taken as 1200 Btu/hr-ft²-°F.

Koenig³ also calculated the axial temperature distribution in element 018 for conditions corresponding to the average power-to-flow ratio. Table IV shows the results.

TABLE IV. Axial Temperature Profile for Element 018
with Average Power-to-Flow Ratio

Length Fraction of Fuel Column ^a	Peak Linear Power, kW/ft	Temperature, °F				
		Coolant	Cladding Outside Surface	Cladding Inside Surface	Fuel Surface ^b	Fuel Centerline ^b
0 (bottom)	12.06	700	736	818	1342	3802
0.05	12.47	707	744	828	1370	3885
0.10	12.86	713	752	838	1397	3957
0.15	13.21	720	760	848	1423	4023
0.20	13.55	728	768	858	1447	4085
0.25	13.81	735	776	868	1468	4135
0.30	14.03	742	784	877	1487	4177
0.35	14.19	750	792	886	1503	4210
0.40	14.30	758	800	894	1516	4232
0.45	14.33	765	808	902	1525	4244
0.50	14.31	773	816	909	1531	4244
0.55	14.23	781	823	916	1535	4235
0.60	14.08	788	830	922	1534	4213
0.65	13.89	796	837	928	1531	4185
0.70	13.64	803	844	932	1525	4146
0.75	13.34	810	850	937	1517	4100
0.80	13.01	817	856	940	1506	4047
0.85	12.65	824	862	944	1494	3989
0.90	12.29	831	868	947	1481	3933
0.95	11.92	837	873	950	1468	3870
1.0 (top)	11.56	844	878	953	1455	3806

^aFraction of total length of 10.91-in.-long column.

^bHeat-transfer coefficient of fuel-cladding gap taken as 1200 Btu/hr-ft²-°F.

III. NONDESTRUCTIVE EXAMINATION AT HOT FUEL EXAMINATION FACILITY

Subassembly X106 was transferred to the HFEF on December 27, 1971, after it was found to be responsible for the release of gaseous fission products to the EBR-II primary cover gas during runs 51C, 52A, 52B, and 53A. The HFEF examination had two objectives: (1) identifying the leaking element, and (2) evaluating the sensitivity of the available techniques for locating the site of the defect in the element. The HFEF examination and its results were described in Ref. 3; they are summarized here:

1. Sampling of the cover gas in the interbuilding coffin (IBC) during transfer of the test from the reactor to the examination site showed that the ^{133}Xe activity in the IBC was 30 times greater than the ^{133}Xe activity in the reactor cover gas. A similar result (100 times the reactor-cover-gas activity) was obtained when subassembly X085, containing the intentionally predefected mixed-oxide element, was in the IBC. These results are encouraging, since both defects were small and yet produced a positive indication in the IBC that the subassembly contained a failed fuel element.

2. The initial visual examination of the element exteriors showed no unusual features that could be associated with either the defected cladding site or damage to surrounding elements. The relative ^{133}Xe activity in the gas-plenum regions of all seven elements was then measured with the precision gamma scanner in the hope that the leaking element would show significantly less ^{133}Xe present. The results of this gamma scan were inconclusive, but did provide a baseline measurement, which subsequently helped to identify the probable leaker.

3. All seven elements were then transferred to the HFEF argon cell for leaktesting. For this test, each element was placed in a sealed chamber filled with argon. The element was then heated to 350°F, the chamber pressure was cycled a number of times, and the argon was analyzed for krypton and xenon. The results of this test were negative.

4. At this point, the plenum regions of all seven elements were gamma-scanned again for ^{133}Xe to determine if fission gas had been lost during the transfer operation and/or leaktesting. The results of this scan indicated that gas was leaking from element 018, as it had lost ~2.5 times as much activity as could be accounted for by radioactive decay of ^{133}Xe .

5. Element 018 was given a second leaktest at 700°F. The results again were negative.

6. A third gamma scan of all elements for ^{133}Xe showed only the expected decrease due to decay between the second and third scans.

7. Bow, length, weight, diameter, and balance-point measurements were made on all elements, followed by neutron radiography at the TREAT reactor. The radiographs revealed no unusual features. The diameter increases ($\sim 2\%$) were normal for Type 304 stainless steel-clad elements at 7 at. % burnup. The profilometer traces showed no unusual features.³ There were no preirradiation data on element weight, so the postirradiation weights were compared with the average of the weights measured during the two previous examinations. Although the data had substantial scatter, they did suggest that element 018 lost about 0.5 g. The weight of fission gas in the plenum of element 018 at 7 at. % burnup was calculated to be about 0.6 g. The balance-point measurements showed a shift in the balance point toward the top of the element; this was expected as a result of an increase in fuel length. However, the amount of the shift for element 018 was ~ 0.030 in. less than the average for the other six elements. The direction of this difference in balance points (i.e., element 018 showed less shift toward the top) was consistent with a loss of fission gas from element 018. However, the magnitude of the difference (0.030 in.) was five times as great as could be accounted for by the loss of 0.6 g of fission gas.

Table V summarizes the most significant results of the HFEF examinations.

TABLE V. Summary of Results of HFEF Examination
of Elements from Subassembly X106

Element Number	Maximum Diameter Increase, ^a % $\Delta D/D_0$	Weight Change, ^b g	Balance- point Shift, ^c in.	Ratio of ^{133}Xe Gamma Scans (1st scan/2nd scan)	
				Measured	Calculated ^d
003	1.83	-0.2	+0.034	9.4	9.5
004	1.58	-0.1	+0.037	8.4	9.5
011	2.24	-0.2	+0.038	9.5	9.5
014	2.28	-0.2	+0.038	9.6	9.3
016	1.89	-0.15	+0.032	9.7	9.4
018	2.00	-0.65	+0.006	25.3	9.3
024	2.17	-0.15	+0.029	10.2	9.5

^aBased on D_0 equal to average diameter near top of plenum.

^bPresent weight minus average of weights during first and second examinations.

^cPresent balance point minus balance point at second examination; measured from bottom of element.

^dAssuming loss in activity is due only to radioactive decay.

IV. NONDESTRUCTIVE EXAMINATION AT ANL-EAST

After the examination at the HFEF, the seven elements were shipped to the alpha-gamma cells of the Materials Science Division at ANL-East for detailed examination. Element 018 and unfailed element 024 were extracted from the shipping cask for examination, and the other five elements were hermetically sealed in gastight containers pending the results of the examination of elements 018 and 024. Unfailed element 024 was chosen for examination to provide a performance baseline for study of element 018 since the two elements were similar in design and operational characteristics.

To facilitate handling and inspection of the elements in the hot cell, the 21-in.-long solid steel end pieces were shortened to ~6 in. In addition, the spacer wires were removed following the initial visual inspection.

Because experience in locating small cladding defects in irradiated fuel elements was limited at the time, detailed nondestructive examinations were performed on element 018 in an effort to locate its defect. All methods used--both successful and unsuccessful--are discussed here. The sequence of inspections is described in the order in which they were performed, not necessarily in the order of importance in establishing the leak location.

A. Visual Examination

The entire cladding surface of element 018 was visually examined through a stereomicroscope at magnifications of 5X-25X. Several areas were considered suspect in that their visual appearance suggested such things as circular stains, small pinholes, and, in one area, even a hairline crack. Photographs were taken of eight areas deemed to be the most probable locations of the leak. However, it was later determined by other methods that none of the areas that appeared suspect coincided with the actual defect site. Figure 3 shows photographs of three suspect areas.

