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INTRODUCTION

The character and extent of fuel-cladding chemical interaction (FCCI) was established for UO_2-25 wt% PuO_2 clad with 20% cold worked type 316 stainless steel irradiated at high cladding temperatures to peak burnups greater than 8 atom %. The data base consists of 153 data sets from fuel pins irradiated in EBR-II with peak burnups to 9.5 atom %, local cladding inner surface temperatures to 725°C, and exposure times to 415 equivalent full power days.[1-5] As-fabricated oxygen-to-metal ratios (O/M) ranged from 1.938 to 1.984 with the bulk of the data in the range 1.96 to 1.98. HEDL P-15 pins provided data at low heat rates, ∿200 W/cm, and P-23 series pins provided data at higher heat rates, ∿400 W/cm.

A design practice for breeder reactors is to consider an initial reduction of 50 microns in cladding thickness to compensate for possible FCCI.[1] This approach was considered to be a conservative approximation in the absence of a comprehensive design correlation for extent of interaction. This work provides to the designer a statistically based correlation for depth of FCCI which reflects the influences of the major fuel and operating parameters on FCCI.

CHARACTER OF THE INTERACTION

The nature of the FCCI was characterized through metallographic examinations of samples removed from irradiated fuel pins at numerous axial locations. The FCCI was classified[3] (Figure 1) as predominately matrix, evolved matrix, intergranular, or combined matrix and intergranular interaction. In matrix interaction, the attack is uniform with no strong preference for attack along the grain boundaries. The reaction product is a mixture of metallic and nonmetallic compounds in the fuel-cladding gap. In evolved matrix interaction there is a definite segregation of the cladding constituents in the reaction product layer.[2] For intergranular interaction, attack is predominantly along the grain boundaries with metallic and nonmetallic reaction products present in the fuel-cladding gap. Intergranular and matrix type interaction sometimes occur simultaneously with the intergranular attack preceeding the matrix interaction in the reaction zone. This form of interaction is designated as combined interaction. The data from the HEDL P-23 test series pins are summarized in Figure 2 according to initial fuel O/M and burnup.

