Effects of Operational Parameters on Nodular Corrosion Characteristics

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Received January 17, 1989
Revised May 1, 1989

Zirconium oxide nodules formed on BWR fuel rods were characterized quantitatively and correlated statistically with the rod operational parameters. Cladding specimens were obtained from fuel rods irradiated in a commercial BWR. Their burnup and fast neutron fluence ranged 17~38 GWd/t and 4×10^{25}~8×10^{25} n/m^2, respectively. Characteristic variables of the nodules such as maximum thickness $T_{\text{max}}$ (μm) were measured on metallographs of the cladding cross sections. These variables were correlated by multiple regression analyses with the operational parameters, such as irradiation time $t$ (d), linear heat rate $p$ (kW/m) and fast neutron flux $\phi$ (n/m^2-s). For example, the maximum thickness depended on linear heat rate and showed a saturating tendency with burnup $B$ (GWd/t) ($T_{\text{max}} \propto t^{0.8\pm0.05} p^{2.3\pm0.9}$ or $T_{\text{max}} \propto B^{0.8\pm0.4} p^{1.5\pm0.5}$). This decrease of growth rate with irradiation time was interpreted in terms of a microstructure change of Zircaloy-2 during neutron irradiation. Results of transmission microscopy and energy dispersive X-ray spectroscopy indicated that the alloying elements such as Fe, Cr and Ni dissolved from intermetallic precipitates into the base metal during neutron irradiation. Dissolution of the alloying elements might be effective in decreasing the growth rate of nodules.

KEYWORDS: nodular corrosion, multiple regression analysis, fast neutron flux, linear heat rate, neutron beams, irradiation time, Zircaloy-2, fuel rods, BWR type reactors, TEM, EDX

I. INTRODUCTION

Waterside surfaces of Zircaloy fuel claddings are oxidized during irradiation in LWR owing to exposure to high-temperature and high-pressure water. Moreover, the in-pile oxidation is accelerated in comparison with the out-pile one\(^{(1)-(3)}\). Especially in BWR, local oxidation progresses and produces ellipsoidal or spherical zirconium oxide known as nodular corrosion. Although the influence of material factors on the nucleation and growth of these nodules has been widely examined, few data on the effects of in-pile irradiation conditions are available.

This paper characterizes the nodular corrosion generated in a commercial BWR and gives statistical evaluations of the effects of irradiation conditions upon its nucleation and growth. Metallographs obtained from fuel cladding outer surfaces were used to characterize the nodules quantitatively and then correlations with operational parameters were investigated.

II. PROCEDURES

Metallographic observations were made for characterization of the oxide nodule. Samples were taken from fuel rods irradiated for 2 and 4 cycles in a commercial BWR. Cladding tubes were Zircaloy-2 of three different manufacturing lots. They were finally annealed at 577°C for 2.5 h. The chemical compositions of lots A and C are given in Table I. Their burnup and fast neutron fluence ranged 17~38 GWd/t and 4×10^{25}~8×10^{25} n/m^2, respectively. These samples were taken from outer fuel rods in a fuel assembly and different axial positions of fuel rods.
Table 1 Chemical compositions of fuel claddings

<table>
<thead>
<tr>
<th>Lot</th>
<th>Chemical composition (%)</th>
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<tbody>
<tr>
<td></td>
<td>Zr</td>
</tr>
<tr>
<td>A</td>
<td>bal.</td>
</tr>
<tr>
<td>C</td>
<td>bal.</td>
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These samples were observed using metallographs, magnified 125 times, along the outer surface of the fuel claddings. Photograph 1 (a) and (b) show examples of the metallographs of nodular corrosion. From these photos, thickness $T_i$ (μm) and circumferential length $L_i$ (μm) were measured as shown in Fig. 1.

Using these values, characteristic parameters were defined as follows. Almost all of the distribution profiles of thickness and circumferential length of nodules in one radial cross section of fuel cladding conformed very well to a log-normal distribution. Figure 2(a) and (b) show examples of their distributions on log-normal probability papers. In these figures, data obtained from 2 and 4 cycle irradiated claddings are compared. Two cycle data of both thickness and circumferential length conformed very well to the log-normal distribution, however their 4 cycle data deviated from the log-normal distribution at less than 10 μm and more than 100 μm, respectively. It was considered that these deviations were due to coalescence of nodules and the nucleation of new, small nodules. When nodules coalesced, apparent circumferential length of nodules increased and the number of nodules which had a long circumferential length increased. New, small nodules had a flattened shape and the number of thin nodules increased, although the number of nodules which had a small circumferential length did not increase.
From this result, medians of thickness and circumferential length $T_{\text{med}}$ ($\mu$m) and $L_{\text{med}}$ ($\mu$m) were selected as characteristic parameters, because a median is a distribution parameter of a log-normal distribution. Maximum thickness $T_{\text{max}}$ ($\mu$m) was defined as maximum value of thickness in one cross section. Linear coverage $C$ (%) was defined as

