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A TECHNIQUE FOR EXAMINING THE FUEL/CLADDING INTERFACE BY TEM

Hanford Engineering Development Laboratory

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Assistant Secretary for Nuclear Energy

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Hanford Engineering Development Laboratory

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L.E. Thomas
May 1983

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A TECHNIQUE FOR EXAMINING THE FUEL/CLADDING

INTERFACE BY TEM

W. J. S. Yang
B. J. Makenas
L. E. Thomas

ABSTRACT

Fuel and fission-product interactions with the fuel-pin cladding is an area of concern and has been evaluated in the past principally by in-cell optical metallographic and electron-microprobe examinations. The applicability of three techniques for preparing specimens to reveal the microstructural details and local microchemistry of the fuel/cladding interface under conditions of high-resolution-scanning transmission-electron microscopy has been investigated. The specimen preparation techniques were designed to preserve the fuel/cladding interface and provide and maintain a specimen surface free from smearable alpha contamination. One of the techniques, Ni plating of a fuel-cladding sample, preserved the entire cladding cross-section for examination. An Fe-oxide layer on the cladding inner surface was found in specimens prepared by this method. All three techniques of specimen preparation are described in some detail, along with their advantages and disadvantages. It is concluded that the Ni-plating technique can be used for examining the inner surface of cladding from fuel pins and that cracks produced in the cladding during irradiation can be characterized in detail, both chemically and microstructurally.

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I. SUMMARY

Three specimen preparation techniques were developed to reveal the microstructural details and the local microchemistry of the fuel/cladding interface. Specimens were prepared from sections of three fuel pins. The specimen preparation techniques were designed to meet two criteria: 1) preserve the fuel/cladding interface and 2) maintain the foil surface free of alpha contamination. The first specimen preparation process involved electrolytically jetting the TEM disc from the OD surface inward to 2/3 of the cladding wall thickness with the inner surface protected by a layer of lacquer. This step was followed by removal of the lacquer and electrolytically polishing both surfaces of the disc to perforation. The fission elements were moved along in the laminar liquid over the polished surface during perforation and accumulated at precipitates exposed on the foil surface and at the grain boundaries. This problem was avoided in specimens prepared by the second method, where the cladding inner surface was protected during thinning by an evaporated layer of Au. However, the quality of the micrographs was affected by the appearance of Au nodules on the background. The third approach, Ni-plating, proved to be a satisfactory method for producing specimens for fuel/cladding interface examination. Nickel was directly plated on the fuel cladding specimen without prior cleaning. Thin foils were prepared by ion milling sections from the plated specimen. The principal result obtained by applying this technique is that the cladding inner surface becomes coated by an oxide film.

II. OBJECTIVE

The objective of this study is to develop a dependable specimen preparation technique to reveal the microstructural details and the microchemistry of the fuel/cladding interface.

III. ACCOMPLISHMENTS AND STATUS

A. INTRODUCTION

One of the requirements of a fuel pin cladding material is that the cladding must not react with the fuel to the extent that the mechanical properties of the cladding are degraded beyond design allowances. In a typical irradiation environment, cladding/fuel interactions may consist of cladding/mixed (U,Pu) oxide and cladding/fission product interactions. The classic interaction results in either a uniform oxidation of the cladding inner surface or an intergranular penetration by oxygen into the cladding surface.⁽¹⁻³⁾ The latter interaction may also include the intergranular penetration by fission products into the cladding inner surface.⁽¹⁻⁶⁾ The intergranular attack by either oxygen or fission products will inevitably affect the cladding mechanical properties.

Examinations of the results of fuel/cladding interactions so far have been limited to optical metallography and electron microprobe analyses.⁽¹⁻⁶⁾ The present study was designed to explore and to demonstrate the feasibility of examining the fuel/cladding interface by using a JEM 200B scanning transmission electron microscope (STEM). The primary advantage of using a STEM is to increase the resolution by orders of magnitude and to reveal the microstructural details and the local microchemistry.

B. SPECIMENS

Fuel cladding specimens were selected from three mixed oxide fuel pins clad with 20% CW 316 stainless steel.

1. Thin Foil Preparation Techniques and the Examination Results

Three thin foil preparation processes were developed. The development was designed to meet two major objectives, namely, to preserve the fuel/cladding interface and to provide a foil surface free of alpha contamination.

2. Two-Step Jetting

In this process, fuel pin segments 0.64 cm in length were first freed of fuel by pushing out the fuel mechanically. Cleaning was accomplished ultrasonically with methanol. The cleaned cladding sections were then sliced longitudinally in half. TEM discs were punched out from the half tubing for final thinning. The above described steps are illustrated in Figure 1. In the final thinning, the disc inner surface was first protected with a coating of lacquer. Then, the disc was jetted electrolytically from the OD surface to a depth of 2/3 of the cladding wall thickness. The layer of lacquer on the ID surface was then removed and the disc was electrolytically jet polished from both sides to perforation. This is illustrated in Figure 2. The thin foils prepared by this method represent a region of material within 25 to 76 μm (0.001 to 0.003 in.) from the cladding inner surface. Specimens used for this process were from fuel pin A (sections -II, -NN, -DDD) and fuel pin B (sections -P, -FF). Ten thin foils were prepared, two thin foils from each cladding section. The irradiation conditions for these specimens are given in Table 1.