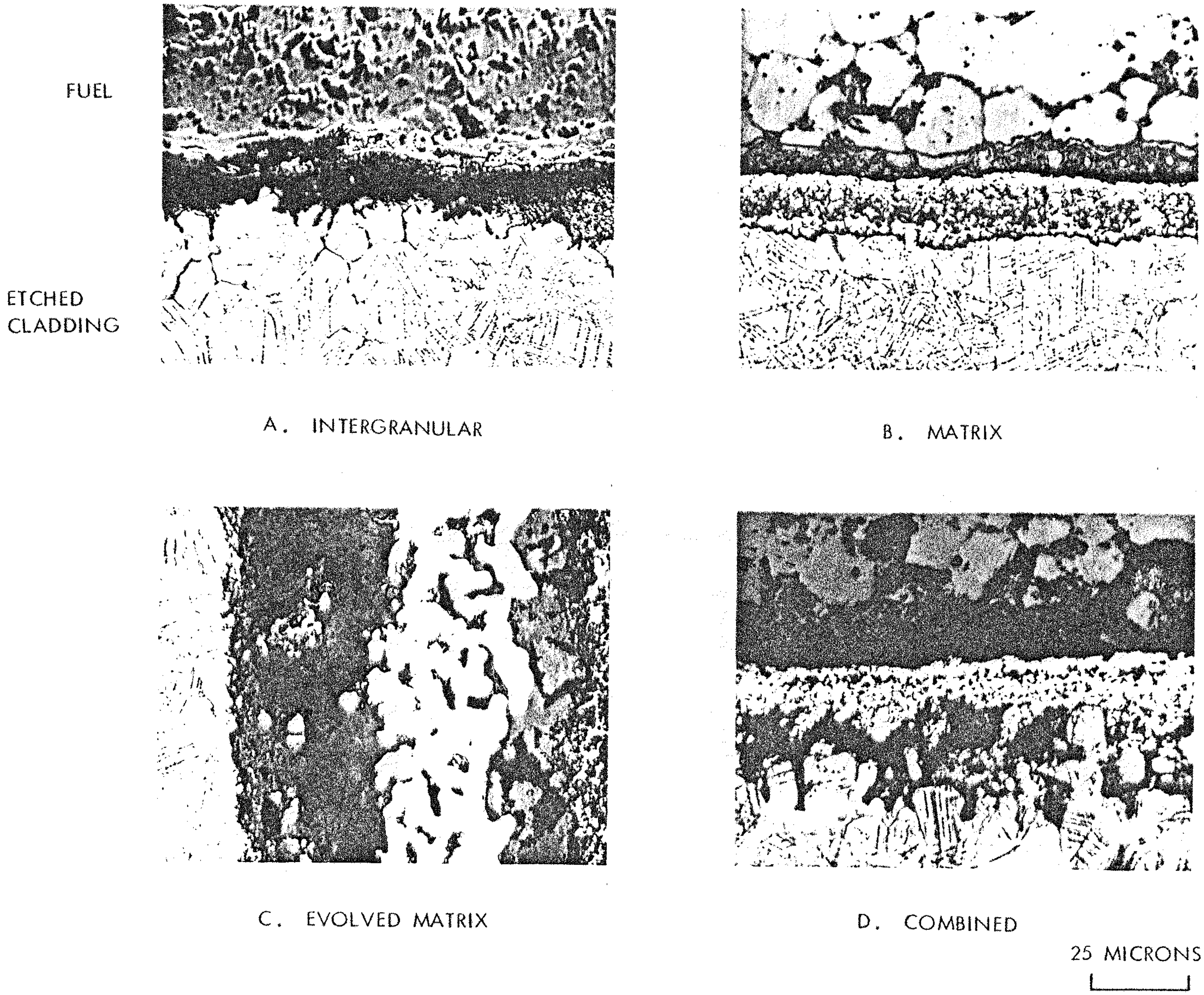

Figure 1. Examples of the Four Types of Fuel-Cladding Chemical Interaction Characterized for the Mixed-Oxide Fuel Pins with Type 316 Stainless Steel Cladding.

O/M	BURNUP		
	LOW (0-3 at.%)	MODERATE (3-6 at.%)	HIGH (6-10 at.%)
HIGH (1.98-1.99)	>675°C** INTERGRANULAR <675°C MATRIX <500°C NO FCCI 7 PINS *	>675°C EVOLVED MATRIX <675°C MATRIX <500°C NO FCCI 2 PINS	>500°C EVOLVED MATRIX <500°C NO FCCI 4 PINS
MODERATE (1.96-1.97)	> 550°C MATRIX < 550°C NO FCCI 10 PINS	> 550°C MATRIX < 550°C NO FCCI 3 PINS	> 650°C COMBINED > 525°C MATRIX < 525°C NO FCCI 4 PINS
LOW (1.94-1.95)	>700°C SHALLOW MATRIX <700°C NO FCCI 3 PINS	>625°C SHALLOW INTERGRANULAR < 625°C NO FCCI 4 PINS	>600°C SHALLOW INTERGRANULAR AND MATRIX < 600°C NO FCCI 4 PINS

* NUMBER OF FUEL PINS EXAMINED WITH INDICATED O/M's AND BURNUPS

** CLADDING INNER SURFACE TEMPERATURE

Figure 2. Characterization of Fuel-Cladding Chemical Interaction in 41 Fuel Pins from the HEDL P-23 Test Series