B. Profilometry

Contact profilometry (in addition to that done previously at HFEF) was performed on element 018 at 10° rotational intervals and on element 024 at the 0, 45, 90, and 180° orientations. The general shape of the diametral profiles and the maximum diameter increases observed were consistent with the results of the previous HFEF examination. The large number of traces was performed on element 018 to determine if there was any evidence of local cladding deformation that might indicate the location of the defect. The profilometry traces were examined in detail, but they indicated no pronounced deformation of the cladding that could be correlated with the area where the leak occurred. Figure 4 shows the profilometer trace at the approximate angular orientation where the leak was eventually found to be. The total cladding-diameter increase at the elevation of the leak varied within the range 0.30-0.35%. For the operating conditions of the element, the diameter increase

Fig. 3

Photographs of Suspect Leak Areas on Exterior Surface of Element 018. Neg. Nos. MSD-162286 (6X), -162284 (4.25X) and -162288 (8.5X).

Fig. 4. Profilometer Trace of Element 018 at Angular Orientation Corresponding to Location of Leak

due to stainless steel swelling was calculated to be 0.28% using the PNL Theta correlation* for annealed Type 304 stainless steel.⁷ Thus, within the uncertainties involved in such a calculation, essentially all the diameter increase observed at the leak location could be attributed to stainless steel swelling.

The peak diameter increases observed on elements 018 and 024 were 1.93 and 2.07%, respectively.

C. Gamma Scanning

Elements 018 and 024 were gamma-scanned for gross, ⁹⁵Nb, ⁹⁵Zr, ¹⁰³Ru, ¹⁰⁶Rh, and ¹³⁷Cs activities. The gross axial scans of the fuel elements were made through a mechanically variable and collimated horizontal slot with the element about 40 in. from the face of a Ge(Li) detector. A 2048-channel analyzer was used for identification of the gross collected spectrum. Scans for specific fission-product elements identified from the gross collected spectrum were made through a single-channel analyzer.

Qualitatively, the axial activity profiles for the two fuel elements were similar. As shown by the scans of element 018 in Fig. 5, the gross scan was fairly regular, some local valleys being associated with interpellet gaps and

* $\Delta V/V$ (%) = $[(T-40) \times 10^{-10}][\phi t][2.05-(27/\theta)+(78/\theta^2)] \exp[32.6-(5100/T)-0.015T]$, where $[\phi t] = 10^{22}$ neutrons/cm² ($E > 0.1$ MeV), $T = ^\circ K$, and $\theta = T - 623$.

Fig. 5. Axial Gamma Scans of Element 018

Fig. 5 (Contd.)

"shutdown cracks" caused by thermal cycling. Evident on all traces was the sharp peak at each end of the fuel column caused by the broad Compton scattering from the tantalum disks. The ^{95}Nb and ^{95}Zr profiles were symmetrical about the core midplane and showed local deviations in activity similar to those observed in the gross scan. The ^{103}Ru and ^{106}Rh traces were similar in shape to the gross scan. These nuclides exhibited peaks at the bottom of the fuel column, contributing significantly to the peaks observed in the gross scan at the same location. Subsequent metallography of a transverse section through

the bottom fuel pellet of 018 revealed the presence of metallic-fission-product ingots at the location of the peaks. Cesium-137 had a very irregular profile, with numerous peaks and valleys appearing along the length of the fuel column. In some instances, the ^{137}Cs peaks correlated with valleys in the gross profile, suggesting that cesium was transported into gaps and cracks in the fuel. This same behavior was observed earlier in a sister element from subassembly X040A at a slightly lower burnup.⁵ A large ^{137}Cs peak was observed near the interface of the upper UO_2 insulator pellet and the top fuel pellet of element 018, and a much smaller peak was observed at the corresponding location at the bottom of the element. Similar large ^{137}Cs peaks were observed at both ends of element 024. Metallography of the upper UO_2 insulator from that element showed the presence of a cesium-uranium oxide chemical-reaction product, very likely cesium uranate.

Full gamma-ray spectra were taken from regions in the upper and lower UO_2 insulator pellets and tantalum disks to ascertain the possible presence of species that might be correlated later with the occurrence of the cladding defect. No unexpected nuclides were detected in any of the areas scanned. There were no qualitative differences in spectra between the upper and lower ends of the element. The two ^{182}Ta peaks (1.122 and 1.222 MeV) were the most predominant ones associated with the tantalum disk. The UO_2 insulator pellets exhibited peaks from ^{95}Nb , ^{95}Zr , ^{103}Ru , ^{106}Rh , ^{134}Cs , and ^{137}Cs , indicating migration of some fission products short distances into the insulator regions. Similar observations were made on element 024.

D. Eddy-current Examinations of Element Claddings

An attempt was made to locate the cladding defect in element 018 with the point-probe eddy-current scanning technique developed by Renken.⁸ The test technique had previously been used in prefabrication examination of tubing for inner- and outer-surface defects. After that, results on sister irradiated elements had demonstrated the capability of the technique for detecting intergranular fission-product penetration on the inner surface of fuel-element cladding.⁶

The equipment was first calibrated with a defect standard, a 0.230-in.-OD, 0.015-in.-wall Type 304 stainless steel tube, that had the following artificial defects: (1) a 20%-wall-thickness internal defect (0.003 in. deep, 0.030 in. long, and 0.003 in. wide); (2) a 50%-wall-thickness internal defect (0.0075 in. deep, 0.030 in. long, and 0.003 in. wide, and (3) a 20%-wall-thickness external defect (0.003 in. deep, 0.030 in. long, and 0.003 in. wide). The equipment sensitivity for this examination is shown in the traces of standard defects shown in Fig. 6. The point probe incorporates one field coil and two pickup coils. The information is extracted by discrete time sampling of a series of voltage pulses. These pulses are smoothed, filtered, and displayed on separate recorders. The information discrimination is such that one recorder traces the characteristics of the inner surface of the cladding while the other traces the characteristics of the outer surface.

Fig. 6. Response of Point-probe Eddy-current Tester to Standard Cladding Defects

The measured effective angle of "view" for the probe was 18° ; longitudinal scans were therefore made at 15° rotational intervals to ensure complete coverage of the element surface. Figure 7 shows the recorded traces at the orientation at which the cladding failure was eventually located. Although situated near the upper tantalum disk and the upper portion of the UO_2 insulator pellet, the defect could not be unequivocally related to the eddy-current trace. This was due to the presence of objects inside the cladding, such as the tantalum disk, insulator pellet, and plenum spring. Indications of the condition of the inner surface of the cladding were masked by the boundary between these dissimilar materials.

Similar traces were obtained from the corresponding region of undetected element 024.

E. Recovery of Fission Gas

The plenums of elements 018 and 024 were punctured, and the plenum gas was recovered. Element 018 had 10.40 cm^3 (STP) of gas, 91.4% of which was xenon and krypton fission gas. Table VI gives the results of spectrometric analysis of the recovered gas. Based on an assumed 100% release of the fission gas produced after a peak analyzed burnup of 6.95 at. % and a peak/average power ratio of 1.125, 9% of the gas in the plenum of element 018 at the time the cladding failure occurred was recovered. The volume of helium recovered represented 8% of the original fill volume of 3.7 cm^3 (STP).

TABLE VI. Composition (vol %) of Gas Recovered from Plenum of Element 018

^{83}Kr	1.9	Ar	0.7
^{84}Kr	3.3	CO_2	<0.05
^{85}Kr	0.8	He	2.7
^{86}Kr	6.0	H_2	<0.1
^{131}Xe	12.4	N_2	4.6
^{132}Xe	17.6	O_2	0.5
^{134}Xe	26.9	H_2O	<0.1
^{136}Xe	22.5		

The plenum of element 024 contained 103.8 cm^3 (STP) of fission gas. This corresponded to 92% release of stable fission gases at the calculated peak burnup of 7.30 at. %.