Only three thin foils among the ten prepared were free of smearable alpha on the surface and therefore could be transferred into the microscope for examination. The three thin foils were from A-II, B-P and B-FF. The microstructures observed in these three specimens were similar to those observed in the unfueled RS-1 irradiation experiments.⁽⁷⁾ Voids and precipitates were heterogeneously distributed. Precipitates, mainly M_{23}C_6 and eta-silicide, were preferentially precipitated at grain boundaries and twin bands. Some examples of the voids and precipitates in specimens A-II and B-P are given in Figure 3. EDX analysis showed that the fission products Ag, Cd, Mo, Pd, Se and Te were concentrated at precipitate particles and at grain boundaries, in specimens A-II and B-P. In addition to these fission product elements, Pb was also consistently detected at precipitates and grain boundaries. Figure 4 gives an example of the X-ray spectrum obtained from precipitates and grain boundaries containing fission products and Pb. No fission products were detected in specimen B-FF, however. A large scale

FIGURE 1. Preparation of a TEM Disc from Irradiated Fuel Cladding.

FIGURE 2. Two-Side Jetting Procedure.

FIGURE 3. Microstructures of Pins A-II and B-P. Neg 8302478-1

FIGURE 4. Fission Product Elements in Carbide Precipitates. Neg 8302478-2

TABLE 1
SPECIMENS PREPARED BY THE FIRST METHOD

Specimen	In. From Bottom of Fuel To Middle of Sample	Local Burnup (Atom Percent)	Fluence (10^{22} n/cm ² , E > 0.1 MeV)	Time-Averaged Cladding Midwall Temp. (°C)
A-II	7.87	11.07	9.36	494
-NN	9.12	10.71	9.03	507
-DDD	13.12	8.87	6.14	546
B-P	6.25	8.80	11.37	472
-FF	12.12	7.55	8.69	551

All samples were 0.25 in. long and approximately 0.230 in. in diameter.

deposit present on the ID had flaked off during testing for smearable contamination prior to thinning this specimen and final examination involved a region very likely removed from the inner surface.

Careful re-examination of the specimen prepared from A-II revealed that a large number of fine particles had accumulated at twins, voids and precipitates in regions close to the perforation, as shown in Figure 5. The fine particles are fission product debris. The accumulation of fission product debris on the foil surface is due to their release from the inner surface during the final stage of the thinning. Fission products in the fuel/cladding interface are swept along with the laminar liquid film, a consequence of the electrolytical polishing, at the time of perforation due to surface tension forces. This gives an erroneous indication that fission product elements may have penetrated into the cladding. The element Pb, which was also concentrated at precipitates and at grain boundaries, may simply be an impurity from the fuel or from some external source and is swept along like the fission products and deposited on the cladding surface.

FIGURE 5. Fission Product Particles on the Thin Foil Surfaces During Final Thinning Stage. Neg 8302767-3

3. Single-Step Jetting

In this process, the cleaning process of the cladding sections was similar to that applied in the previous two-step jetting process, except that the step involving ultrasonic cleaning in methanol was eliminated. After the TEM discs were punched out from the half tubing, the inner surface of the cladding was coated with an evaporated layer of Au (in vacuum) to fix loose alpha-active particles. The final thinning consisted of electrolytic jet polishing from the OD to perforation. Thin foils were prepared by this method from cladding B-D, -E, -G, -O, -U, -BB, -CC and -DD. Considerable thin areas were found in foils prepared from claddings -G, -U and -DD. The irradiation conditions of these sections are listed in Table 2.

TABLE 2
SPECIMENS PREPARED BY THE SINGLE-STEP JETTING METHOD

Specimen	In. From Bottom of Fuel To Middle of Sample	Local Burnup (Atom Percent)	Fluence (10^{22} n/cm ² , E > 0.1 MeV)	Time-Averaged Cladding Midwall Temp. (°C)
B-C	.87	7.57	8.29	396
-D	1.12	7.64	8.57	399
-E	1.37	7.72	8.85	403
-F	1.62	7.79	9.13	406
-G	1.87	7.86	9.41	410
-H	2.12	7.93	9.69	413
-N	5.62	8.75	11.32	463
-O	5.87	8.77	11.34	467
-S	7.37	8.76	11.34	488
-T	7.62	8.74	11.31	492
-U	7.87	8.72	11.28	495
-AA	10.87	7.95	9.95	536
-BB	11.12	7.87	9.78	539
-CC	11.37	7.79	9.55	542
-DD	11.62	7.71	9.26	545
-EE	11.87	7.63	8.98	548

The adhesion of Au onto the cladding inner surface was excellent. This results in effectively holding the loose fission product particles on the cladding surface. However, the quality of the micrographs was substantially reduced due to the presence of Au nodules on the foil surface. Figure 6 presents representative micrographs taken from B-G, -U and -DD. Patches of fuel/cladding interface layer sandwiched between the Au layer and the cladding were found to be enriched in Fe, as well as Te, Pd, I, U and Pu. The layer could be some form of Fe-oxide. This is shown in Figure 7. No fission product elements or Pb were detected at precipitates and at grain boundaries. Only in one instance were fission product elements detected at a precipitate attached at the foil edge and at a grain boundary crack (specimen B-U). This confirms that the fission product element found at precipitates and at grain boundaries in specimens prepared by the first method were due to elusion of these particles from the cladding inner surface during the final thinning process.