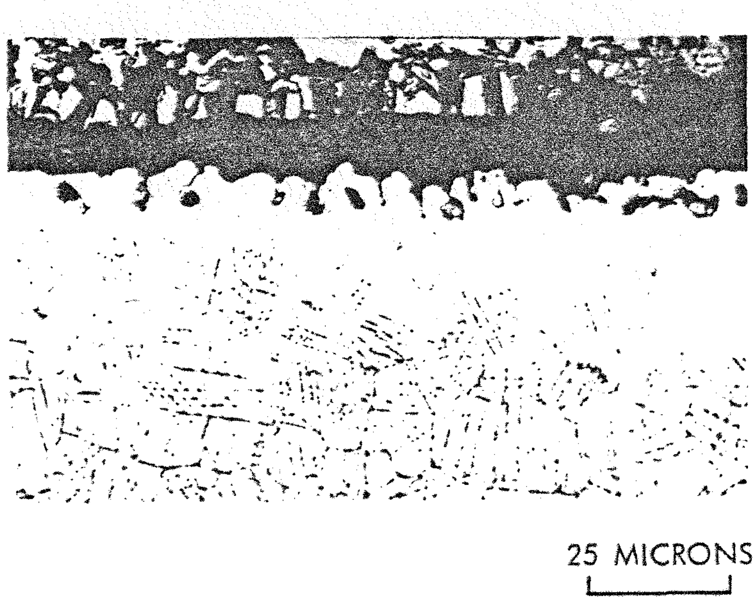

Figure 3. Shallow Intergranular Attack at 5.5 at.% Burnup and a Cladding Inner Surface Temperature of 645°C for an Initial O/M = 1.948

In the case of the high O/M fuel pins, i.e., 1.98 to 1.99, cladding interaction occurs above ∿500°C. For cladding temperatures greater than 675°C intergranular attack is predominant at the lower burnups (Figure 1A). Whole grains on the cladding edge are surrounded and the carbides begin to disappear from within grains as well as the grain boundaries. Electron microprobe examinations show the chromium to be depleted at the grain boundaries from which the carbides have disappeared. The interaction in the high O/M pins changed from intergranular to an evolved matrix interaction as burnup increased. Similarly, the matrix interaction observed at low and moderate burnups for temperatures less than 675°C changed to the evolved matrix interaction (Figure 1C). The metallic-appearing reaction product was found to be predominantly iron and nickel with the nonmetallic layer next to the unreacted cladding containing chromium and cesium most likely as an oxide compound. In some cases, several layers of cesium-chromium reaction products were found to be located between corresponding iron and nickel layers. Molybdenum and palladium, when found, were generally in a layer located on the surface of the unreacted cladding. Tellurium was associated with the cesium when found in detectable quantities.

For moderate O/M fuel pins, i.e., 1.96 to 1.97, the threshold temperature for the interaction was somewhat higher and the interaction was generally matrix (Figure 1B) except at higher burnup for the higher temperatures. The reaction product consisted of the cladding constituents with the chromium content approximately half that of the cladding. In some cases chromium enriched layers were observed on the apparently unreacted cladding coincident with depleted iron and nickel layers. Enriched manganese and molybdenum layers were seen with the depleted iron and nickel layers. Fission product cesium and tellurium were in the fuel-cladding gap and in the depleted iron, nickel layers. For the higher burnups, and cladding temperatures, i.e., >650°C, the attack was characterized as combined (Figure 1D). Chromium was depleted in the middle of the reaction product layer and enriched on both the outer surface of the reaction product layer and the inner surface of the cladding. Iron and nickel were found to be depleted on the cladding side of the reaction zone. For the moderate burnup range the number of samples examined at cladding temperatures ≥650°C were too limited to establish whether or not combined interaction was the dominant form of interaction in preference to matrix attack.

For the lowest O/M range, i.e., 1.94 to 1.95, no FCCI (>2 microns) was observed for cladding temperatures to ∿700°C for burnups to ∿3 atom %. For temperatures >700°C a shallow matrix type interaction was seen in the only two samples examined with these conditions. As burnup increased, a shallow intergranular form of interaction (Figure 3) was observed at lower cladding temperatures. The attack front proceeded along grain boundaries which intersected the cladding surface. The grain boundaries depleted in carbides were found to be enhanced in iron and nickel and depleted in chromium compared to the bulk cladding compositions. The attack changed from shallow intergranular to a shallow matrix attack at ∿8 atom % burnup.