After the puncturing and gas collection were completed, the plenum void volume of element 024 was determined to be 5.16 cm^3 . The measurement was made by allowing the evacuated plenum to come to pressure equilibrium

Fig. 7. Axial Eddy-current Scans of Element 018 at Angular Orientation Corresponding to Leak Location

with the hot-cell nitrogen atmosphere, repuncturing the cladding at 90° from the original puncture, and determining the volume of the nitrogen recovered from the plenum. The same procedure was repeated with element 018, but either a leak in the seals of the puncturing apparatus or the leak in the element cladding prevented pumping down the system enough to allow the plenum volume to be measured.

F. Helium Leaktest with Mass Spectrometer

Another technique used in the attempt to isolate the defect site in element 018 was helium leaktesting. A saddle valve was used to seal the holes that had been introduced into the plenum during puncturing. The valve was connected through a small-diameter pressure line to a three-way valve system outside the hot cell. The external hookup was made in such a way that the element plenum could first be purged with a vacuum pump and then pressurized from a pressure-regulated helium supply.

The sensor probe for the mass spectrometer was improvised from an oversize (with respect to cladding OD) pressure-fitting coupling and a Veeco N-9K sensor tip. The fitting was drilled out so that it could slide over the end of the element, and Neoprene O-rings were substituted for the steel ferrules. The calibrated sensor tip was mounted in a tube connected to the midsection of the fitting. Figure 8 shows the arrangement as installed in the hot cell. The probe was connected by flexible tubing to the vacuum lines of the in-cell puncturing system, which in turn, was connected to the helium mass spectrometer outside the cell.

Fig. 8. Scanning of Element 018 with Helium-leak-detector Probe for Indication of Cladding Defect. Neg. No. MSD-162779.

The element was scanned at 1/2-in. intervals, with the probe held at each position for 5 min. The entire element (except at the location occupied by the saddle valve) was scanned three times in this manner at internal helium pressures of 98, 250, and 400 psig. There was no positive indication of helium leaking from the element at any location.

After the defect site had been located by the immersion pressurization tests discussed in Sec. III.G below, additional helium leaktests were performed with the probe connected directly to the spectrometer through an 18-ft-long, 1/4-in.-ID vacuum line, instead of through the somewhat more tortuous path of the vacuum lines of the puncturing apparatus. Tests with this setup showed that 1 min was required for evacuation

of helium and that the line length had a 15-sec-response delay time. Element 018 was scanned axially at an internal helium pressure of 500 psig, and the location of the leak was positively identified. Whether the success in this instance was due to the change in the sampling line or to the possible removal of flow restrictions from the defect during the immersion pressurization tests was not clear.

G. Immersion Pressurization Tests

Previous efforts having failed to determine the leak location in element 018, immersion pressurization tests were performed. An immersion tank was fabricated from a conical, clear plastic sleeve, closed at the apex and supported vertically in a ring stand. The wide mouth was in the up position and held open with a rigid collar. The tank was filled with 3 liters of alcohol, and the entire element 018 (including the saddle valve) was immersed in the

Fig 9. Photograph of Bubble-check Apparatus Used for Locating Breach in Cladding of Element 018. Element appears bowed because of light refraction in alcohol. Neg. No. MSD-162778.

liquid, as shown in Fig. 9. The helium pressure in the element was raised to 400 psig, and the surface of the element was scanned visually with a 6X magnification. The internal element pressure was then elevated to a maximum of 670 psig, and the entire length of the element was systematically examined at 45° intervals of rotation. By this procedure, a small stream of bubbles was seen emanating from the cladding at $12 \frac{5}{16}$ in. above the bottom-end-plug weld (see Fig. 10). The streaming continued with the pressure lowered to 200 psig, but at a reduced bubble-formation rate. The bubble diameter, as measured from photographs, was about 0.003-0.004 in. at a pressure of 480 psig. The axial location of the leak corresponded to a

region near the interface between the top tantalum disk and the top UO₂ insulator pellet, as shown in Fig. 1.

Movie films were taken of the magnified bubble train in order to study the rates of bubble formation and emission and to identify the origin of the bubbles.

H. Measurements of Gas Flow Rate through Cladding Defect

The flow rates of helium and argon gas through the breach in the cladding of element 018 were measured as a function of pressure. The measurement was made with the element clamped in the in-cell puncturing rig and with the suspect leak area open to the vacuum system of the rig. The element

was pressurized through the hole in the plenum. The results of the test, presented in Fig. 11, were discussed in Ref. 3 in relation to the magnitude and nature of the gaseous-fission-product signals observed when leaking element 018 was in EBR-II.

Fig. 10

Small Stream of Bubbles (boxed) Rising through Alcohol Bath from Cladding Defect in Element 018. Mag. 3.75X. Neg. No. MSD-162955.

I. Precise Determination of Leak Location

Although the axial and circumferential orientation of the leak was fairly well defined during the alcohol-immersion pressurization, the defect had to be precisely located so it could be identified easily during the metallography to follow. The element was therefore mounted on the photographic stage in the cell, and the general area of the leak was swabbed with soapwater while the internal element pressure was maintained at 600 psig. Within 3 sec after application of the solution, a small area of white froth appeared, marking the leak. The froth disappeared within 10 sec. Figure 12 shows the appearance of this froth. The area of the leak was circled with an indelible marker to aid in the surface replication that followed. In this test, it was discovered that the soap solution dried on the surface and sealed the leak if the internal pressure was allowed to drop below 50 psig. The leak could be reopened, however, by raising the plenum pressure to 670 psig and swabbing the leak area with fresh solution.

Following the swabbing test, a modified helium-bubble test was performed under an in-cell stereoviewer. A small, portable bubble tester, consisting of a tank, a helium pressure bottle, and an alcohol supply reservoir (a bottle), was built

Fig. 11

Measured Leak Rates of Helium and Argon Gas through Defect in Element 018 as a Function of Internal Pressure

Fig. 12. Results of Soapwater-swabbing Test of Element 018, Showing White Froth (Boxed) Marking Location of Leak. Neg Nos. MSD-162722 (3X) and -162721 (0.75X).

for the test, as shown in Fig. 13. The element was inserted horizontally through O-ring seal fittings located about $3/4$ in. below the open top of the tank. The level of alcohol in the tank could be varied by raising or lowering the alcohol bottle. The helium pressure bottle was pressurized to 200 psi and had no regulation other than a shutoff valve. The tester was clamped to the stage of the stereoviewer. As the stage was being raised into the viewing position, the alcohol bottle was manually elevated with a slave manipulator.

Fig 13. Portable Bubble Tester for Examining Defect in Cladding of Element 018 under In-cell Stereoviewer. Neg. No MSD-162962

The results of the examination were as follows:

1. Bubbling came from not one source, but two sources about 0.035 in. apart and longitudinally oriented one above the other as shown in Fig. 14. This fact was not evident from still photographs or from movies of the bubbles streaming from the element while it was being pressurized in the vertical position. Nor was this condition apparent during the swabbing test.

2. The points on the cladding surface from which the bubbles came could not be visually distinguished as being different from any other surface markings in the areas.

Fig. 14. Photograph of Two Bubble Streams 0.035 in. Apart on Cladding of Element 018. Photograph was taken through one eyepiece of remote stereoviewer. Mag. 28X. Neg. No. MSD-163074.

Movie films were taken of the bubbling as seen through one eyepiece of the stereoviewer. Because of low illumination, the film speed had to be reduced to 2 frames/sec, but the sequence clearly showed the location of the two leaks.