4. Nickel Plating

After successful trials of Ni-plating unirradiated 316 tubing, surface oxidized 316 tubing, and finally, chemically cleaned cladding from an irradiated pin, as shown in Figure 8, Ni plating was performed on a piece of the 316 fuel cladding fragment. This fuel cladding fragment, 0.3 cm in diameter, was removed mechanically from a breached fuel pin. The fragment was located 5.5 in. from the bottom of the fueled section of the pin. The neutron fluence accumulated was $2.9 \times 10^{22} \text{ n/cm}^2$ ($E = 0.1 \text{ MeV}$) and the time-averaged midwall temperature was 465°C . No cleaning of the fragment was attempted. To preserve the fuel/cladding interface, Ni-plating was performed in a NiSO_4 solution. A nugget 1.5 cm long with a cardioid shaped cross-section, 0.6 cm in the short distance and 0.9 cm in the long distance, formed after five days of plating. The thickness of the plating is illustrated in Figure 9, a SEM micrograph taken from a cross-section of the nugget. The bonding between the Ni-plating and the specimen was exceptionally good, as shown in Figure 10. A large number of grain boundary cracks were revealed on the cladding surface. A number of large cracks were filled with Ni,

FIGURE 6. Microstructures of Au Coated B-DD, -U and -G. Gold nodules affect the quality of the micrograph. Neg 8302767-5

FIGURE 7. Fuel/Cladding Interface Layer Enriched in Fe and Fission Elements.
Neg 8302767-6

FIGURE 8a. Ni-Plating of Oxidized, Unirradiated 316 Tubing (50X).

- b. Bounding Surface Between Ni Plating and Chemically Cleaned Cladding from an Irradiated Fuel Pin (200X). Neg 8302767-4

FIGURE 9a. Cross-Section of the Ni Nugget Surrounding the Cladding Specimen from a Section Near a Breach.

b. Bounding Surface Between Ni Plating and the Uncleaned 316 Fuel Cladding Specimen. Neg 8302767-2

FIGURE 10a. Grain Boundary Cracks in Cladding ID Surface.

b. Ni Plating Filling in the Surface Cracks. Neg 8302767-1

assuring good plating. Sections 1.0 mm thick were then sliced from the nugget and subsequently mechanically polished to a thickness of 0.26 mm. TEM discs were obtained by electrolytically polishing off the excess material and preserving a 3-mm diameter disc by masking this area with tape on both sides of the slice. The steps in this process are illustrated in Figure 11. The final thinning was performed in a GATAN Model 600 ion mill. Two thin foils were prepared by this method. No fission product elements had accumulated at the precipitates or at the grain boundaries. An electron-opaque layer between the Ni plating and the cladding was observed. Diffraction ring patterns obtained from this layer are from an fcc structure with a lattice parameter $a = 0.42$ nm (Figure 12); these patterns match the structure of FeO formed at high temperatures. Extraction replicas taken from the cross-section of the cladding revealed a large number of Fe-rich acicular precipitates (Figure 13) on the cladding inner surface. These are a form of Fe-oxide, as an oxygen peak was detected using a thin window X-ray detector.

It is apparent that Ni plating of fuel cladding provides a technique for revealing the entire cladding cross-section. The technique of thin foil milling must be refined further in order to produce extensive thin areas for examination. The principal result obtained, namely finding the Fe-oxide layer on the cladding inner surface, illustrates the value of this method for examining and characterizing the fuel/cladding interface.

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FIGURE 11. TEM Specimen Preparation Procedure for Ni-Plated Cladding Specimens.

FIGURE 12. Selected Area Diffraction Ring Pattern of Fuel/Cladding Interface.

FIGURE 13. Fe-Oxide Particles From Cladding ID Surface (Extraction Replica of Cladding Cross-Section). The attached X-ray spectrum was obtained from thin window X-ray detector. Neg 8302767-8

IV. CONCLUSION

Three different techniques for preparing thin-foil TEM specimens which reveal the fuel/cladding interface in irradiated fuel pins have been evaluated. The best method is one which utilizes Ni-plating a fuel cladding fragment which, after slicing and thinning, permits examination of the entire cladding cross-section. The principal observations and results from an examination of a cross-section of a piece of cladding from a breached area in an irradiated fuel pin are: 1) a large number of grain boundary cracks are present on the inner surface of the cladding and 2) an Fe-oxide layer forms on the cladding inner surface next to the fuel during irradiation.

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