DEPTH OF INTERACTION

Measurement of Depth of Interaction

A "nominal" depth of interaction was obtained by averaging the measurements of the minimum thickness on 225X photographs of the cladding at eight equally spaced locations on the circumference of each metallographically prepared sample and subtracting this value from a similarly established reference cladding thickness. The photographic coverage was on a regular grid for each sample. Each of the eight photographs covered $\sim$2% ($\sim$8°) of the cladding circumference; i.e., about 18% of the total circumference of each sample was examined in detail at 225X. In addition, if there were major variations within a given sample the photographic coverage was increased accordingly. Samples for determining the reference thickness were removed from each fuel pin at a location $\sim$25 cm above the top of the fuel column. Examinations of unirradiated cladding have shown significant variations (i.e., on the order of ±10-12 microns) in total cladding thickness[2] around the circumference of the samples due primarily to manufactured tubing eccentricity. The averaging technique used to define the depth of interaction tends to reduce the data scatter due to as-fabricated cladding thickness variations.

A maximum depth of interaction was also determined for each sample. In the cases of little cladding interaction the maximum depth of interaction was measured using previously developed techniques of extrapolation of the cladding inner surface.[3] For these measurements the uncertainties in total cladding thickness are eliminated, however some uncertainties are introduced in locating the original unreacted cladding interface. In general, this measurement technique introduces the least amount of error for an individual measurement for those cases where the interaction was slight. In the case of extensive cladding interaction, such as for high burnup and high initial fuel O/M's it was necessary to define the maximum depth of interaction as the thinnest location on the circumference of the sample. Therefore, these data are subject to the uncertainty of a typical 10 to 12 micron variation in as-fabricated tubing thickness in a given sample.

Selection of Operating Conditions

A local axial burnup was calculated for each fuel pin sample. Measured burnup values have been shown to agree within $\sim$±3% with values calculated from EBR-II fission rates, corrected by a 0.91 factor to normalize to the correct reactor power.[6] Irradiation temperatures at the fuel-cladding interface were calculated using the COBRA code for the temperature distributions within the 37 pin subassemblies and the SIEX[7] code for temperatures within the fuel pins. Irradiation conditions were calculated for each

EBR-II operating period for each fuel pin used in the data base. These detailed run-to-run histories for each fuel pin show small variations in both cladding temperature (±20°C) and linear heat rate (±25 W/cm) due to changes in the irradiation environment from cycle-to-cycle, alterations in the subassemblies due to scheduled interim examinations, and the depletion of fissile atoms with burnup. A time averaged cladding inner surface temperature, along with the calculated local fuel burnup, was selected to represent the operating conditions for the fuel samples for the data correlation.

Data Analysis

Linear modeling techniques were first used to establish the important parameters for the correlation of depth of interaction. Stepwise regression calculations for burnup, temperature, oxygen-to-metal ratio, and power including all cross product terms suggested the initial forms of the equation with non-linear regression techniques used to determine the final correlation.

The correlation was based on the nominal depth of FCCI. Upper confidence levels for the correlation were initially obtained for maximum depth of FCCI using standard techniques. However, a few instances of deep localized intergranular interaction at low burnups, i.e., <2.0-3.0 atom %, prevented establishing a single distribution function for both the maxiumum and the nominal values. The addition of a constant value to the burnup, i.e., B + K, was found to properly weight the early-in-life contributions of the deep localized interaction and allow a single expression to be developed.