From the photographs taken through the stereoviewer, the two leaks could be located in relation to an identifiable pattern of surface scratches. To obtain higher resolution of the defect areas and possibly observe fine cladding cracks on the surface, replicas were prepared using cellulose acetate tape. Many replicas had to be taken to get a few that were free of wrinkles and bubbles in the region of interest. Figure 15 shows a replica composite, with the location of the two leaks circled. It is apparent that there are no outstanding surface peculiarities that uniquely define the leak sites.

Just before element 018 was sectioned for destructive examination, a line was scribed into the cladding surface a known distance from the leaks. This line was used as a guide to preclude the possibility of missing the leaks during grinding and polishing. The line, which served its purpose successfully, was made by lightly applying a small-tubing cutter to the cladding surface. After the line had been scribed, the element was returned to the portable

Fig. 15. Composite Surface Replica from Element 018.
Circled areas mark location of leaks. Mag. 68X.

bubble tester on the stage of the stereoviewer, and a photograph was taken that showed the location of the bubbles with reference to the scribed line (see Fig. 16).

Fig. 16. Location of Scribed Line Used as Reference Mark on Cladding of Element 018 during Grinding and Polishing. Mag. ~15X. Neg. No. MSD-163071.

V. DESTRUCTIVE EXAMINATION AT ANL-EAST

A. Examination of Fuel Region of Elements 018 and 024

Element 024 was examined by metallography to provide a performance baseline in the investigation of the cause of failure of the cladding of element 018. Element 018 was studied in great detail, especially at regions near the failure site, and the results were compared with those from element 024 to establish any significant differences that might be related to the occurrence of the failure.

Metallographic sections of element 018 were taken from the interface of the bottom UO_2 insulator pellet and the fuel; near the core midplane; near the top of the fuel column; and through the transition region of the upper UO_2 pellet, upper tantalum disk, and element plenum, where the leak occurred. A burnup-analysis sample was also taken from near the core midplane of the element. Specimens were taken from element 024 at locations about $2\frac{1}{2}$ in. above and $2\frac{1}{2}$ in. below the core midplane; about $2\frac{1}{2}$ in. below the top of the fuel column; at the interface of the upper UO_2 pellet and the fuel; and from the region of element 024 corresponding to the failure region in element 018. Silicon carbide abrasive disks were used for grinding, and Hyprez diamond paste and lubricant were used during vibratory polishing. Metallographic results from the fueled sections are discussed in this section. A detailed account of the study of the failed region is given in Sec. V.B below.

Fig. 17. Transverse Section of Element 018 Taken near Core Midplane. Area within rectangle is shown magnified in Fig. 19. As-polished. Mag. $\sim 10\times$. Neg. No. MSD-163590.

The behavior of the fuel and cladding in the core regions of both elements was generally as expected based on past experience with similar elements. Transverse and longitudinal sections taken near the core midplane and near the top of the fuel column of element 018 are shown in Figs. 17 and 18. Typical observable features are fuel-restructuring effects such as the central void and columnar, equiaxed, and unrestructured fuel zones. Near the core midplane, the central void was ~ 0.090 in. in diameter. Very evident in Fig. 17 are radial and circumferential fuel cracks caused by thermal cycling.

The outlined rectangular area of Fig. 17 is shown at a higher magnification in the radial composite micrograph of Fig. 19. This figure

Fig. 18. Longitudinal Section Taken near Top of Fuel Column of Element 018. As-polished. Mag. $\sim 18X$. Neg. No. MSD-163591.

shows the effects mentioned above in addition to the white, globular fission-product inclusions apparent in the columnar-grain region of the fuel. Although these inclusions were not examined by microprobe, similar fission-product particles in another mixed-oxide fuel element irradiated in EBR-II were found to contain molybdenum, ruthenium, technetium, rhodium, and palladium.⁹

Figure 20 shows the central void as it terminates at the bottom of the active fuel column in element 018. The diameter of the void at this location was ~0.055-0.065 in., somewhat less than at the core midplane. Fission-product ingots can be seen at the bottom and along the sides of the void. The location of these ingots corresponded to ^{103}Ru and ^{106}Rh peaks observed during axial gamma scanning. Other, unidentified species may also have been present. Lambert et al.⁶ found that similar ingots in mixed-oxide fuel irradiated in EBR-II contained the same elements (molybdenum, ruthenium, rhodium, technetium, and palladium) found in the smaller columnar-grain inclusions mentioned above.

Element 024 exhibited an effect that was not observed metallographically in element 018. This was the chemical reaction between the top UO_2 insulator pellet and cesium that had migrated from the fuel to this region. The reaction product, which some evidence suggests may be cesium uranate (Cs_2UO_4),¹⁰ was seen as a gray phase in the gap between the insulator pellet and the cladding and along thermal cracks in the pellet, as shown in Fig. 21. Some of the reaction product within the pellet itself appears

Fig. 19

Radial Composite across Fuel Section near Midplane of Element 018; Corresponds to Rectangular Area in Fig. 17. As-polished. Mag. ~85X. Neg. No. MSD-166968.

to have been lost during metallographic preparation. The location of this reaction product coincided with a ^{137}Cs peak observed during gamma scanning.

Fig. 20. Termination of Central Void near Bottom of Fuel Column of Element 018. Note accumulation of porous fission-product ingots. As-polished. Mag. $\sim 10\times$. Neg. No. MSD-163595.

Fig. 21. Interface of Top Fuel Pellet and UO_2 Insulator Pellet in Element 024, Showing Nature of UO_2 -Cesium Chemical Interaction. As-polished. Mag. $\sim 9\times$. Neg. No. MSD-163598.

The cladding of element 018 exhibited intergranular oxidation caused by fission-product compounds, especially over the upper portion of the fuel column, where the operating temperatures were the highest. Figure 22 shows the nature and extent of the most severe grain-boundary penetration in a cladding section from near the top of the fuel column. The temperature of the inner surface of the cladding at that point had been $\sim 950^\circ\text{F}$ during irradiation in subassembly X106. The temperature had been $\sim 1050^\circ\text{F}$, however, during most of the irradiation life of element 018 (while it was in subassemblies X040 and X040A). The maximum measured depth of penetration was 0.008 in. into the 0.020-in.-thick material. Electron-microprobe analysis on an attacked region of cladding showed the presence of significant amounts of molybdenum, cesium, and oxygen and trace amounts of tellurium in the corroded grain boundaries. Cesium, molybdenum, and tellurium were found in extensive concentrations in the fuel-cladding gap. Small, isolated spots of iodine were also detected in the gap, but not in the cladding. The concentrations of cesium and molybdenum in the gap appeared to be unrelated to the depth of attack of the adjacent stainless steel. However, tellurium was detected in higher concentrations in areas of maximum cladding attack.

Fig. 22. Area of Element 018 near Top of Fuel Column, Which Experienced Most Severe Intergranular Attack by Fission-product Compounds. As-polished. Neg. Nos. MSD-163174 (400X) and -163173 (85X).

Cladding attack was also observed in the midplane section from element 018, where the temperature of the inner surface of the cladding had been $\sim 910^{\circ}\text{F}$ in later life and $\sim 1010^{\circ}\text{F}$ during earlier irradiation. The maximum depth of penetration of fission products at this location, as determined by metallography, was 0.0035 in. Figure 23 is a photomicrograph of the attacked cladding from this section.

Fig. 23. Intergranular Cladding Attack in Section of Cladding of Element 018 Taken from Near Core Midplane. As-polished. Mag. 85X. Neg. No. MSD-163152.

No cladding deterioration was observed in the section taken from the bottom of the fuel column of element 018, where the temperature of the inner surface of the cladding had been only $\sim 830^{\circ}\text{F}$ during irradiation.

