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AEC RESEARCH
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8/19/69

**COMPATIBILITY OF
URANIA-PLUTONIA FUELS WITH
STAINLESS STEEL AND SODIUM**

MASTER

T. LAURITZEN

U. S. ATOMIC ENERGY COMMISSION
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ADVANCED PRODUCTS OPERATION

GENERAL ELECTRIC

SUNNYVALE, CALIFORNIA **P2208**

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COMPATIBILITY OF URANIA-PLUTONIA FUELS WITH STAINLESS STEEL AND SODIUM

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ABSTRACT

The elevated temperature compatibility of mixed plutonia-urania fuels with austenitic stainless steel cladding was evaluated. The results of both out-of-pile and in-pile tests are summarized below.

- Out-of-Pile Compatibility

- 1) The austenitic alloys 304, 316, 321, 347 and Incoloy 800 were observed to be fully compatible with stoichiometric and slightly substoichiometric fuel for durations of at least 1000 hours at 1400°F in inert atmosphere systems as well as in systems containing sodium vapor.
- 2) All alloys exhibited slight incompatibility with hyperstoichiometric fuel in similar environmental systems. Incompatibility was manifested primarily in cladding surface oxidation with reaction zones ranging in depth from trace quantities in Incoloy 800 to 35 microns in Type 347.

- Compatibility in a Radiation Environment

Although several types of reaction were observed in irradiated fuel pin cladding, none could be attributed to incompatibility between fuel and cladding alone. The most common effect noted was the heavy grain boundary precipitation along the inner surface of the cladding, which was attributed to the thermal migration of carbon. Instances in which cladding was observed to have been severely attacked were related in most cases to tests that had experienced overpower conditions, resulting in excessively high interface temperatures.

SECTION I

INTRODUCTION

Austenitic stainless steel has long been considered the most applicable material for use as thin wall cladding of fast reactor fuels. Selection of this class of materials—in particular, several of the 18-8 grades—for development as prospective cladding for a sodium-cooled fast ceramic reactor (FCR) was based on factors such as neutron economy, mechanical properties at elevated temperatures, compatibility with liquid sodium and commercial availability. Two important and potentially decisive properties of the material remain to be established: (1) susceptibility to radiation damage in a predominantly fast neutron flux and (2) compatibility with internal components of the fuel pin. This report will be restricted primarily to the latter and will discuss radiation damage only in the context of its effect on system compatibility.

A fundamental function of any fuel pin cladding is that of isolating the fuel body from the potentially corrosive environment of the coolant. Extensive chemical interaction at either the inner or the outer surface of the cladding tube can limit fuel lifetime either by loss of

material or by changes in local temperature and stress patterns, or a combination of these effects.

The present FCR program is currently evaluating two basic fuel pin designs: gas-bonded and sodium-bonded pelleted mixed oxide fuel encased in thin wall stainless steel tubing. A modification of both is the vented pin, in which fission gases are allowed to escape to the coolant. With regard to compatibility, therefore, the component systems of interest are: fuel-cladding and fuel-coolant-cladding.

The purpose of this work was (a) to examine the type and magnitude of interactions occurring between fuel and cladding and between fuel and cladding in the presence of sodium, (b) to explore the mechanisms whereby a given reaction occurs, and (c) to assess the effect of observed interactions on long-term cladding stability. The results of these experiments will be used as one of the bases for selecting the most favorable materials and operating limits for mixed oxide fuel pins.

SECTION II

SUMMARY OF RESULTS

The solid-state compatibility of uranium-plutonium mixed oxide fuel with austenitic stainless steel has been evaluated in a series of out-of-pile isothermal anneals. The work to date,

performed at 1400° F for annealing times as long as 1000 hours, has indicated excellent compatibility of stoichiometric and substoichiometric fuel with all austenitic alloys tested. Shallow

reaction layers (not more than 35 microns in thickness) were noted along some stainless steel surfaces in a capsule loaded with hyperstoichiometric fuel but no reaction was observed in the adjacent fuel. Precipitate-free zones of the same magnitude were also observed along the surfaces of cladding materials annealed in this capsule.

A group of fuel-cladding capsules containing sodium vapor, annealed under the same conditions, yielded similar results. Metallographic data revealed that cladding underwent no obvious attack in capsules containing stoichiometric and hypostoichiometric fuel but did sustain minor attack in hyperstoichiometric fueled capsules. In all cases, the majority of sodium vapor in the capsules had reacted with the fuel, with only slight reaction product formation in the fuel-clad gap.

Several distinct types of reaction have been observed between components of the fuel-cladding system annealed in an irradiation environment. A common occurrence is that of heavy precipitation of complex carbides in grain boundaries along the inner surfaces of cladding tubes. Since this structural condition has been noted in both short-term and long-term irradiation tests, the precipitation is most likely caused by the rapid movement of carbon within the cladding under the influence of a thermal gradient rather than an interaction between cladding and fuel.

The mechanism responsible for the severe reactions sometimes observed at the fuel-cladding interface in failed fuel pins has not yet been established. However, the fact that some of these pins experienced over-power conditions during irradiation suggests that the reactions are associated with reactions at considerably higher temperature.

SECTION III

OUT-OF-PILE COMPATIBILITY STUDIES

3.1 GENERAL

The primary purpose of the out-of-pile evaluation of fuel-cladding compatibility has been to assess the type and magnitude of interaction occurring under maximum design conditions, i.e., fuel and cladding are maintained in intimate contact at an interfacial temperature of 1400°F. The tests were performed in an out-of-pile environment to allow close thermal control, to facilitate handling and analysis and to isolate the effect of a purely thermal anneal versus that of an irradiation test on the compatibility of fuel with cladding. Three such tests have been performed to date. The first two tests

consisted of alternate discs of fuel and cladding held in compression in inert atmosphere capsules; the third test consisted of a stack of standard size fuel pellets contained in reference design cladding. The latter capsules contained a reservoir of sodium to provide a sodium vapor environment at the fuel-cladding interface.

Test materials in all three anneals were the same: urania-plutonia fuel of three stoichiometries (1.97, 2.00, and 2.04 O/M) and the five FCR candidate cladding alloys Types 304, 316, 321, 347, and Incoloy-800. Specific details of each

of the tests are discussed below. (Representative metallography of as-received and control cladding material is contained in the appendix.)

3.2 FUEL-CLADDING COMPATIBILITY

The first test in the current series of fuel-cladding compatibility evaluations consisted of three capsules of the form shown schematically in Figure 3-1. Design of the capsule was patterned after that used by Murdock.⁽¹⁾ The diffusion couple "sandwich"—in this case, alternating discs of (U-20wt%Pu)O₂ fuel and cladding—is positioned within a thick-walled cylindrical tube of 410 stainless steel with the disc mating surfaces normal to the axis of the tube. A Type 304 stainless steel rod rests upon the specimen column and abuts the inside surface of the screw-on cap. The capsule is loaded and sealwelded in a helium environment. The diffusion couple is axially constrained at the annealing temperature by pressure exerted on the couple by the Type 304 stainless steel rod. (The coefficient of thermal expansion of Type 304 is higher than that of Type 410.) To satisfy a basic requirement of the fuel-cladding test, namely, to evaluate the effect of fuel stoichiometry on system compatibility, each capsule contained fuel of identical stoichiometry. This assured that the oxygen environment in a given capsule was not confounded by annealing fuel of several stoichiometries in the same capsule.

The capsules of the first fuel-cladding compatibility test (FC-1) were annealed at 1400°F for 100 hours in a tube furnace equipped with continuous temperature control and read-out. Destructive examination of the capsules was performed by cutting each capsule transversely through the heavy-walled region above the couple (Figure 3-1). Each entire couple was mounted longitudinally in epoxy and ground to the axial mid-plane, thereby revealing simultaneously all fuel-cladding interface combinations in each capsule.

Observations of the as-polished sections revealed no evidence of gross chemical instability at any of the fuel-cladding interfaces. No diffusion at any mating surface was noted. Preferential etching of the cladding discs (10% oxalic, electrolytic) revealed that the surface of each disc contained a thin (less than 0.0006 inch) dense layer of heavy carbide precipitation. This effect has been attributed to a cold-worked surface structure that was not completely removed by pickling prior to capsule assembly. Since susceptibility of austenitic alloys to sensitization is enhanced by cold working, it is not surprising that the carbide precipitation is well pronounced along alloy disc surfaces which experienced some degree of cold working during fabrication. Only in the Type 316 stainless steel disc, however, does the carbide precipitation extend much beyond the cold-worked zone. In this material, a distinctive grain boundary carbide was observed as deep as 4 mils from the cold-worked surface of the disc. Photomicrographs representative of the fuel-clad interfaces of the capsule containing stoichiometric fuel are shown in Figure 3-2. No variation in the magnitude or distribution of carbides with fuel stoichiometry could be detected.