The final equation which describes both the nominal and maximum depths of interaction is:

$$D = .4521\ (B + K)(O/M - 1.942)(T - 728) \quad \text{for } B > 0,\ O/M > 1.942,\ T > 728$$

(for conditions outside this range, D is zero)

where:

D = Depth of cladding interaction (microns)
B = Local fuel burnup (atom %)
K = Constant (A function of the confidence level for maximum depth of interaction)
O/M = Initial as-fabricated fuel oxygen-to-metal ratio
T = Local time averaged cladding inner surface temperature (°K)

In the case of K ≡0 the value predicted for D is the median value for the "nominal" depth of interaction. The maximum depth of interaction for the full 360° of the circumference of an axial section is less than or equal to the value predicted by the correlation, with the confidence level determined by the value of K.

K	Confidence Level
12.23	95%
9.45	90%
6.66	80%
5.04	70%
3.00	50%

A given value of K specifies the associated fraction of the population which has a maximum depth of interaction less than the prediction.

The predicted and measured maximum depths of interaction at a 95% confidence level (K = 12.23) shows (Figure 4) that the model adequately accounts for the deep localized interaction without being overly conservative.

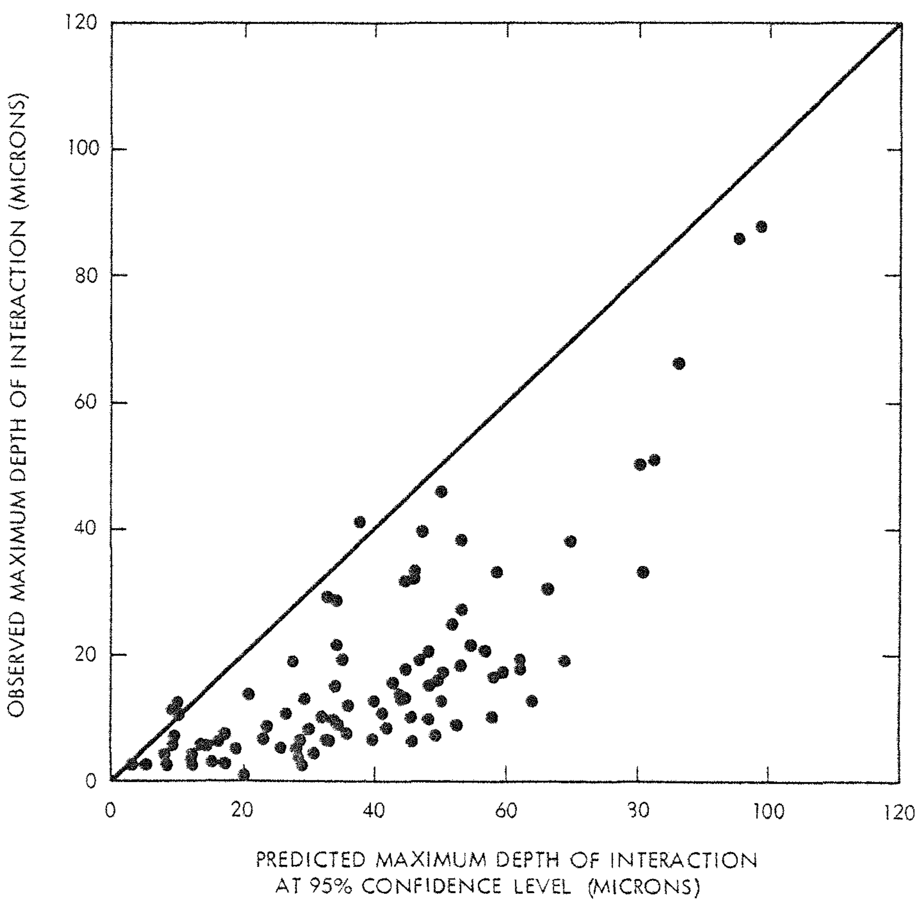

Figure 4. Comparison of Observed Maximum and Predicted Maximum Depth of Interaction for a 95% Confidence Level (K = 12.23)

DISCUSSION

Change in Character of Interaction

The change in character of the interaction (Figure 2) is consistent with oxidation of the cladding constituents.[3] Early in the irradiation (≤ 1 atom %) of hypostoichiometric fuels, the protective oxide film is disrupted by the chemical action of Cs and Te fission products. The exposed cladding grain boundaries are then attacked, exposing greater surfaces to the reactants. Eventually, whole grains become surrounded and removed from the cladding. Chromium is apparently preferentially oxidized in advance of the reaction zone.