The general depth of cladding penetration along the length of the element could be qualitatively correlated with the magnitude of the eddy-current signals obtained earlier, as can be seen by comparing the micrographs of Figs. 22 and 23 with the axial signal variation in Fig. 7. The results are similar to those obtained by Asamoto et al.,¹¹ who demonstrated that the eddy-current technique

is very sensitive and can, with proper adjustment and calibration of the equipment, be a valuable technique for nondestructive evaluation of irradiated fuel elements.

An interesting feature was observed metallographically in a cladding section from near the top of the fuel column in element 018. A fine network

Fig. 24. Widmanstätten Pattern Observed in Cladding of Element 018 near Top of Fuel Column. As-polished. Mag. $\sim 350\times$. Neg. No. MSD-163357.

of precipitates, oriented in a Widmanstätten pattern along definite crystallographic directions, was apparent to a depth of 0.004-0.006 in. in isolated areas. The precipitates and the intergranular penetration were evident in the as-polished condition, as shown in Fig. 24. Microhardness readings indicated that the cladding regions containing the precipitates were no harder than the unaffected matrix. Although the precipitates were not identified, microprobe analysis showed that they contained high concentrations (~ 20 wt %) of molybdenum, presumably of fission-product origin.

B. Examination of Defect Site in Element 018

A transverse metallographic specimen containing a portion of the plenum-region cladding, the upper tantalum disk, and a portion of the upper UO_2 pellet was prepared from the section known to contain the defect. As mentioned in Sec. IV.I, the cladding surface in this area had a scribed line about 0.106 in. above the upper leak site. This surface marking was successfully used as a reference in relating the location of a particular examination surface to the leak sites during successive grinding and polishing. The specimen was obtained by sectioning 0.150 in. above the scribed line and $\sim 3/4$ in. below the bottom leak. The section was embedded in a metallographic mount. The reference mount thickness was 0.954 in.

The cladding defect was first observed metallographically on a surface 0.162 in. above the upper surface of the tantalum disk. The defect consisted of two intergranular cracks extending from the inner surface outward to depths of about 0.009 and 0.015 in. They were located about 90° circumferentially away from the weld seam of the cladding. As in all the sections studied, a significant amount of carbide precipitation--probably as $(\text{Fe,Cr})_{23}\text{C}_6$ --was observed in the grain boundaries after electrolytic etching in oxalic acid solution. This was expected, since the austenitic stainless steel had been in the sensitization-temperature range for an extended period of time. Figure 25 shows the nature of the cracks where they were first observed in the plenum region.

Fig. 25

Nature and Extent of Intergranular Cladding Cracks as First Observed in Plenum Region of Element 018, 0.162 in. above Top of Tantalum Disk. Cladding etched in oxalic acid. Mag. 80X. Neg. No. MSD-163097.

At 0.074 in. above the upper surface of the tantalum disk, the defect was observed to be a single crack at the inner cladding surface, branching into two cracks near midwall. Figure 26 shows the appearance of the crack at this location. In all, the crack was observed metallographically at nearly 20 elevations extending from the plenum area, through the tantalum-disk region, and partially into the insulator-pellet region. The crack ran longitudinally, at nearly the same circumferential orientation, for at least 0.291 in. but not more than 0.322 in. The exact length of the crack could not be determined, because the upper end of the crack terminated where the element was sectioned for metallography with a 1/32-in.-thick abrasive cutoff wheel. Figures 27 and 28 show the entire element cross section where the crack was near the tantalum disk and the UO_2 pellet, respectively, along with more highly magnified views of the crack. Significant gaps exist between the cladding and the disk and between the cladding and the pellet: a 0.020-in. diametral cladding-disk gap, and an average 0.008-in. diametral cladding-pellet gap.

Fig. 26

Appearance of Cladding Crack 0.074 in. above Top of Tantalum Disk of Element 018. As-polished. Mag. 100X. Neg. No. MSD-163103.

Etched in $(\text{NH}_4)_2\text{S}_2\text{O}_8$

As-polished

Fig. 27. Crack in Cladding of Element 018, as Observed near Upper Tantalum Disk. Neg. Nos. MSD-164763 ($\sim 9X$) and -163623 ($\sim 115X$).

As-polished

Etched in $(\text{NH}_4)_2\text{S}_2\text{O}_8$

Fig. 28. Crack in Cladding of Element 018, as Observed in UO_2 -insulator Region. Neg. Nos. MSD-164699 ($\sim 8X$) and -163645 ($\sim 112X$).

The as-polished appearance of the tantalum disk was somewhat surprising; precipitate platelets were distributed throughout the material. Figure 29 shows the microstructure of the tantalum. For comparison, an unirradiated archive disk from the same lot of material used in the element fabrication was also examined by metallography. This material was free of such precipitates and had a normal recrystallized grain structure. Microprobe

analysis of the irradiated tantalum base metal and precipitates revealed that there was no significant difference in tantalum concentration in the two phases.

Fig. 29. Precipitates Observed in Upper Tantalum Disk of Element 018. As-polished. Mag. 175X. Neg. No. MSD-163244.

This suggested that the precipitate phase was a compound of tantalum and another element of low atomic weight. Based on this observation and on comparison with the microstructures of various hydrided refractory metals, it was concluded that the phase was a tantalum hydride, most likely TaH. There was no evidence to suggest that the hydrided tantalum was in any way associated with the failure of element 018, because the tantalum disk in unfailed element 024 had the same microstructure. Off-gassing of hydrogen or water from the fuel or insulator pellets was considered to be the most likely source of hydrogen in the elements.

Many areas of the defected specimen were examined by electron microprobe as metallography pro-

ceeded along the crack length. The microprobe examinations were done to determine the distribution of elements in the crack and adjacent cladding regions and to investigate other effects observed metallographically in the element.

The defected section was first microprobed at the elevation corresponding to the upper surface of the tantalum disk, where a branched crack extended about 0.017 in. into the cladding. At this axial location, intergranular cladding penetration was observed at the inner surface in the as-polished condition, but only in the vicinity of the crack. No penetration was observed at areas more than $\sim 30^\circ$ circumferentially away from the large crack. Figure 30 shows the slight (0.0005-in.-deep) intergranular penetration associated with the cracked area and compares this area with the unattacked inner surfaces at 120° either side of the crack.

The large crack and nearby areas showing intergranular attack were examined by microprobe, using a slightly defocused beam impinging on the areas of interest. Full-spectrum scans revealed the presence of cesium, oxygen, and chlorine in the penetrated inner-surface grain boundaries. These three elements were also detected in the large gap associated with the cladding crack. Cesium and chlorine were found to be adsorbed on the stainless steel inner surface at several areas near the crack. Linear count-rate scans for chlorine showed this element to be adsorbed on the fractured stainless steel surfaces. Neither molybdenum nor tellurium was detected at this axial location of element 018. Figure 31 shows electron and X-ray scanning images from the mouth of the cladding crack.

0°

120°

240°

Fig. 30

Condition of Inner Cladding Surface of Element 018 at Locations near Crack (0°), and 120 and 240° Circumferentially Away from Crack. Note intergranular penetration of surfaces near defect. As-polished. Mag. 375X. Neg. Nos. MSD-163238, -163234, and -163236.