3.3 FUEL-CLADDING COMPATIBILITY II

The second fuel-cladding compatibility test (FC-2) utilized the same materials and capsule design as the FC-1 tests. Test FC-2 consisted of three fueled capsules and one capsule containing only cladding to provide a cladding thermal control. Unlike FC-1, the cladding materials used in FC-2 were annealed at 1800°F for 20 minutes prior to capsule assembly to relieve the effects of cold working introduced in disc fabrication. The three capsules were annealed for 1007 hours at 1400 ± 10°F in an assembly shared with the capsules of FC-3 (Section 3.4). Preparation of the fueled capsules for optical metallography was identical with that used on the FC-1 capsules.

FIGURE 3-1. FUEL-CLADDING COMPATIBILITY CAPSULE (X4)

INCOLOY-800

347 STAINLESS STEEL

X4

316 STAINLESS STEEL

321 STAINLESS STEEL

304 STAINLESS STEEL

MAGNIFICATION: 250x
ETCHANT: 10 PERCENT OXALIC ACID

FIGURE 3-2. REPRESENTATIVE FUEL-CLADDING INTERFACES AFTER 100 HOURS AT 1400°F (STOICHIOMETRIC FUEL, OUT-OF-PILE).

Examination of the several fuel-cladding interfaces revealed varying degrees of reaction at cladding surfaces adjacent to hyperstoichiometric fuel (Figure 3-3). The general appearance of the reaction zones is similar in all cases: a gray, porous-appearing layer contiguous with the cladding underlying a bright metallic deposit in the fuel-clad gap. The combined thicknesses of the two-zone scale on the Type 304 stainless steel is approximately 1 mil and is fairly continuous. The reaction zones on the stabilized Types 321 and 347 stainless steel are somewhat thinner and discontinuous while the Incoloy 800 specimen exhibits virtually no surface reaction products. (Type 316 was not tested with hyperstoichiometric fuel). Although much of the gray layer is unattacked, virtually none of the metallic deposit is retained after etching. This indicates that the chemistry of this material is different from that of the matrix. It should be emphasized that these reactions were observed in capsules containing hyperstoichiometric fuel: no evidence of reaction could be detected in systems containing stoichiometric or substoichiometric fuel.

In addition to the well-defined surface layers, the metallographic examination also revealed a precipitate-free zone approximately 30 microns wide along the surfaces of all cladding discs adjacent to hyperstoichiometric fuel. The zone is most prominent in Types 321 and 347 in which the stabilizing carbides and a precipitate phase identified by electron microprobe analysis as sigma are uniformly distributed throughout the matrix but are absent near the surface. In the unstabilized grades, the precipitate-free zone is evident in the absence of grain boundary precipitation at and adjacent to the surface in the otherwise fully sensitized structure. This effect is shown in the etched microstructure, Figure 3-3. No gradation in the density of precipitates was observed in the cladding material annealed with stoichiometric or hypostoichiometric fuel.

In an attempt to identify the composition of the reaction layers observed, an electron microprobe analysis was performed on the Type 304 stainless steel reaction zone. The qualitative data from this examination are shown in the x-ray image display of Figure 3-4. The components of the region analyzed are shown in the light optical image and the corresponding specimen current image (the latter also provides a visual indication of the relative density of the several components since the specimen current intensity is proportional to atomic number). Thus, the chromium x-ray image shows that the gray surface layer is enriched in chromium while the adjacent metallic deposit contains virtually none. The x-ray image for iron, on the other hand, shows that the metallic deposit is rich in this element while the gray surface deposit is somewhat depleted of iron. The nickel image is similar to that of iron. The apparent high nickel content in the fuel is not real. This is thought to be due to the fact that the nickel spectral line occurs at a diffraction angle where the peak-to-background ratio is poor. This is confirmed by the spectral line profiles shown in Figure 3-4. Note that the line profile intensities of all three elements are reduced to background at the periphery of the fuel. This indicates that no measurable diffusion of these elements occurred into the fuel. Similar x-ray imaging of uranium and plutonium showed no trace of either element along the cladding surface.

The elemental composition of these cladding surface zones, gathered by a point-by-point microprobe traverse, is represented graphically in Figure 3-5. The path of the traverse is shown on the adjoining photomicrograph. A diagonal path across the interface was used to increase the relative thickness, thereby achieving a better resolution of the surface zones. The data show that the total metallic content of the gray surface layer is approximately 75 percent by weight and that of the metallic layer approaches 100 percent. No

AS-POLISHED

ETCHED

INCOLOY-800

AS-POLISHED

ETCHED

321 STAINLESS STEEL

AS-POLISHED

ETCHED

347 STAINLESS STEEL

AS-POLISHED

ETCHED

304 STAINLESS STEEL

MAGNIFICATION: X500
ETCHANT: 10% OXALIC ACID

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FIGURE 3-3. REPRESENTATIVE FUEL-CLADDING INTERFACES AFTER 1000 HOURS AT 1400°F (HYPERSTOICHIOMETRIC FUEL, OUT-OF-PILE)

① X-RAY INTENSITY SCAN, ② TRACE OF THE ELECTRON BEAM, ③ BACKGROUND INTENSITY SCAN.

FIGURE 3-4. ELECTRON MICROPROBE EXAMINATION OF SURFACE LAYERS ON TYPE 304 STAINLESS STEEL ADJACENT TO A HYPERSTOICHIOMETRIC (U-20 WEIGHT PERCENT Pu)O₂ FUEL

67-01457

304 SS/HYPERSTOICH. FUEL
ANNEALED 1400 F, 1000 h.

FIGURE 3-5. COMPOSITION OF REACTION LAYERS ON 304 SS: ELECTRON MICROPROBE ANALYSIS

plutonium or uranium could be detected in either surface layer.

3.4 FUEL-COOLANT-CLADDING COMPATIBILITY

The third fuel-cladding compatibility test (FC-3) was performed to investigate the effect of a sodium vapor environment on the compatibility of fuel and cladding. The objective of the test was to produce, in an out-of-pile isothermal environment, a reaction similar to that observed in several irradiated fuel pins which contained sodium or NaK. The test consisted of 15 capsules—three capsules of each of the five cladding alloys, each capsule containing (U-24wt%Pu)O₂ fuel of one of the three stoichiometries. The capsule design is depicted schematically in Figure 3-6. The capsule wall consisted of 0.250-inch diameter, 0.015-inch wall tubing of the five candidate cladding alloys. Each capsule contained three 200-mil-high fuel pellets bounded on each end by a 200-mil-high solid cylinder of the same material as the cladding tube. The capsule was capped at both ends with welded end plugs. The bottom end plug contained a sodium reservoir which was loaded with approximately 50 mg of metallic sodium. A nominal as-fabricated fuel-clad gap of approximately 4 mils was used. To assure intimate fuel-cladding contact at the test temperature, the capsule tube walls were designed to collapse along the length of the fueled region at an external pressure of 1500psi.

Both FC-2 and FC-3 capsules were annealed simultaneously in the annealing rig shown in Figure 3-7. The alpha container was required to allow the anneal to be performed in an uncontrolled free access area. The annealing rig was inserted into an argon-pressurized autoclave and heated at a rate of 100°F per hour. Pressure in the autoclave during the heating period was held at 600 psi. This allowed sodium vapor permeation into the fuel-cladding gap prior to collapse of the wall. Pressure was adjusted to 1500 psi after thermal equilibrium at 1400°F was attained. Temperature was controlled at 1400±10°F throughout

the 1007-hour test. The test system is shown in the schematic diagram, Figure 3-8.

The test was terminated by controlled cooling at a rate of approximately 100°F per hour. At room temperature, the argon was exhausted through a millipore filter. Once the filter was judged to be free of alpha contamination, the autoclave was opened, the annealing rig extracted and transferred to an inert atmosphere box for sectioning and examination.

Prior to destructive examination, each capsule was gauged to determine the extent of diametral change that occurred in the fueled region as a result of the anneal. Although one would have intuitively assumed that the capsule diameter would have been reduced by the 1500-psi external pressure applied during the anneal, this was not generally true. Indeed, of the 15 capsules tested, only five showed a diametral reduction greater than one-half mil. All contained hypostoichiometric fuel. Six of the remaining 10 capsules were observed to have undergone diametral swelling greater than one-half mil. Four contained hyperstoichiometric fuel.

Destructive examination of the capsules utilized two transverse sections: a section immediately above the sodium reservoir and a section in the central fueled region. Visual examination of the former revealed that virtually all the sodium supplied to the reservoir had been consumed. Of the 40-60 milligrams of sodium loaded, only a thin film could be detected along the walls of the reservoirs.

Metallographic examination of each capsule, performed on a transverse section through the center fuel pellet, yielded some evidence of sodium intrusion or sodium-fuel reaction in all three fuel stoichiometries tested. The reaction appeared to be most severe, however, in capsules containing hyperstoichiometric fuel. The product may be characterized as a homogeneous gray material, generally occurring in fissures at or near the fuel periphery. A reaction product typical of that observed in all fuel compositions is shown

FIGURE 3-6. FUEL-COOLANT-CLADDING COMPATIBILITY CAPSULE (X4).