The observations of little or no FCCI for the low O/M fuels at <3 atom % burnups are consistent with estimates of oxygen redistribution, and O/M increases with burnup. Evans[8] calculated (for a fuel pin under very similar conditions) that for O/M of 1.94 the O/M at the fuel surface would be 1.98 which is below the estimate of 1.998 necessary for oxidation of the chromium in the cladding. The increase in overall O/M with burnup has been estimated to be between 0.001 and 0.005 O/M units per atom % burnup,[9] with 0.003 O/M units/atom % burnup the recommended value. Thus an initial O/M of 1.94 would increase to approximately 1.95 after 3 atom % burnup. This corresponds to a fuel surface O/M $\simeq$ 1.990, still below the threshold for oxidation of the Cr in the cladding.[8] However, as burnup progresses beyond 3 atom % the bulk fuel O/M increases to $\sim$1.96 with a corresponding increase in the surface O/M to a value greater than that necessary to oxidize the chromium in the cladding. A consideration of only the initial fuel O/M and an increase of 0.003 O/M units/atom % burnup results in several inconsistencies when compared to the classification of interaction (Figure 2). For example, for the low O/M, high burnup case, the average O/M is calculated to be $\sim$1.975 which corresponds to the moderate O/M, low burnup category. The character of the FCCI and the threshold temperatures are different in these two categories. This illustrates that in addition to the initial O/M and the corresponding O/M increase with burnup the quantity of reactants is an equally important consideration.

Depth of Interaction

The extent of FCCI is controlled by the following three steps; supply rate - a generation and release of reactive fission products and oxygen, transport rate - transport of reactive fission products and oxygen to the cladding inner surface, and reaction rate - direct reaction between reactive fission products, oxygen, and the cladding. If the supply rate and transport of reactive fission products and oxygen is more rapid than their reaction with the cladding, the reaction rate is the controlling step. This is generally considered to be the case for low cladding temperatures, i.e., $\sim$600°C. However, increasing cladding inner surface temperatures result in increased reaction rates. A point is then reached at which the supply of reactive fission products and oxygen may become rate limiting.

The dependence of the depth of interaction on burnup (or reaction time) should provide information on the rate-controlling step in the process leading to FCCI. If the burnup, or time dependence, is parabolic, then the kinetics of the reaction are generally considered to be those of bulk diffusion of the reactants to the area of the fuel-cladding gap. Adamson has shown in out-of-reactor studies[10] that the kinetics of the reaction varied between parabolic and linear depending upon temperature and oxygen activity. High oxygen activities were found to favor parabolic behavior. If the FCCI process involved diffusion through a thickening layer, say an oxide, then parabolic behavior would be expected. Low oxygen activities would inhibit the formation of the barrier layer, thus allowing the reactants access to the cladding. Such a condition is expected to result in a linear depth of reaction with time.

When the broad range of burnups and initial fuel O/M's in the data base were considered, a linear dependence of burnup on depth of FCCI was established. This suggests that the reactants are in close contact with the cladding and that the reaction rate is most likely the rate controlling step.

Selection of Equation for Depth of Interaction

The following two correlations for depth of FCCI in terms of temperature, O/M, and burnup fit the data nearly as well as did the equation selected

$$D = 1.62 \times 10^{4} B\ (O/M - 1.948) e^{\frac{-13416}{RT}} \quad (R - 1.987\ \text{Cal/mole K})$$

$$D - 1.65 \times 10^{-3} B\ (O/M - 1.948)(T - 666)^{2}\ .$$

In each case a linear O/M and burnup dependence provided the best fit to the data. In the case of O/M, a linear dependence is also consistent with earlier P-23 data from a limited number of fuel pins[4,5] and preliminary FCCI data from the GA F-1 irradiation test series.[11] For burnup, both linear and square root dependences have been used in other FCCI correlations and either can be justified on mechanistic grounds. Local pin power was not included as a variable in the current analysis because of the lack of a clear understanding of the effects of pin power on FCCI as well as adequate data in which local pin power is not intimately related to local burnup. Because of the latter, local pin power was not determined to be a significant parameter in the data correlation.