Electron Scanning Image
Near Mouth of Cladding
Crack

Cladding Inner Surface →

Chlorine X-ray Image Super-
imposed on Specimen Current,
Showing Cl in Crack and in
Grain Boundaries at Inner
Surface

Cesium X-ray Image, Showing
Isolated Spots of Cs in
Crack Area

Chlorine X-ray Image, Showing
Concentration of Cl on Cladding
Inner Surface Near Crack

Cladding Inner Surface →

Fig. 31. Results of Electron-microprobe Examination of Crack in Cladding of
Element 018 at Elevation Corresponding to Top of Upper Tantalum Disk

The presence of cesium and oxygen above the active fuel region was not unexpected, since axial migration of these elements had previously been observed. However, the presence of chlorine in and near the crack at the concentrations observed was surprising, and the initial indications of chlorine were met with skepticism. It was suspected that chlorine contamination may have occurred subsequent to the failure. However, further investigation showed a very low probability of this happening. Questioning of individuals concerned revealed that no chlorine-containing reagents were knowingly used on the fuel element during cleaning and preliminary examination at ANL-West or during metallographic preparation at ANL-East. The metallographic procedure used at ANL-East was reviewed in detail as a possible source of chlorine. The specimen in which chlorine was detected was repolished in the routine manner, along with an identically prepared specimen of archive stainless steel tubing. Subsequent microprobe examination again showed chlorine in the specimen containing the cladding defect, but none in the archive material. Several other specimens from different axial locations of element 018 were examined for the presence of chlorine, with negative results. These findings tended to confirm that the chlorine was not introduced during hot-cell metallographic preparation at ANL-East. Although it was realized that the mounting epoxy contained chlorine, the concentration levels observed in the specimen were much greater than that in the epoxy, which was thus eliminated as a potential source.

As the examination at this axial location continued, microhardness readings were taken across the cladding wall parallel to the crack and at the 120 and 240° orientations relative to the crack. At all orientations, the inner and outer surfaces exhibited somewhat higher hardness values (~250 VHN) than metal nearer the midwall (~225 VHN), presumably because of residual cold work at the surface. An exception to this pattern was seen ~0.002 in. from the cladding inner surface near the crack, where hardnesses of 430-535 VHN were recorded. Figure 32 shows the hardness variation across the wall thickness near the crack. No local hardness variations of this magnitude were observed anywhere else in the fuel element.

Fig. 32. Radial Cladding-microhardness Profile near Crack at Elevation Corresponding to Top Surface of Upper Tantalum Disk of Element 018

Several microprobe examinations were performed to determine the cause of the localized hardness increase. Full-spectrum X-ray emission scans of the hardened stainless steel matrix were made and compared with similar scans of unirradiated archive cladding material. No qualitative differences were observed between the two materials; both exhibited X-ray peaks for iron, chromium, nickel, silicon, and manganese--the major cladding constituents. No foreign elements with atomic numbers greater than 12 (magnesium) were detected in the hardened stainless steel matrix. Next, linear scans for the elements mentioned above were performed along the hardness gradient. No variations in the concentrations of the elements across the wall thickness were detected.

Finally, an attempt was made to detect the possible presence of any of the interstitial elements oxygen, nitrogen, and carbon in the hardened stainless steel matrix. Nitrogen and carbon could not be detected in the cladding at any of the locations examined, including the hardened region. Oxygen levels higher than background were detected at and just below (~ 0.0005 in.) the cladding inner surface in the area exhibiting hardening. However, the depth of oxygen penetration into the cladding--as determined by simultaneous linear scans for iron and oxygen--was not as great as the total depth of stainless steel hardening (~ 0.005 in.). No similar increase in subsurface oxygen concentration was observed 120 and 240° away from the crack, where no hardening occurred. The cause of the hardening could not be explained on the basis of the results of the metallographic and microprobe examinations.

At this point, metallography of the defected cladding was continued. Light repolishing of the surface that had just been microprobed yielded another surprising result. A gray phase of foreign material--easily distinguished from the mounting material--was observed to fill much of the cladding crack and was also in intimate contact with the inner cladding surface adjacent to the crack. This observation was made 0.006 in. below the top of the tantalum disk. As shown in Fig. 33, the gray material appeared to be fairly dense in some areas, but exhibited porosity in others. Extensive microprobe examination revealed that the material (1) had a very low average atomic number, (2) was electrically conductive and physically stable under the electron beam, and (3) consisted mainly of carbon, a reasonable approximation being ~ 80 wt % carbon. Silicon and chlorine were also found in the material, but at much lower concentrations. Any other elements that may have been present in the material either were at concentrations below the detectability limits of the instrument or were not amenable to detection because their atomic number was less than four (beryllium). Figure 34 shows the X-ray scanning images obtained for carbon, chlorine, and silicon from several areas in the foreign material.

A review of previous metallography results at higher axial elevations showed traces of the same foreign material within the crack that had not been distinguished at those elevations when the metallography had been done. The material was not observed in any areas of the defected specimen away from the crack, nor was any seen in any other metallographic specimen prepared from

Fig. 33. Foreign Gray Material Found in and near Crack 0.006 in. below Top of Tantalum Disk of Element 018. Cladding etched in oxalic acid. Neg. Nos. MSD-163486 (350X) and -163481 (105X).

Fig. 34

X-ray Scanning Images of Carbon (top left), Chlorine (topright), and Silicon (bottom left) at Various Locations on Foreign Material in Crack Shown in Fig. 33

elements 018 and 024. The presence of the chlorine-containing material in the crack was believed to be real, not an artifact introduced during metallographic preparation. A probable explanation of the source of the material was not available at the time, however.

Grinding and polishing were continued; 0.204 in. below the location where the crack was first observed, the crack completely traversed the thick-

ness of the cladding and reached the outer surface. At this location, the crack was not branched. The crack was about ~ 0.0004 in. wide near the inner surface and was a grain-boundary crack estimated from photomicrographs to be about 4.5μ wide at the outer surface. Figure 35 shows the as-polished appearance of the crack as it first penetrated the wall thickness.

Fig. 35. Intergranular Crack Extending to Outer Surface of Cladding of Element 018. As-polished. Mag. 325X. Neg. No. MSD-163643-44.

At this time, the specimen was removed from its mount and polished from its lower surface upward toward the bottom end of the major crack. After several grind-polish operations, the bottom of the crack was found to be in the UO_2 -pellet region; from this, it was determined that the total length of the crack was about 0.3 in., as discussed earlier in this section. The UO_2 pellet was examined by microprobe at this level. A full X-ray emission spectrum of the bulk UO_2 for elements of atomic number greater than 12 indicated the presence of only

uranium. However, scanning images revealed the presence of chlorine on the outer periphery of the UO_2 pellet and on the inner surface of the cladding.

What remained of the defected specimen--a cladding section 0.085 in. long--was removed from the metallographic mount, the UO_2 pellet was taken out, and the cladding was cut into a semicircular ring for examination under the scanning electron microscope. The fractured surface was exposed by breaking the half-ring into two pieces by propagating the defect. Figure 36 is a scanning image of the inner cladding surface before the defected specimen was broken. Figure 37 shows the brittle, intergranular nature of the fracture. Evident on the grain faces of the fractured surface are small pit marks from which grain-boundary carbide precipitates were presumably removed by previous etching and ultrasonic cleaning. The crack that formed during irradiation was clearly brittle, and there was no evidence of local

Fig. 36. Scanning Electron Micrograph of Cladding Ring from Element 018 Containing Defect, before Crack Was Completely Propagated for Study of Fractured Surface

Fig. 37. Scanning Electron Micrograph of Fractured Surface of Cladding of Element 018, Showing Brittle, Intergranular Nature of Crack

plastic deformation near the crack. However, when the crack was propagated into previously good material ahead of it for the examination by the scanning electron microscope, that material deformed in a ductile fashion. This suggested that some aspect of the irradiation environment was responsible for promoting the brittle behavior observed.