A. CAPSULE RADIOGRAPHS

B. THE ANNEALING RIG

FIGURE 3-7. COMPONENTS OF THE FC-2/FC-3 COMPATIBILITY TESTS.

FIGURE 3-8. THE FC-2/FC-3 TEST SYSTEM (SCHEMATIC).

in Figure 3-9. The material was rapidly attacked by aqueous etching solutions causing severe grain pullout, particularly in the fine-grained hypostoichiometric fuel.

Attack of the inner cladding surface occurred in all capsules although, like the sodium-fuel reaction, the attack was most prominent in capsules containing hyperstoichiometric fuel. The reaction product in the as-polished state is characterized by an irregular gray layer overlain by a fairly continuous thin metallic layer, the latter being adjacent to and generally in contact with the fuel. The inner layer was observed to be readily attacked

by cladding etchants whereas the outer metallic strand was not. Representative metallography of all fuel-cladding combinations tested is shown in Figure 3-10. Although there is some evidence of surface irregularity on cladding annealed adjacent to stoichiometric and hypostoichiometric fuel, it is obvious that the only significant attack occurred with hyperstoichiometric fuel. The metallic material along the Type 321 stainless steel surface adjacent to stoichiometric fuel, as shown in Figure 3-10, constitutes an extremely local effect and is most likely cladding material removed and re-deposited during cutting and grinding. The results of the FC-3 cladding examination are summarized in Table 3-1.

TABLE 3-1

EXAMINATION RESULTS OF FC-3 CAPSULES

<u>Cladding</u>	<u>Fuel O/M</u>	<u>Fuel-Clad Gap</u>	<u>Fuel-Clad Reaction (max)</u>	<u>General Cladding Condition</u>
304	1.97	~16 μ	None	The structure is lightly sensitized throughout, with an average grain size of ASTM #8.
304	2.00	0	None	
304	2.04	0	None	
316	1.97	~8 μ	None	The structure is lightly sensitized throughout, with an average grain size of ASTM #8.5.
316	2.00	0	None	
316	2.04	0	~20 μ	
321	1.97	0	None	The structure contains a heavy precipitation of sigma phase. There is insufficient grain boundary delineation to determine grain size.
321	2.00	0	None	
321	2.04	0	~12 μ	
347	1.97	0	None	The structure contains a heavy precipitation of sigma phase. There is insufficient grain boundary delineation to determine grain size.
347	2.00	0	Trace	
347	2.04	0	~35 μ	
I-800	1.97	0	Trace	The structure is moderately sensitized throughout the cross-section. The material has an average grain size of ASTM #10.
I-800	2.00	0	Trace	
I-800	2.04	0	~15 μ

(REDUCED TO 75%
FOR REPRODUCTION)

AS-POLISHED

500X

FIGURE 3-9. SODIUM-FUEL REACTION PRODUCT IN TYPE 316 STAINLESS STEEL-CLAD CAPSULE CONTAINING HYPERSTOICHIOMETRIC FUEL

FIGURE 3-10. INTERACTION OF AUSTENITIC STAINLESS STEEL WITH MIXED OXIDE FUEL IN THE PRESENCE OF SODIUM. COUPLES ANNEALED FOR 1000 HOURS AT 1400°F. ALL PHOTOMICROGRAPHS: AS-POLISHED, 500X

A precipitate-free zone along the cladding surface, similar in appearance to that noted in the fuel-cladding compatibility test (FC-2), was also observed in this test. Like FC-2, the effect is evident in material containing large quantities of the sigma phase, as shown in the Type 347 stainless steel cross-sections of Figure 3-11, and is restricted to cladding annealed with hyperstoichiometric fuel.

3.5 DISCUSSION OF RESULTS FROM OUT-OF-PILE TESTS

3.5.1 Fuel-Cladding Interaction

The observation of measurable surface reaction in 18-8 austenitic stainless steel materials annealed with hyperstoichiometric fuel and the absence of reaction in capsules containing lower stoichiometry fuels strongly suggests that the reaction product is an oxide of one or a combination of components comprising the fuel-cladding system. Indeed, the electron microprobe data have established that iron, chromium, and nickel account for 75 percent by weight of the content of the gray surface layer and iron, 100 percent of the outer metallic layer. Neither plutonium nor uranium could be detected beyond the periphery of the fuel.

Typical oxide scales forming on austenitic stainless steel in air consist of an inner layer of Cr_2O_3 or a spinel-type compound of the form $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and an outer layer of Fe_2O_3 or Fe_3O_4 . The chromium content of the inner layer, 30-40 percent, observed by microprobe on the Type 304 sample is too low to be represented by Cr_2O_3 which has a chromium content of approximately 68 percent. The metallic content of the spinel, however, closely approximates the combined iron-chromium content of the layer (71.4 w/o versus 72.8 w/o). The iron contents of both oxides, Fe_2O_3 and Fe_3O_4 , are substantially lower than that observed in the outer layer, 80-90 percent. This discrepancy suggests that, in the absence of adequate oxygen activity (oxygen partial pressure) or a reduc-

tion in activity with time, any iron oxides formed would decompose (over long periods of time) to FeO and finally to metallic iron. This assumes, of course, that since the capsule was sealed in an inert environment the oxygen present was liberated from the fuel and therefore available in a very limited amount consistent with the partial pressure in equilibrium with the fuel at the test temperature.

The fact that the oxygen activity at the surface of the fuel does indeed diminish with time has been experimentally established. An electrical conductivity probe across the fuel, parallel to the diffusion direction, revealed a reduction in fuel conductivity in a surface zone 100 microns wide. Since fuel conductivity is proportional to its oxygen content, this reduction represents a loss of oxygen. This work suggests that the rate-controlling step in the oxidation of stainless steel in this system was the diffusion of oxygen to the surface of the fuel.

The observations noted in the examination of the FC-2 capsules were corroborated by the results of the fuel-coolant-cladding compatibility tests (FC-3), the latter differing primarily in magnitude of reaction. Since the only major difference in the two tests was the inclusion of sodium in FC-3, the greater reaction occurring in FC-3 may have been due to sodium-enhanced oxygen transport.

3.5.2 Sodium-Fuel Interaction

The extent of cladding attack observed in the two series of tests discussed above is somewhat minor when one considers that the test parameters were selected to represent temperature and pressures well beyond those of anticipated normal operation. A more significant effect could likely be that posed by the observed sodium-fuel interactions. At the present time, two fuel pin design concepts are being explored which could be strongly influenced by the effects of sodium-fuel incompatibility. In the vented to-coolant design, which could conceivably allow

a. 347 SS — STOICHIOMETRIC FUEL

b. 347 SS — HYPERSTOICHIOMETRIC FUEL

FIGURE 3-11. SIGMA PHASE PRECIPITATE DISTRIBUTION IN 347 STAINLESS STEEL.
VILELLA'S ETCH, X500.

sodium vapor ingress into the fueled region of the pin, and, of course, in the sodium-bonded pin, fuel-coolant reaction could produce fuel degradation as well as contribute to changes in thermal conductivity. Both could eventually lead to gross failure of the fuel pin.

A particularly significant observation in this regard is the apparent increase in fuel swelling with stoichiometry in the presence of sodium. This correlation was suggested in the measurements of capsule diametral changes previously discussed. It can now be evaluated on the basis of the metallographic examination. Fuel swelling data were collected on each capsule on the basis of the following three assumptions:

1. The fuel-cladding gap is filled or otherwise closed.
2. The cladding thickness was not altered during the anneal.
3. Both longitudinal and diametral swelling occurred.

Both diametral and volume swelling were determined: diametral swelling being represented by the cladding diametral changes plus the as-fabricated width of the fuel-clad gap, volume swelling being equated to three times the per cent diametral swelling. The data are listed in Table 3-2 and plotted in Figure 3-12. The values for "per cent total void" were obtained by adding the observed swelling to the initial fuel porosity. This figure provides a measure of the total volume available for sodium intrusion. Note that fuel swelling occurred in all capsules, in contrast to the post-anneal dimensional data which could only detect fuel swelling as evidenced by an increase in as-fabricated capsule diameter. The trend in swelling—increasing with stoichiometry—corroborates the previous data.

The source of fuel swelling may be related to one or a combination of several possible

mechanisms: Na_2O had penetrated the fuel, sodium had reacted directly with the fuel, or metallic sodium had penetrated the fuel by capillary action and had formed Na_2O during subsequent metallographic preparation.

Sodium impregnation by capillary action is considered the least likely mechanism in view of the fact that fuel swelling occurred against a 1500-psi external pressure. Moreover, since the sodium reservoirs were not completely filled and the capsules were heated in an upright position, a gap existed between the sodium level and the steel slug supporting the fuel column (see Figure 3-6). It would be difficult to conceive of capillarity in such a system.