Linear, quadratic, and exponential temperature dependences resulted in very similar statistical correlations of the data because the exponential and quadratic equations are reasonably well approximated by a linear function over the temperature range of the data base, i.e., 650 K to 1000 K. Previous FCCI correlations, both domestic and foreigh, have generally included an exponential (Arrhenius) temperature dependence in recognition of the fact that thermally activated processes such as corrosion usually obey an Arrhenius relationship. Laboratory studies have verified that under well characterized and controlled conditions cladding corrosion follows an Arrhenius type behavior.[10] However, in the fuel pin data base the temperature dependence of the corrosion process is less certain although there is still some reason to believe it would be of the Arrhenius type.

A linear temperature relationship was chosen for three reasons: 1) simplicity while providing a good statistical fit to the data, 2) ability to account for early-in-life intergranular corrosion through inclusion of a simple linear term (K) and, 3) ability to account, semiquantitatively, for the observed axial variation of FCCI in short (EBR-II) fuel pins and long (Phenix-French) fuel pins.[12]

Limitations of Data from EBR-II Irradiations

The P-23 series fuel by necessity contains enriched U in the $(U, Pu)O_2$ fuel, i.e., 65 wt% $^{235}U/U$, to produce heat rates in the range of 400 W/cm in EBR-II. Calculations predict a greater oxidizing potential for a fuel where the majority of the fissions occur in plutonium rather than from both uranium and plutonium as is the case in EBR-II. The reason for this is the greater yield of noble metal atoms for plutonium fissions compared to uranium. To date no irradiated fuel pin data exists to substantiate these predictions. The P-15 fuel pins contained fuel with normal uranium (0.71 wt% $^{235}U/U$). Examinations of pins irradiated to peak burnups of 1.8 at.% have not shown any FCCI at peak cladding temperatures of $\sim$700°C which is most likely a result of the low heat rates but suggests no major effects of all plutonium fissions on extent of FCCI.

Predictions of a Breeder Reactor Fuel Pin

The depth of interaction was calculated for a typical breeder reactor fuel pin operating at a peak cladding inner surface temperature of 700°C to a peak burnup of 8 atom % (Figure 5). Axial burnup and cladding temperature profiles are shown in the upper curves. For "nominal" depth of interaction (K = 0), the predictions for O/M's of 1.95 and 1.97 are less than 20 microns. The maximum depth of interaction is $\sim$50 microns at the 95% confidence level (K = 12.23) for an O/M = 1.97, considered to be the upper end of most fuel specifications and occurrs approximately 3/4 of the way up the fuel column where a combination of burnup (or heat rate) and cladding temperature produces the most severe conditions. Therefore, the correlation demonstrates that the design practice of an initial reduction of 50 microns in cladding thickness to compensate for possible FCCI is conservative since it corresponds to maximum depth of interaction at the 95% confidence level for an O/M at the upper end of the specification. Effects on creep properties are unknown however, burst rupture tests of irradiated cladding indicated no drastic reduction in strength for localized interaction through as much as 35% of the cladding thickness.[13]