C. Burnup Analysis

A specimen was taken for chemical determination of fuel burnup from just below the core midplane of element 018, a region corresponding to the location of peak fission rate in the element. Based on a ^{148}Nd fission yield of 1.725 at. % from fully enriched UO_2 -20 wt % PuO_2 fuel,¹² the peak burnup as determined by isotope dilution-mass spectrometry was 6.95 at. %.¹³

VI. ANALYSIS OF CLADDING FAILURE OF ELEMENT 018

The results of the examination of element 018 were somewhat surprising in that the cladding failure was in a location away from the active fuel region, in the vicinity of the upper UO_2 insulator pellet and tantalum disk. The failure therefore occurred in a cladding section operating under less severe thermal and mechanical conditions than the cladding adjacent to the fuel. The cladding temperature was about 900°F at the defect during the end-of-life irradiation, as compared with a temperature of 945°F at the inner cladding surface near the top of the fuel column during the same period. There were essentially no cladding thermal stresses at the defect location; in comparison, there was a 13,500-psi thermal stress in the cladding at the top of the fuel column, caused by the 75°F temperature gradient across the cladding wall at the point.³ Koenig³ calculated that the local axial bowing stresses in that vicinity could be as high as 34,000 psi as a result of a circumferential temperature gradient of 170°F at the top of the restrained element. The only mechanical stress imposed on the defected cladding was that due to released fission gas and original helium fill gas. Based on 100% release of all stable fission-gas atoms produced during irradiation to 6.95 at. % peak burnup--104.9 cm^3 (STP)--and the assumption that the plenum gas was at the same 844°F temperature as the exit sodium, the calculated plenum pressure at end-of-life power was 1160 psi. This gas-pressure loading corresponds to a cladding hoop stress of 8410 psi, much less than the yield stress of irradiated stainless steel.

Since the defect occurred near the upper tantalum disk, some consideration was given to the possibility that the highly activated tantalum may have been heated enough by gamma decay during shutdown to contact and stress the cladding by thermal expansion. Based on the assumption that the tantalum thermally expanded while the cladding ID remained constant at 0.250 in., calculations showed that the tantalum would have melted before reaching a temperature sufficient to allow it to fill the 0.020-in. tantalum-cladding diametral gap observed metallographically. It was thus concluded that no mechanical interaction occurred between the tantalum and the stainless steel cladding.

In terms of the metallurgical condition of the cladding, the defected section showed only slight (~ 0.0005 -in.-deep) intergranular penetration near the defect, in areas near the foreign gray substance observed metallographically. In contrast, 0.0035- and 0.008-in.-deep intergranular fission-product penetrations were observed in the cladding near the core midplane and the top of the fuel column, respectively.

Not only did the failure in element 018 occur at an unexpected location, but failure at a burnup level as low as 7 at. % was also unusual. Review of all mixed-oxide fuel elements irradiated in EBR-II through run 62 (July 1973) shows that more than 200 unencapsulated elements containing that fuel have reached peak burnups of 7-12 at. % without experiencing spontaneous cladding failure. The failure-frequency histogram of Fig. 38 shows that element 018

is the only spontaneously failed unencapsulated mixed-oxide element out of about 1150 irradiated to burnups up to 12 at. %. The only other spontaneous failure of unencapsulated mixed-oxide element has been element D-5 from sub-assembly X084. The cladding of that element failed at about 16.5 at. % burnup.

Fig. 38

Irradiation Experience with Unencapsulated Mixed-oxide Fuel Elements in EBR-II, as of Run 62, July 1973. Does not include failure of purposely predefected element.

These facts, combined with the observations of chlorine and a highly carbonaceous foreign material in and near the defect, suggested that these substances were related to the occurrence of the cladding cracks. In pursuit of this hypothesis, an extensive review of the materials and techniques used in the fabrication of the group of fuel elements to which element 018 belonged was conducted to determine possible sources of chlorine- and/or carbon-containing substances that could be linked to the failure. The results of that review follow.

The cladding was welded and annealed Type 304L stainless steel tubing that had a 0.290-in. OD and a 0.020-in. wall thickness. The steel was produced by Armco Steel Corporation (heat number 840505), and the tubing was manufactured by Wall Tube and Metal Products Company. Table VII gives the chemical analysis of the cladding.

TABLE VII. Chemical Analysis of Type 304L Stainless Steel Cladding
Used for Group of Elements to Which Element 018 Belonged

Chemical Element	Amount Present, wt %	Chemical Element	Amount Present, wt %	Chemical Element	Amount Present, wt %
C	0.03	Ni	9.26	Co	0.05
Mn	1.37	Cr	18.29	O	0.005
P	0.010	Ti	0.02	N	0.055
S	0.007	Cu	0.074	B	<0.005
Si	0.62	Mo	0.02	Fe	Balance

The 0.2% yield strength at room temperature was in the range 31,550-34,370 psi. The measured tensile strength was 81,970 and 82,820 psi at elongations of 49.0 and 56.3%, respectively. The average preirradiation micro-hardness was 180 VHN with a 100-g load. Measurements of ASTM grain size yielded average values of 6-7 for the base metal and $8\frac{1}{2}$ for the weld metal.

All the tubing, which was in 60-in. lengths, was subjected to eddy-current inspection for defects at ANL-East, using an encircling coil probe. A 60-in. length was rejected if it contained less than 40 consecutive inches of surface containing no defects greater than 10% of wall thickness. Of the 703 pieces tested, 464 were acceptable along their full 60-in. length, 94 had 40 consecutive inches of acceptable surface, and 145 failed the test. Thus, the reject rate was 20.6%. The defects were later found by metallography to be outer-surface gouges, laps, seams, and nonmetallic inclusions.

The fuel pellets were produced by Nuclear Materials and Equipment Corporation from coprecipitated (U,Pu)O₂ powder. The pellets were purchased according to ANL Metallurgy Specification (U,Pu)O₂-166. The composition of fuel batch 1571, which was used in element 018, was 70.12 wt % uranium, 17.92 wt % plutonium, and 11.94 wt % oxygen, a composition corresponding to an O/M value of 2.00. Table VIII summarizes the impurity content of the fuel, as determined by ANL-East analysis.

TABLE VIII. Impurity Content (ppm)
of (U,Pu)O₂ Fuel in Element 018

Ag	<2	Cr	10	Mg	<2	Sn	<2
Al	30	Cu	<10	Mn	1	Sr	0.2
B	<1	Fe	150	Mo	120	Ti	5
Ba	<0.2	H	2	Na	<2	V	<1
Be	0.5	K	<2	Ni	2	Y	<0.1
C	17	Li	0.005	Pb	<1	Zn	<2
Ca	10	Ga	<0.2	Rb	<0.2	Zr	15
Co	<2	La	<0.2	Sb	<20		

The insulator pellets for all fuel elements in the group were fabricated at ANL-East from ceramic-grade depleted-UO₂ powder supplied by Kerr-McGee (lot number 1-30-36). The O/U ratio of the original powder was determined by the vendor to be 2.06; however, the O/U ratio of the pellets was subsequently adjusted to 2.01 at ANL-East. Table IX summarizes the impurity content of the pellets, as determined by ANL-East analysis.

TABLE IX. Impurity Content (ppm) of
UO₂ Insulator Pellets in Element 018

Ag	<2	Cr	20	Mn	0.5	Sn	<2
Al	10	Cu	10	Mo	0.5	Sr	0.02
B	<2	Fe	30	Na	<2	Ti	2
Ba	0.4	K	<2	Ni	50	V	<2
Be	0.002	Li	<0.004	Pb	<2	Zn	<2
Ca	5	Mg	5	Sb	<20	Zr	0.2
Co	<2						

The tantalum disks used at the extreme ends of the fuel column were fabricated from 0.030-in.-thick ANL sheet stock. As shown in Table X, chemical analysis detected no significant amount of any impurity in the material. Thus, there was no evidence to indicate that any of the materials from which element 018 was fabricated contained chlorine. The stainless steel cladding passed all tests of physical and mechanical properties. The only observation that aroused any suspicion as to the materials used was the high rejection rate (20.6%) of stainless steel tubing by eddy-current testing. This high rate increased the possibility that some defective tubing was mistakenly accepted and used in element 018. It cannot be established in retrospect whether the element 018 cladding was initially defective. As the following discussion suggests, however, the assumption of initially defective cladding is not necessary to explain the probable cause of failure.