Recent analytical work has shown⁽²⁾ that Na_2O would not be expected to form in hypostoichiometric fuel at 760°C (1400°F) since the free energy for formation of the hypostoichiometric mixed oxide is lower than that of Na_2O at 900°C .

The most plausible source of fuel swelling appears, therefore, to involve direct reaction of sodium with the fuel. A number of sodium uranate compounds have been observed and studied in recent years⁽³⁾. Lattice parameter measurements on the compound $\text{Na}_2\text{U}_2\text{O}_7$, for example, have indicated a density of 7.15 gm/cm^3 . This represents an 80 percent volume change upon reaction of sodium with UO_2 to form this compound. The maximum amount of swelling that could be produced by this reaction in any one capsule, assuming total reaction of the contained sodium, is approximately 19 percent. Calculations of initial fuel void and gap space, plus additional volume due to swelling, have shown that the fuel could accommodate from 5.9 to 14.6 percent volume swelling, depending upon the oxygen-to-metal ratio. Since the total amount of sodium present in the as-fabricated capsules is not accurately known, it is felt that the existence of sodium uranates is reasonable based on the swelling data.

TABLE 3-2

CAPSULE SWELLING DATA (FC-3)

Cladding Type	Fuel O/M	Pellet Density % T.D.	Initial Cladding i. d. (inches)	Cladding Thickness (inches)	Initial Fuel-Clad Gap (inches)	Initial Cladding o. d. (inches)	Post-Anneal Cladding o. d. (inches)	Swelling	Percent Diametral Swelling	Percent Volume Swelling	Percent Total Void
347 SS	2.04	93.3	0.2195	0.0330	0.0029	0.2525	0.2524	0.0028	1.30	3.9	10.6
347 SS	2.00	92.5	0.2195	0.0330	0.0025	0.2525	0.2521	0.0021	0.97	2.9	10.4
347 SS	1.97	96.0	0.2191	0.0330	0.0046	0.2521	0.2490	0.0015	0.70	2.1	6.1
304 SS	2.04	94.0	0.2188	0.0294	0.0030	0.2482	0.2514	0.0062	2.87	8.6	14.6
304 SS	2.00	91.6	0.2189	0.0294	0.0015	0.2483	0.2492	0.0024	1.10	3.3	11.7
304 SS	1.97	96.0	0.2189	0.0294	0.0039	0.2483	0.2463	0.0019	0.88	2.6	6.6
321 SS	2.04	93.0	0.2185	0.0310	0.0018	0.2495	0.2510	0.0033	1.52	4.6	11.6
321 SS	2.00	92.1	0.2186	0.0310	0.0020	0.2496	0.2495	0.0019	0.88	2.6	10.5
321 SS	1.97	95.8	0.2188	0.0310	0.0041	0.2498	0.2470	0.0013	0.61	1.8	6.0
316 SS	2.04	93.0	0.2198	0.0302	0.0022	0.2500	0.2524	0.0046	2.11	6.3	13.3
316 SS	2.00	91.5	0.2200	0.0302	0.0026	0.2502	0.2512	0.0036	1.66	5.0	13.5
316 SS	1.97	96.0	0.2198	0.0302	0.0053	0.2500	0.2479	0.0032	1.50	4.5	8.5
Incoloy 800	2.04	93.0	0.2181	0.0302	0.0015	0.2483	0.2522	0.0054	2.49	7.5	14.5
Incoloy 800	2.00	92.8	0.2181	0.0302	0.0013	0.2483	0.2488	0.0018	0.83	2.5	9.7
Incoloy 800	1.97	96.1	0.2181	0.0302	0.0040	0.2483	0.2457	0.0014	0.65	2.0	5.9

GEAP-5633

FIGURE 3-12. FUEL SWELLING IN THE PRESENCE OF SODIUM (1400 F, 1000 h).

3.5.3 Cladding Structural Changes

Two major structural changes, in addition to the surface reactions discussed in 3.5.1, were observed in the cladding materials tested: (1) the precipitation of sigma phase in Types 316, 321, and 347 stainless steel, and (2) the formation of a precipitate-free zone along the surface of all alloys. Correlation of results from the cladding thermal control tests (discussed in Appendix A) and the compatibility tests show that the precipitation of sigma was due solely to the 1000-hour anneal since the quantity and distribution of sigma was similar in both tests. The precipitate-free zones, on the other hand, were not evident on the thermal controls indicating that their formation is due to the surface reaction with the fuel or the environment provided by the fuel.

The formation of the sigma phase in Types 321 and 347 stainless steel annealed for 1000 hours at 1400°F is not unexpected. At this temperature, the nucleation and growth of sigma is strongly favored. However, the mechanism responsible for the formation of sigma in "stabilized" stainless steels is not immediately clear. Two theories relating to a mechanism for sigma formation have been advanced: transformation from delta ferrite and transformation due to the decomposition of $M_{23}C_6$. The delta ferrite transformation mechanism is not plausible with regard to wrought austenitic stainless steels, at least in dealing with the magnitude of sigma observed in these tests. The formation of sigma phase via the decarburization of $M_{23}C_6$ is somewhat more realistic.

This mechanism was first suggested by Goldschmidt⁽⁴⁾ to explain the formation of sigma in a fully austenitic structure. In later work, Lismer, et al.,⁽⁵⁾ proposed that the complex carbide $M_{23}C_6$ breaks down after attainment of some critical size, thereby re-

leasing chromium. This enrichment in chromium in the region once occupied by the carbide provides an environment conducive to sigma formation. The driving force for this reaction is somewhat vague but may be due to the strain energy associated with the transformation or a difference in energy at the sigma-austenitic interface.⁽⁶⁾

With regard to the current work, it is significant to note that, although no complex carbide could be detected in either Type 321 or Type 347 stainless steel annealed for 1000 hours, the same materials annealed for 100 hours showed evidence of sensitization throughout the structure. The latter materials contained no trace of sigma. It is proposed, therefore, that the breakdown of $M_{23}C_6$ occurs at some time after 100 hours at 1400°F, resulting in a local chromium enrichment which subsequently transforms to sigma. The transformation is virtually complete after 1000 hours.

Evidence of such a mechanism for the formation of sigma was observed in the Type 316 stainless steel thermal control specimens. This material contained scattered grain boundary deposits of sigma after 1000 hours. It was noted, however, that the grain boundaries impinging on these sigma deposits were devoid of carbide precipitates (See Figure A-1, Appendix). The overall structure was sensitized.

Neither Incoloy 800 nor Type 304 stainless steel showed metallographic evidence of the sigma phase. Both materials, however, contain elements that are known to influence the position of the ternary phase boundary near which they lie. Silicon and molybdenum, for example, have been found to be three to four times more effective than chromium in the promotion of sigma,⁽⁷⁾ a fact that could explain why small quantities of sigma were observed in Type 316 and none in Type 304 stainless steel, the latter containing substantially smaller amounts of both.

These observations were made on material annealed for only two time periods in the sigma-tizing range. Clearly, it cannot be concluded from this evidence that a material is prone or immune to sigma formation. Previous experimental work has in fact shown that all five materials can be annealed to produce sigma.

The formation of a precipitate-free region, and the apparent oxide layers, at the surfaces of cladding specimens annealed in the long-term compatibility tests represent the only distinguishable features that can be attributed solely to the environment provided by the mixed oxide fuel. Moreover, the fact that these phenomena occurred only in capsules containing hyperstoichiometric fuel strongly suggests that the mechanism responsible for both depends upon the establishment of an oxygen-rich atmosphere at the cladding surfaces.

One mechanism whereby a precipitate-free region may be formed is that of solute depletion.⁽⁸⁾ Although the systems studied here are somewhat complex, an attempt has been made to isolate the variables in order to establish the identity of a common solute.

Based on the comparative metallography, the precipitate phases absent from the surface regions in the Types 321 and 347 stainless steel are the stabilizing carbides, TiC and NbC, respectively, the sensitizing carbide $M_{23}C_6$, and sigma, which are common to both. The precipitate-free regions in the remaining cladding materials, which contained little or no sigma, were restricted to grain boundaries impinging the surface and extending not more than one grain diameter (approximately 40 microns) into the matrix. In addition to the fully-sensitized structure beyond the surface regions, these materials contained a fine dispersion of intragranular precipitates which extended to within 4 microns from the surface.

Except for the components of the sigma phase, the solute element common to all clad-

ding materials exhibiting the precipitate-free region is carbon. It has already been established the hyperstoichiometric fuel provides an oxygen-rich environment at the cladding surface. Thus, the oxidation of all components, including carbon, can occur, the carbon being converted to CO or CO_2 . This surface decarburization establishes a carbon concentration gradient and an outward diffusion of carbon ensues to reduce the gradient. It is proposed, therefore, that the mechanism of solute depletion—in this case, the depletion of carbon by decarburization—is responsible for the precipitate-free surface regions in the cladding alloys exhibiting an overall sensitized structure. The observation that these regions are more pronounced along grain boundaries than at the surface of the cladding alloys is evidence of the fact that the activation energy for grain boundary diffusion is substantially lower than that for volume diffusion.