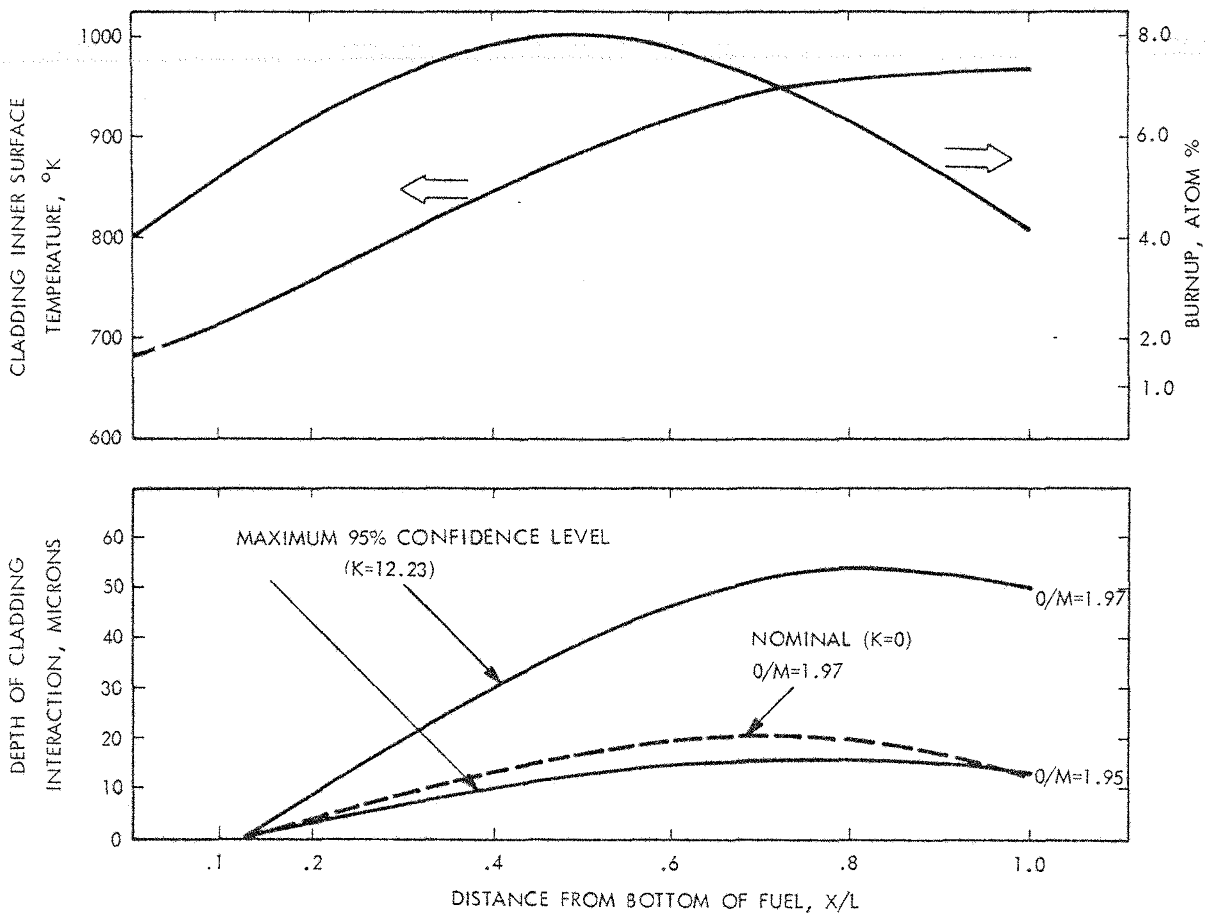

Figure 5. Predicted Nominal and Maximum Depth of Interaction for a Typical Large Breeder Reactor Fuel Pin

CONCLUSION

A statistically based correlation of depth of interaction has been established for mixed oxide fuels irradiated in EBR-II which reflects the influences of the major fabrication and irradiation parameters. The confidence intervals defined for the correlation of maximum depth of interaction do not overly weight the occurrences of a few instances of localized deep intergranular attack. The predominant form of interaction was matrix with intergranular attack occurring only for the highest O/M fuel pins (i.e., 1.98 - 1.99) early in life. The interaction was consistent with the mechanism of oxidation of the chromium in the cladding. The initiation of interaction in the low O/M fuel pins was in agreement with current estimates of oxygen redistribution and O/M increases with burnup.

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