TABLE X. Impurity Content (wt %) of
Tantalum Disks Used in Element 018

Ag	<0.01	Cr	<0.01	Mn	<0.01	Sn	<0.01
Al	<0.01	Cu	<0.01	Mo	<0.001	Sr	<0.01
As	<0.1	Fe	<0.01	Na	<0.01	Ti	<0.1
Ba	<0.01	Hg	<0.01	Ni	<0.01	V	<0.01
Be	<0.01	Hf	<0.1	P	<1	W	<0.1
Bi	<0.01	K	<0.01	Pb	<0.01	Zn	<0.1
Ca	<0.01	Li	<0.001	Sb	<0.1	Zr	<0.1
Co	<0.01	Mg	<0.01	Si	<0.01		

The fabrication techniques for element 018 were reviewed through examination of data record books and interviews with personnel involved in the work. Information gained from this review enabled isolation of the factor most likely leading to the failure.

All internal components of the fuel elements (i.e., fuel pellets, insulator pellets, tantalum disks, and springs) were found to have been loaded by a special technique developed to minimize alpha contamination of the outer surface of the cladding.¹⁴ The elements, whose bottom end plugs had already been welded into place, were interfaced with the plutonium-containing loading box by means of a vinyl plastic membrane. This membrane contained several polyvinyl chloride (PVC) nipples designed so that the open, upper end of the cladding could be slipped up through the bottom portion of a nipple. As shown in the cutaway view in Fig. 39, the upper portion of the nipple was shaped so it would accept a metal funnel that was pushed through it and into the slightly flared end of the element cladding to be loaded. Internal components were thus easily transferred from the alpha loading box, through the funnel, and into the element.

The original loading plans, which were altered in favor of the above technique, called for introduction of the entire element into the loading box.

Fig. 39. Apparatus Used for Loading Internal Components into Fuel Elements Irradiated in Sub-assemblies X040, X040A, and X106

As a prevention of alpha surface contamination during loading by that method, the outer surfaces of all elements had been covered with heat-shrinkable polyethylene tubing. This protective covering was kept on each element until loading through the vinyl membrane had been completed, at which time the element was removed from the nipple, the surface covering was stripped off, and the upper end plug was welded into place.

Samples of these two plastic materials--polyethylene and PVC--were obtained from the fabricators to explore the possibility that a piece of one of them could have gotten into a fuel element. Manipulation of a piece of the heat-shrinkable polyethylene tubing and a piece of archive cladding suggested a low probability of unintentionally incorporating a piece of the plastic in a fuel element. Small chips could not easily be removed,

because the plastic was fairly strong. In addition, it could be put on and taken off the element surfaces without coming in close contact with the open ends of the actual fuel elements.

On the other hand, a piece of PVC nipple appeared to have a much greater chance of making its way into a fuel element during fabrication. Since the PVC used in the nipples was plasticized rather than rigid, it was very pliable. When an archive section of the cladding tubing was inserted at a slight angle into a spare PVC nipple, small pieces of PVC were easily gouged from the inner surface of the nipple by the open end of the tubing, which had relatively sharp edges. The plastic particles thus removed adhered to the tubing and were easily deposited inside the tubing during movement inside the nipple. The possibility of gouging material during the actual element loading appears likely, especially since the open end of the cladding was flared outward slightly to accept the metal loading funnel.

It should be mentioned that PVC and other chlorine-containing materials are no longer used in fabrication of fuel elements in the Fuel Fabrication Facility of the ANL Materials Science Division.

The hypothesis that a small amount of PVC was fabricated into element 018 is consistent with the postirradiation examination of the defected area. A foreign material was found in and near the cladding crack. Carbon

was found by microprobe to be the major constituent of the foreign material, and chlorine and silicon were also detected by microprobe. PVC is a thermoplastic material composed basically of carbon, hydrogen, and chlorine, with repeating structural units¹⁵ of $C_{28}H_{42}Cl_{14}$. Thus, without added plasticizers and heat and irradiation stabilizers, PVC contains ~55 wt % chlorine. At temperatures greater than about 250°F and in gamma-radiation fields, PVC decomposes by giving off HCl gas, leaving a carbonaceous residue. The HCl thus released acts as a catalyst, promoting further breakdown of the polymer. This degradation can be retarded somewhat by the addition of metallic-salt stabilizers containing elements such as lead, calcium, barium, tin, or zinc. These metals remove the HCl generated by forming their respective metal chlorides, and the autocatalytic effect of HCl is reduced.¹⁶

The presence of silicon in the carbonaceous residue in the crack can be explained by the fact that silicate compounds are often added to PVC to produce a white color. Chemical analysis of a white PVC nipple like those used in the fabrication (although not necessarily from the same material lot) did reveal the presence of silicon.

Without experiments, it is not possible to propose a mechanism by which PVC or its decomposition products can lead to failure of austenitic stainless steel in the high-temperature, nonaqueous environment inside a fuel element. However, at least one failure of an austenitic stainless steel component associated with PVC has been reported.¹⁷ A stainless steel pipe in the fuel-reprocessing facility at Hanford failed after five years of service at a slightly elevated temperature and in a gamma-radiation field. The temperature was not high enough to produce grain-boundary carbide precipitation and sensitization of the steel. The failure, a transgranular crack in the nonsensitized material, was attributed to stress-corrosion cracking by chloride decomposition products of the PVC pressure-sensitive tape used on the exterior of the pipe. Research by Kerns and Staehle¹⁸ has also shown that dry environments of Cl_2 or HCl gas can produce accelerated crack propagation in high-strength steels.

VII. SUMMARY AND CONCLUSIONS

Element 018 in subassembly X106 released fission products to the EBR-II primary system after irradiation to about 7 at. % peak burnup, becoming the first instance of an uncontrived cladding failure in the run-to-failure program with unencapsulated mixed-oxide fuel. By immersion pressurization tests, the defect in the element was located to be about 1/2 in. above the top of the column of mixed-oxide fuel, in the region adjacent to a tantalum disk and a UO₂ insulator pellet.

Metallography revealed the cladding defect to be a brittle, intergranular crack that initiated on the inner surface of the tubing and propagated outward. At the axial location where the crack penetrated the entire wall thickness, the defect at the outer surface was a very fine grain-boundary separation, estimated to be only about 5 μ wide. The small separation explains the slow gas depressurization observed while the element was in the reactor.

During destructive examination of the element, a foreign substance was observed in the defect at a number of axial locations. By electron microprobe, chlorine was found to be associated with the foreign material and to be adsorbed on the fractured surfaces. Review of the fabrication history of element 018 showed that it had come into intimate contact with a PVC nipple during loading of the fuel pellets. Inserting a section of archive tubing into a nipple, as was done during fabrication, demonstrated that pieces of the PVC material were easily gouged from the nipple and deposited inside the cladding. It is believed that a piece of PVC was unintentionally incorporated into element 018 during loading and that the chlorine-containing products of PVC decomposition contributed directly to the cladding failure, possibly by a stress-corrosion mechanism.

The location and mode of cladding failure of element 018, as well as the time to failure, are considered atypical of LMFBR mixed-oxide fuel elements.

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