The precipitate phase most conspicuous in its absence from the surface zones of the Type 321 and Type 347 stainless steel specimens is sigma. It is not clear how the removal of carbon from these materials could suppress the formation of sigma. However, if the postulation that sigma formation depends upon the prior precipitation of $M_{23}C_6$ is correct, one might conclude that decarburization occurred in the surface zone before the nucleation of $M_{23}C_6$. Carbon impoverishment of this zone would thus have prevented the formation of $M_{23}C_6$ and, consequently, the formation sigma. On the other hand, elemental depletion in the zone adjacent to the cladding surface is not restricted to carbon. The microprobe analysis previously discussed has in fact shown that the chromium content is depressed by as much as a factor of two in a 20-micron zone adjacent to the gray surface oxide. (This zone corresponds in magnitude and position to the precipitate-free regions.) Since the sigma phase is predominantly chromium, any reduction in chromium would tend to suppress its formation.

SECTION IV

FUEL-CLADDING INTERACTIONS, IN-PILE

4.1 GENERAL OBSERVATIONS

Metallographic examination of a large number of fuel-cladding interfaces in irradiated fuel pins revealed several interactions that were not reproduced in out-of-pile isothermal testing. The effect most commonly observed in irradiated cladding is that of heavy grain boundary precipitation at and adjacent to the inner surface of the cladding. This reaction was first observed in Type 347 stainless steel and has since been shown to occur in Type 316 stainless steel as well. In Type 347 stainless steel cladding, the depth of this heavy precipitate zone is approximately 0.004-inch and is relatively uniform in thickness over the burnup range of 52 to 100,000 MWd/Te. This phenomenon has not yet been fully explored in fuel pins utilizing Type 316 stainless steel claddings but preliminary work shows that the heavy precipitate zone is at least twice as broad in this material than in Type 347 stainless steel after comparable exposures. The mechanism for this reaction is not fully understood at this time. There is some evidence that the reaction is dependent on intimate fuel cladding contact, a condition which may provide a higher thermal gradient across the cladding. In the specimen shown in Figure 4-1, for example, precipitation is restricted to regions where the fuel-clad gap is sufficiently narrow to assure that intimate contact existed at the test conditions. The specimen was cut from Capsule IX-1-P, and early irradiation test of Type 347 stainless steel-clad mixed oxide fuel. A detailed investigation of locally enhanced precipitation in irradiated Type 347 stainless steel cladding is presented in a later section.

Another fairly common effect noted at the fuel-cladding interface is that of a 5-10 micron metallic layer contiguous with the cladding. Some observations of this effect are shown in Figure 4-2. Although the boundary between the layer and the cladding, revealed by etching, is very well defined, the grain boundary network of the adjacent cladding is continuous across the layer. The latter observation suggests that the layer is an integral part of the cladding and its formation involves neither a phase transformation nor a change in the crystallographic orientation of the parent material. The fact that such a layer has not been observed in out-of-pile testing indicates that its formation is due to the radiation environment. Indeed, the thickness of the layer is of the same order as the penetration range of recoiling fission fragments. Similar layers have been observed by other investigators.^(9, 10) Their analyses revealed neither compositional changes in the zone relative to the adjacent cladding, nor could any fission product elements be detected. They did observe, however, that the zone is substantially harder than the cladding matrix and evidences no plastic deformation.

A number of local reactions at the fuel-cladding interface have been observed but the isolated nature of their occurrence indicates that the reactions are caused by extreme test conditions rather than system incompatibility in the range of normal operating conditions. Some of the more severe reactions observed are discussed in the following sections.

FIGURE 4-1. GRAIN BOUNDARY CARBIDE PRECIPITATION IN 347 STAINLESS STEEL CLADDING OF TEST PIN IX-1-P, IRRADIATED TO 47,000 MWD/Te IN GETR. CLADDING SURFACE TEMPERATURE: 1060°F. X250

a. 347 STAINLESS STEEL CLADDING FROM CAPSULE C3E, IRRADIATED TO A BURN-UP OF 63,000 MWD/Te.

b. 316 STAINLESS STEEL CLADDING FROM CAPSULE E2D, IRRADIATED TO A BURN-UP OF 110,000 MWD/Te.

FIGURE 4-2. EXAMPLES OF METALLIC LAYER FORMATION OBSERVED ALONG THE INNER SURFACE OF IRRADIATED STAINLESS STEEL CLADDING. (X250).

4.2 TEST CAPSULE B3B

One of the most striking examples of interaction at the fuel-cladding interface was observed in the failed fuel pin of Capsule B3B.⁽¹¹⁾ The Type 347 stainless steel-clad pin contained stoichiometric (U-25wt%Pu)O₂ fuel and was a "vented-to-plenum" design. It was contained in a convection-circulating capsule; the coolant was NaK*. The capsule was irradiated in GETR and was scheduled to accumulate a burnup of 100,000 MWd/Te. The test was terminated at 18,000 MWd/Te when a drop in fission gas pressure and a series of coolant temperature transients were recorded. Two thermocouples attached to the o.d. surface of the pin (180° apart) monitored the temperature of the hottest region of the cladding. The maximum temperature registered was 1315°F. This occurred within a period of 15 minutes shortly after the observed reduction in fission gas pressure. The average cladding temperature during three hours preceding this excursion was approximately 1170°F. Heat transfer calculations indicated that a 120-degree (F) temperature gradient existed across the cladding. This, coupled with an assumed 50-degree gradient between the radial sensing position of the thermocouple and the cladding o.d. surfaces, indicates that the i.d. surface of the cladding attained a maximum temperature of 1485°F.

Destructive examination revealed a series of longitudinal cracks on one side of the pin extending 8 inches along the fueled

* The utilization of NaK rather than sodium as either a thermal bond or local coolant should not be construed as representing the introduction of an additional significant variable. Previous work on fuel-coolant compatibility has shown no distinguishable difference between sodium and NaK with regard to their compatibility with mixed oxide fuel at elevated temperature.

region. Transverse cross sections in the failed region showed that the cladding ruptured intergranularly. Intergranular cracks were observed at various points along the i.d. surface of the cladding and appear to have emanated from local regions in which the cladding had been attacked. It was further noted that these regions are adjacent to radial cracks in the fuel which, in some instances, were filled with a metallic material that appears to have extruded from the cladding (Figure 4-3). The photomicrographs of Figure 4-4 show what may be considered various stages in the propagation of a cladding crack and eventual rupture. In all cases, the crack appears to have been preceded by a pitting attack on the cladding surface. The composition of the metallic deposit is not yet known. One might logically assume from its metallic luster and its location that the deposit is extruded cladding material. However, as the photomicrographs of Figure 3-10 show, the material is readily dissolved by an etching reagent commonly used to delineate grain boundaries in sensitized stainless steel.

4.3 TEST CAPSULE B8A

A reaction at the fuel-cladding interface, somewhat similar to that seen in B3B, was observed in the failed fuel pin of capsule B8A.⁽¹³⁾ An irradiation test run specifically to assess the long-term compatibility of sodium with mixed oxide fuel, capsule B8A contained two fuel pins: a sodium-bonded pin and a control gas-bonded pin of reference FCR design. Both pins contained stoichiometric (U-25wt%Pu)O₂ fuel; the cladding was Type 347 stainless steel. Although designed to accumulate a burnup of 100,000 MWd/Te, failure of the gas-bonded pin forced termination of the test at 14,400 MWd/Te.

Detailed metallographic survey of the failed pin revealed that the cladding experienced

FIGURE 4-3. AS-POLISHED, 100X.

FIGURE 4-3. OXALIC ACID ETCH, 100X.

FIGURE 4-3. FUEL-CLADDING INTERFACE IN THE FUEL PIN OF CAPSULE B3B. THE PIN WAS IRRADIATED IN GETR TO A BURNUP OF 18,000 MWD/Te. THE TEST WAS TERMINATED DUE TO GROSS CLAD FAILURE.

FIGURE 4-4. SUCCESSIVE STAGES IN THE PROPAGATION OF A CLADDING CRACK (PROPOSED). CAPSULE B3B, X250, ETCHED.

severe intergranular attack adjacent to the fuel body. Destruction of the cladding occurred to a depth of approximately 2 mils, with grain boundary attack extending to 5 mils (Figure 4-5). The as-fabricated cladding wall thickness was 15 mils. Thin stringers of metallic-appearing material were observed to have extended into the adjacent fuel and were not substantially attacked by an electrolytic oxalic acid etch. Cladding grain boundaries in the 5-mil zone along the i.d. surface contained a homogeneous gray deposit, the majority of which was removed by etching. The remainder of the cladding structure was lightly sensitized, as can be seen in Figure 4-6. Cladding attack was observed to diminish with distance from the failed region of the pin. No observable attack was noted at or adjacent to the fuel-insulator interface at the base of the pin. The temperature at the inner cladding surface has not been firmly established. The capsule was designed to attain a temperature of 1215°F in this region.

4.4 TEST CAPSULE C3B

The previous two examples of fuel-cladding interaction occurred in fuel pins which had experienced gross coolant ingress. In the following test, severe destruction of portions of the cladding wall occurred in regions containing no trace of coolant. Indeed, the metallographic examination of the fuel pin failed to disclose any gross cladding failure, although the pin had obviously failed. Capsule C3B was designed to study the effects of fuel densification and pre-irradiation central void on the transient performance of mixed oxide fuel.⁽¹⁴⁾ The capsule was pre-irradiated in GETR to a burnup of 7900 MWd/Te, after which the fuel pin was re-encapsulated and exposed to a single transient in TREAT. Post-irradiation gross examination revealed fission gases in the atmosphere external to the fuel pin, indicating cladding failure. Destructive examination of the pin itself, however, failed to pinpoint the failed region, although partial destruction of the cladding wall was acute

(Figure 4-7). Intergranular cracks were observed along the cladding i.d. and, in one particular region, an apparent reaction at the fuel-cladding interface was noted. This attack, shown in the transverse cross-section in Figure 4-8, occurred in a region of intimate fuel-cladding contact and, although the adjacent fuel does not appear to have reacted, the destruction of the cladding is obvious.

4.5 LOCAL GRAIN BOUNDARY PRECIPITATION

The precipitation of carbides along austenitic stainless steel grain boundaries adjacent to the fuel-cladding interface has been observed in the majority of fuel pins irradiated in GETR. Concern that this precipitation will endanger the long-term integrity of the cladding has prompted an analytical study directed toward the identification of the precipitating species. This effect has been observed in both failed and unfailed fuel pin claddings and shows no substantial change in magnitude with fuel burnup. The following discussion is based on the examination of cladding from the fuel pin irradiation tests: a high burnup test (E2B) which terminated in cladding failure and a low burnup test (B2A) in which total cladding integrity was maintained.

4.5.1 E2B Cladding Examination

Test capsule E2B contained (U-20wt%Pu)O₂ fuel jacketed with 0.250-inch diameter, 0.015-inch wall Type 347 stainless steel. The purpose of the test was to evaluate the in-pile swelling behavior of mixed oxide fuels under typical fast reactor operating conditions. The capsule was irradiated in GETR and accumulated a burnup of 70,000 MWd/Te before termination of the test due to a monitored overpower condition. A detailed discussion of this experiment, as pertains to fuel behavior, is contained in a previous report.⁽¹⁵⁾

Post-irradiation examination of the hyperstoichiometric (2.04 O/M) pin of E2B

FIGURE 4-5. FUEL-CLADDING INTERACTION IN THE FAILED PIN OF CAPSULE B8A. X100, AS-POLISHED.

FIGURE 4-6. GRAIN BOUNDARY ATTACK ALONG THE INNER SURFACE OF B8A CLADDING, IN THE REGION SHOWN IN FIGURE 11. X250, ETCHED.

FIGURE 4-7. DESTRUCTION OF CLADDING STRUCTURE IN THE C3B FUEL PIN. X100, ETCHED.

FIGURE 4-8. FUEL-CLADDING REACTION IN THE C3B FUEL PIN. X250, AS-POLISHED.

revealed a longitudinal clad rupture immediately adjacent to a spacing wire attached to the outer cladding surface. Failure was attributed to a reduction in clad yield strength due to local overheating in this region. Metallographic examination of the failed region revealed considerable necking at the o.d. surface (Figure 4-9) suggestive of ductile fracture. The remainder of the cladding failed intergranularly. Metallography of the i.d. surface of the cladding near the failure showed a region consisting of heavy grain boundary precipitation extending to a depth of approximately 3 mils. Although this surface is highly irregular due to the breakaway of precipitate-enveloped surface grains (Figure 4-10), no gross chemical attack was observed at any point along the fuel-clad interface. The o.d. surface of the cladding showed no abnormal exposure effects.

A full thickness section of cladding was removed from the E2B pin and prepared for electron microscopy and x-ray analysis. (Details of the specimen preparation technique are contained in the appendix.) Precipitates were extracted by replication from three regions along the clad cross-section: (1) the i.d. region of high density grain boundary precipitation, (2) the region adjacent to and including the o.d. surface, and (3) the central portion of the section. Electron microscopic examination of the extraction replicas showed that the o.d. surface and central region of the cladding contained a random distribution of massive globular precipitates characteristic of those found in a stabilized stainless steel. The i.d. surface, however, exhibited a continuous grain boundary array of thin angular precipitates, as well as the globular forms. Transmission electron micrographs of replicas from the three regions are shown in Figure 4-11.

Analysis of the bulk-extracted precipitates by x-ray diffraction (Debye-Scherrer) revealed only one discrete phase in both extractions: a face-centered cubic structure with a lattice parameter of $4.434 \pm 0.005 \text{ \AA}$.

This value agrees fairly well with NbC but suggests non-stoichiometry. Pearson⁽¹⁶⁾ reports that a lattice parameter of this value would match a composition of approximately $\text{NbC}_{0.72}$. The possibility exists, however, that the phase contains nitrogen in solution, corresponding to a composition $\text{Nb}(\text{C}, \text{N})$ which contains approximately 30 mole percent nitrogen. The fact that the primary constituent of the phase is niobium was substantiated by x-ray fluorescence analysis of the extracted precipitates, which identified niobium as the only major element present. A weak trace of iron was also detected (x-ray fluorescence does not detect carbon or nitrogen).

Since the x-ray diffraction of the bulk extraction failed to show the presence of a second precipitate, an electron diffraction analysis of the two precipitates observed in the carbon extraction replica from the cladding i.d. surface was performed. Although the large precipitates were too thick for electron transmission, the thin angular particles yielded good diffraction patterns, the spot-spacings of which correspond to the compound M_{23}C_6 . Since this compound could not be resolved by x-ray diffraction of the precipitates removed by bulk extraction, it is reasonable to assume that a much larger volume of niobium-base particles than M_{23}C_6 particles was present in the fuel cladding. A subsequent x-ray diffraction analysis of an extraction replica of the i.d. surface revealed both phases.

It was concluded, therefore, that the majority of the M_{23}C_6 precipitates occur in the narrow zone at the inside surface of the cladding and constitute the heavy grain boundary precipitate phase observed in optical metallography.

4.5.2 B2A Cladding Examination

An examination of grain boundary precipitation similar to that discussed in the previous section was performed on Type 347

FIGURE 4-9. CLADDING FAILURE IN E2B FUEL PIN.
X250, ETCHED.

FIGURE 4-10. TRANSVERSE CROSS-SECTION OF 317 STAIN-
LESS STEEL CLADDING FROM THE FUEL PIN
OF CAPSULE E2B. X250, ETCHED.

FIGURE 4-11. TRANSMISSION ELECTRON MICROGRAPHS SHOWING THE TYPE AND DISTRIBUTION OF PRECIPITATES IN 347 STAINLESS STEEL CLADDING, CAPSULE E2B.

stainless steel cladding from a very low burnup pin to assess the effect of radiation on the type and distribution of precipitate phases occurring in thin wall tubing. Capsule B2A was irradiated in GETR to a burnup of 52 MWd/Te. The i.d. surface of the cladding was in contact with (U-20wt%Pu)O₂ fuel and attained a maximum temperature of 1260°F. The o.d. surface was exposed to static sodium. The pin operated intact for the duration of the test. Optical metallography of a representative transverse cross-section of B2A, Figure 4-12, revealed a zone of heavy grain boundary precipitation along the i.d. surface of the cladding, similar in appearance to that seen in the high burnup pin previously discussed and typical of the many observed occurrences in irradiated fuel pin claddings. A somewhat narrower zone of grain boundary precipitation was also noted at the o.d. surface. Carbides were collected from three zones in the cladding—i.d. surface, center, and o.d. surface—by carbon extraction replication. The entire sample preparation procedure was identical to that used in the E2B examination.

The majority of the precipitates extracted from the three cladding zones were observed to have rounded shapes typical of the carbides of a stabilized stainless steel. Representative photomicrographs (transmission electron images) are shown in Figure 4-13. Arrows in the lower micrograph point to a few angular precipitates of the form generally associated with M₂₃C₆. Electron diffraction patterns of the three precipitate samples showed that both the i.d. and o.d. regions of the cladding contained M₂₃C₆ and NbC while the central region contained only NbC. The results are summarized in Table 4-1. The fact that excellent correlation of diffraction lines with the complex carbide was observed without a strong visual indication of typically-shaped M₂₃C₆ suggests that these carbides may have been modified by heating, subsequent to the irradiation anneal, from sharp angular to rounded globular shapes. There is, however, no evidence to support this assumption. Nevertheless, the diffraction data clearly show that,

although the stabilizing carbide exists throughout the structure, M₂₃C₆ is found only in the region of heavy grain boundary precipitation.

4.5.3 Chemical Analysis of Grain Boundary Precipitate

Electron microprobe analysis was performed on two specimens from the cladding of capsule E2B in an effort to further define the i.d. surface reaction discussed 4.5.1. In particular, the additional analytical work was intended to evaluate the distribution of primary alloying constituents in the region of heavy grain boundary precipitation and to determine the composition of the cation constituent of the complex carbide. The specimens included a full cladding cross-section (a 1/8-inch disc) and a carbon extraction replica of the i.d. surface of the cladding. Both were prepared in the manner previously described.

Microprobe analysis of the cladding cross-section in the region shown in Figure 4-4 showed no gradients in the compositions of chromium, nickel, or iron. The specimen current image of this region, Figure 4-14 shows a uniform distribution of bright spots which were identified by the microprobe to be rich in niobium. Since the specimen surface was coated with a carbon layer for the electrical conduction required in microprobe analysis, carbon in the specimen could not be measured. It was obvious, however, that the niobium-rich particles were the niobium carbides previously detected by electron microscopy and x-ray analysis. Although the scanned region represented the area of heavy grain boundary precipitation, no evidence of the carbide M₂₃C₆ could be detected. This was not expected, however, since the cation component is generally composed of primary elements of the matrix. X-rays emitted from the matrix would thus mask the contribution from these particles.

FIGURE 4-12. TRANSVERSE CROSS-SECTION OF 347 STAINLESS STEEL CLADDING FROM THE FUEL PIN OF CAPSULE B2A. X500, ETCHED.

FIGURE 4-13. TRANSMISSION ELECTRON MICROGRAPHS SHOWING THE TYPE AND DISTRIBUTION OF PRECIPITATES IN 347 STAINLESS STEEL CLADDING, CAPSULE B2A.

TABLE 4-1

d-SPACINGS OF EXTRACTED PRECIPITATES FROM B2A
MEASURED BY ELECTRON DIFFRACTION

<u>Inside</u>	<u>Outside</u>	<u>Center</u>	<u>M₂₃C₆</u>	<u>hkl</u>	<u>NbC</u>	<u>hkl</u>
			6.15	111		
	5.44		5.33	200		
3.76	3.78		3.77	220		
3.25	3.22		3.21	311		
3.088			3.07	222		
2.64	2.67		2.66	400		
2.58	2.57	2.58			2.58	111
	2.52*					
2.43	2.44		2.44	331		
	2.38		2.38	420		
2.28*						
2.24	2.20	2.24			2.23	200
2.19	2.18		2.17	422		
2.08	2.04		2.05	511, 333		
1.925*						
1.87	1.88		1.88	440		
	1.79		1.80	531		
(1.77	1.78		1.77	600, 442		
(1.76						
1.69	1.68		1.68	620		
			1.62	533		
	1.605		1.60	622		
1.59	1.58	1.57			1.580	220
	1.41		1.42	642		
	1.34	1.35)			1.348	311
		1.34)				
	1.27	1.29			1.290	222

*Unidentified spots.

FIGURE 4-14. DISTRIBUTION OF NIOBIUM CARBIDES IN 347 STAINLESS STEEL CLADDING, CAPSULE E2B. ELECTRON MICROPROBE SPECIMEN CURRENT IMAGE.

One way of circumventing this problem is to isolate the carbides, as was done in the earlier work, by extraction replication. Microprobe analysis of such a replica prepared from the i.d. surface of the cladding showed strong traces of iron and chromium in a particle (or group of particles) extracted from the specimen. Figure 4-15 shows the specimen current image and the corresponding CrK_α and FeK_α x-ray

images of such a particle. Trace amounts of nickel and manganese were detected in the particle. No indication of niobium was present. Clearly, the cation component of the M_{23}C_6 , observed as a heavy grain boundary precipitate along the i.d. of irradiated cladding, consists primarily of iron and chromium. A detailed discussion of the microprobe analyses is contained in an earlier report.⁽¹⁷⁾

SPECIMEN CURRENT IMAGE

FeK_α X-RAY IMAGE CrK_α X-RAY IMAGE

FIGURE 4-15. ELECTRON MICROPROBE SCANNING IMAGES OF PRECIPITATES EXTRACTED FROM IRRADIATED 347 STAINLESS STEEL CLADDING, CAPSULE E2B.

SECTION V

GENERAL DISCUSSION OF FUEL-CLADDING COMPATIBILITY

The isothermal out-of-pile compatibility tests have clearly shown that no metallurgical bonding occurs between mixed oxide fuel and the several austenitic stainless steels at temperatures considered to be near the extreme range of normal operating temperatures. Indeed, no evidence has yet been collected in this investigation that would suggest a mutual interaction or diffusion of primary components across the interface which would normally be accompanied by a transformation of the region in both fuel and cladding immediately adjacent to the interface. Electron microprobe analysis has shown that the cladding adjacent to the interface contains no uranium or plutonium, nor does the corresponding region in the fuel contain measurable quantities of iron, nickel, or chromium. Within the limits of the current series of tests, therefore, we can state with some degree of assurance that the several cladding alloys tested (Types 304, 316, 321, 347 stainless steel, and Incoloy 800) are fully compatible with stoichiometric and hypostoichiometric mixed oxide fuel in an isothermal system. The anomaly that was observed at the surfaces of these alloys annealed with hyperstoichiometric fuel is an oxidation reaction caused by the establishment of an oxygen-rich environment in the capsule. The source of oxygen in this system is the fuel.

The formation of an oxide scale on austenitic stainless steel is, of course, not unexpected and certainly not unique when such material is annealed in an oxygen-bearing environment. Moreover, the extent of layer growth in 1000 hours is minor when considering the long-term application of austenitic stainless steel as fuel cladding. What may prove to be a more important cladding effect, however, is that represented by the absence of precipitates in the cladding surface zones adjacent to the fuel. This is a substantially larger and more widespread effect than that of the scale. In Type 321 stainless steel material, for instance, the precipitate-free zone has an average width

of 38 microns. In terms of reference design FCR cladding, this represents 10 percent of the nominal wall thickness. Since this effect is also restricted to the cladding materials annealed in an environment of hyperstoichiometric fuel, it is apparent that it is associated with, or may be attributed to, the oxygen-rich atmosphere provided by the fuel.

One of the foremost objectives of the out-of-pile work was to isolate the effects of a purely thermal environment from the more complex irradiation environment. Except for the influence of fissioning species, however, the only major difference between the two, if maximum temperatures are similar, is the imposition of a thermal gradient in the irradiation test. The thermal diffusion work of Shewmon⁽¹⁸⁾ has indicated that, under the influence of a thermal gradient, carbon migrates toward the higher temperature zone in austenitic alloys. In the case of a fuel pin cladding, this corresponds to the inner surface of the tube. We propose, therefore, that the observed heavy precipitation of carbon (in the form of complex carbides) at or near this surface is influenced largely by the diffusion of carbon from the cooler to the warmer region of the cladding. The absence of any observable local carbide buildup in identical cladding materials annealed in isothermal out-of-pile fuel-cladding compatibility tests lends firm support to this theory.

In contrast to the migration direction of carbon in the cladding is the transport of volatile fission products in the fuel. Previous work at GE⁽¹⁹⁾ has shown, for example, that cesium concentrates at the periphery of urania-plutonia fuels under operating conditions. Such an enrichment of a chemically-reactive species adjacent to the cladding may affect surface reactions and have some influence on the long-term integrity of operating

fuel pins. The reactions observed in the B3B and B8A capsules may be associated in part with the deposition of fission products such as cesium and iodine at the fuel-cladding interface. Examinations at ANL⁽²⁰⁾ of similar appearing reaction zones (at the interface between Type 304 stainless steel and urania-plutonia fuel) also revealed the

presence of cesium at the fuel-cladding interface and along cladding grain boundaries as well. In previous studies⁽²¹⁾ on sodium penetration into grain boundaries, the occurrence of such penetration was shown to be associated with high carbon content in the stainless steel. This may explain the absence of such observations on B3B and B8A.

SECTION VI

ALLOY SELECTION

The results of the compatibility work herein discussed have revealed a number of structural transformations that can occur in cladding materials annealed in the presence of mixed oxide fuel at representative maximum operating temperatures. These interactions, listed in order of importance, include

1. Formation of precipitate-free regions
2. Reaction with the fuel

3. Reaction with fuel in the presence of sodium
4. Formation of the sigma phase
5. Sensitization

Although all would be considered objectionable in principle, the severity of a given reaction and its effect on long-term cladding integrity provides the only realistic basis for alloy selection. The susceptibility of each of the candidate cladding alloys to these transformations is indicated in Table 6-1.

TABLE 6-1

BEHAVIOR OF CLADDING ALLOYS IN OUT-OF-PILE TESTING: 1400°F FOR 1000 HOURS

<u>Material</u>	<u>Sensitization*</u>	<u>Sigma*</u>	<u>Precipitate Free Zones</u>	<u>Reaction with Fuel</u>	<u>Reaction with Sodium-Fuel**</u>
304	Moderate	None	30 microns (g. b.)	12 microns (max.)	10 microns (max.)
316	Light	Light	Not tested	Not tested	20 microns (max.)
321	None	Heavy	20 microns (matrix)	6 microns (max.)	12 microns (max.)
347	None	Heavy	30 microns (matrix)	6 microns (max.)	35 microns (max.)
I-800	Moderate	None	40 microns (g. b.)	Trace	15 microns (max.)

*Observed in thermal control (unfueled) specimens as well as in compatibility specimens containing fuel of all three stoichiometries. The remaining interactions were observed only in compatibility specimens containing hyperstoichiometric fuel. All cladding alloys, including Type 316 stainless steel, were shown to be fully compatible with the lower stoichiometry fuels.

**Hyperstoichiometric fuel (2.04 O/M).

Based on the criteria stated above, Type 304 stainless steel and Incoloy 800 show the most favorable overall properties with Type 316 stainless steel slightly inferior. Although hyperstoichiometric mixed oxide is not presently considered as a candidate fuel composition, the results of the out-of-pile compatibility work with hyperstoichiometric

fuel are believed to be relevant to the selection of a cladding for lower stoichiometry fuels. The testing of hyperstoichiometric fuel in an isothermal environment is analogous to the testing of a lower stoichiometry fuel in a thermal gradient, since both configurations would provide an oxygen-rich atmosphere at the fuel-cladding interface.

APPENDIX A

CHARACTERIZATION OF FCR (FAST CERAMIC REACTOR) CANDIDATE CLADDING ALLOYS

A.1 MICROSTRUCTURE OF CONTROL MATERIALS

Metallographic examination of the several austenitic stainless steel alloys used in the long-term compatibility tests revealed anomalous structural changes in some of the alloys tested. The most outstanding changes occurred in the stabilized Types 321 and 347 stainless steel, which showed a high density distribution of angular precipitates in addition to their stabilizing carbides, and Type 304 stainless steel which contained evidence of severe non-uniform grain growth. Neither Incoloy 800 nor Type 316 stainless steel showed any obvious structural change, except for a precipitate-free surface zone which was observed (primarily in the FC-2 test) in all grades tested.

To better characterize the changes occurring in the cladding and attempt to isolate conditions which might contribute to these alterations, a series of isothermal cladding control tests were run. Since all cladding material specimens used in the long-term tests were given a stress relief anneal prior to the compatibility anneal, a prime objective of the study was to assess the effect of this anneal on the cladding structure. The stress-relief anneal used in the current study—20 minutes at 1800°F—is a standard treatment to eliminate the effect of cold working in austenitic stainless steels. It was applied in the FC-2 compatibility test since all specimens were subjected to cold working during specimen preparation. To assess the effect of this anneal, four groups of specimens were prepared with the following treatments: (1) as-received (fully annealed), (2) stress-relief annealed after fabrication (20 minutes at 1800°F), (3) stress-relief annealed followed by the compatibility anneal (1000 hours at 1400°F), and (4) compatibility anneal without prior stress-relief anneal.

The results of each treatment are indicated in Figure A-1 and discussed below.

A.1.1 As-Received. All materials exhibited a twinned grain structure typical of a fully-annealed austenitic stainless steel. The approximate ASTM grain size of each material is as follows: Types 304 and 316 stainless steel: 7; Types 321 and 347 stainless steel: 9.5; Incoloy 800: 2.5. A uniform grain size was noted in each case.

A.1.2 Stress-Relief Annealed. The 20-minute 1800°F anneal re-established the as-received structure in all materials except Type 304 stainless steel, although twinning was not as pronounced. A severe non-uniform grain growth occurred in Type 304. No effects of surface cold working were evident in any of the materials tested.

A.1.3 Stress-Relief Annealed Followed by the Compatibility Anneal. Incoloy 800: The twinned grain structure was retained after the 1000-hour anneal at 1400°F. Grain boundaries and twin planes are decorated with carbide precipitates, typical of a lightly sensitized structure. There is no apparent alteration in grain size from that of the as-received material.

Types 321 and 347 stainless steel: The most prominent annealing effect noted in these materials is the formation of massive angular precipitates at grain boundary triple points, in addition to the stabilizing carbides. This second phase material is uniformly distributed throughout both materials and has subsequently been identified as the iron-chromium compound, sigma. There is no evidence of sensitization in either material.

Type 316 stainless steel: The material is heavily sensitized throughout. Only slight

FIGURE A-1. FCR CANDIDATE CLADDING ALLOYS-CONTROL MATERIAL. ALL PHOTOS x250.

evidence of a twinned grain structure remains. Long thin stringers of a second phase material have formed at random points, along grain boundaries. Like the second phase noted in the stabilized grades, this material is thought to be sigma. A dense distribution of intragranular dot carbides is evident throughout the structure. The density of both dot carbides and grain boundary carbides is greatly reduced in regions adjacent to individual sigma particles.

Type 304 stainless steel: The non-uniform grain size, first noted after the stress relief anneal, has been maintained and accentuated by sensitization. The material is peppered with an intragranular precipitation of dot carbides but contains no evidence of sigma phase.

A. 1. 4 Compatibility Anneal with No Prior Stress Relief Anneal

The appearance of Types 316, 321, and 347 stainless steel and Incoloy 800 is identical with the structure produced by the 1000-hour 1400°F anneal with prior stress relief anneal. The Type 304 stainless steel structure, on the other hand, is quite different. The material has a typically cold-worked structure throughout, as the numerous carbide-decorated slip lines give evidence. There is no indication that the sigma phase has formed. The grain structure is equiaxed and corresponds to an ASTM grain size number approximating that of the as-received material.

A. 2 TECHNIQUE FOR IDENTIFYING CLADDING PRECIPITATES

Positive identification of precipitates occurring in a thin cross-section of material, such as that observed in reference FCR cladding tubes, and determination of its distribution throughout the cross section, is best achieved by the controlled extraction of discrete particles

from various thicknesses of the cross-section and subsequent analysis. This is a particularly attractive method when dealing with radioactive materials, since one must endeavor to minimize the activity of the specimen to facilitate handling procedures and optimize analytical sensitivity. Gross separation and collection of precipitates such as carbides from matrix material requires nothing more than proper selection of chemical reagents that attack only the matrix. However, maintenance of proper orientation and distribution of precipitates requires replication, a commonly-used but somewhat more complex technique. Although both techniques were used in this examination, only the procedure involved in replication need be discussed.

The steps involved in preparing irradiated tubular cladding specimens for surface replication were:

- (a) Fuel removal from the pin section. This was achieved by a combined mechanical and chemical extraction, the latter utilizing hot nitric acid.
- (b) Slitting and flattening of the cladding tube.
- (c) Punching of 1/8-inch diameter discs (the size of the electron microscope specimen holder, into which the replica is inserted).
- (d) Final cleaning of the cladding (by nitric acid leaching and ultrasonic washing). An alpha count of 1500-2000 DPM was judged to be an acceptable level for out-of-cell handling.

The activity of an individual disc (approximately 22 mg) was 1000 mrad/h or 300 mR/h, at 2 inches. At the time of the activity survey, the specimen had accumulated a cooling time of nine months.

The disc surface to be examined was lightly etched with a 10 percent bromine alcohol solution, then covered with a thin film of carbon by vacuum evaporation. The disc was then immersed in the bromine-alcohol solution to dissolve the matrix metal under the carbon film. (The solution does not attack carbides or other non-metallic inclusions.) When matrix material along the carbon film is totally dissolved, the film floats free. Partially imbedded in the film are the non-metallic precipitates from the thickness of cladding material removed, arranged in roughly the same orientation as they existed in the as-irradiated specimen.

Analysis of particles in an extraction replica may be performed by a number of non-destructive methods. In the E2B-B2A examination, three discrete analytical techniques were applied to fully identify the complex iron-chromium carbide: electron metallography to establish precipitate morphology; electron diffraction to identify structure; and electron

microprobe x-ray analysis to determine elemental content. All three techniques utilized the extraction replica.

In the event that techniques of electron microscopy are incapable of analyzing precipitates, total extraction of precipitates can often be performed by analysis by x-ray diffraction and fluorescence techniques. In the examination discussed above, for example, the suspected stabilizing carbides were too massive to be effectively identified by electron diffraction. Therefore, to fully identify all precipitating species in the cladding, total matrix dissolution of a complete cross-section was performed. The recovered particles were then analyzed by x-ray techniques.

In summary, complete characterization of the precipitates occurring in the Type 347 stainless steel examined in this work required five discrete techniques. These are shown in Figure A-2.

FIGURE A-2. TECHNIQUES USED IN THE ANALYSIS OF CLAD PRECIPITATES

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