$$C = \frac{\sum_{i=1}^{N} L_i}{2\pi r},$$  \hspace{1cm} (1)$$

where $2r$ is the outer diameter of the fuel cladding. Linear number density of nodules per cross section $N$ (number/cross section) were also obtained from metallographs. Cross-sectional area $S_i$ of a nodule $i$ was calculated on the assumption that the cross-sectional shape of a nodule is an ellipse, so

$$S_i = \frac{\pi T_i L_i}{4}. \hspace{1cm} (2)$$

Cross-sectional shape factor $R_i$ of the nodule $i$ was defined as the ratio of thickness to circumferential length, namely

$$R_i = \frac{T_i}{L_i}. \hspace{1cm} (3)$$

These two values were also log-normally distributed. Therefore, medians of cross-sectional area and shape factor $S_{\text{med}}$ ($\mu$m$^2$) and $R_{\text{med}}(T_i/L_i)$ were defined as characteristic parameters as well as total cross-sectional area $S_{\text{tot}}$ (mm$^2$). Total cross-sectional area was defined as

$$S_{\text{tot}} = \sum_{i=1}^{N} \frac{\pi}{4} T_i L_i. \hspace{1cm} (4)$$

The above 8 characteristic parameters were quantitatively examined in correlation with operational parameters, such as irradiation time $t$ (d), linear heat rate $p$ (kW/m), and fast neutron flux $\phi$ (n/m$^2\cdot$s) using multiple regression analyses. Linear heat rate and fast neutron flux were average values during irradiation calculated from burnup $B$ (GWd/t) and fast neutron fluence $F$ (n/m$^2$), respectively. The axial position of fuel rods were also considered as an operational parameter be-

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**Fig. 2(a), (b) Distributions of nodule thickness and nodule circumferential length on log-normal probability paper**
cause it represent the void effect. But it did not show any correlations with characteristic parameters. Therefore, its effect was not described in this paper.

III. RESULTS

1. Burnup Dependence of Characteristic Parameters

Correlations of each characteristic parameter with burnup were investigated first. Maximum thickness, linear coverage, total cross-sectional area, and linear number density had weak correlations with burnup, but medians of thickness, circumferential length, cross-sectional area, and cross-sectional shape factor showed none. Figure 3(a), (b) shows burnup dependence of median of thickness and maximum thickness.

![Graph of burnup dependence of characteristic parameters.](image)

Chain lines represent fitting curves calculated using linear regression analyses and solid lines show the range of $2\sigma$ ($\sigma$ is a standard deviation). The symbol "a" shows the data obtained from spacer contact position.

Fig. 3(a), (b) Burnup dependence of characteristic parameters of nodular corrosion formed on Zircaloy-2 claddings irradiated in BWR.
Distribution parameters of medians of the above 4 characteristic parameters obtained from samples irradiated for 2 cycles were compared with those for 4 cycles. The results showed that there were no significant differences, within the 5 percentile significance level, between these distribution parameters for the 2 and 4 cycle irradiated samples. This result meant that medians of the above 4 characteristic parameters were unchanged during the latter half of the irradiation period.

The other 4 characteristic parameters increased slightly during the latter half. The increasing rate of these characteristic parameters during the first half and the latter half of the irradiation were calculated using linear regression analyses. These results are summarized in Table 2. For example, increasing rate of total cross-sectional area per irradiation time was about 0.2 mm²/yr in the first half and 0.03 mm²/yr in the latter half.

Table 2 Increasing rates of characteristic parameters

<table>
<thead>
<tr>
<th>Characteristic parameters</th>
<th>Increasing rate (yr)</th>
<th>First half</th>
<th>Latter half</th>
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<tbody>
<tr>
<td>Maximum thickness (µm)</td>
<td>26</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Linear coverage (%)</td>
<td>31</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Linear number density (number/cross section)</td>
<td>150</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Total cross-sectional area (mm²)</td>
<td>0.2</td>
<td>0.03</td>
<td></td>
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</table>

2. Multiple Regression Analyses

Multiple regression analyses led to establishment of the following relationships between characteristic parameters and operational parameters. To investigate the contribution of the individual operational parameters, each one was normalized by the other correlating operational parameters. For example, to analyze the correlation between maximum thickness and linear heat rate, maximum thickness was normalized by irradiation time. Values used for normalizing were 1,193 days for irradiation time, 30 kW/m for linear heat rate, and $7 \times 10^{17}$ n/m²-s for fast neutron flux.

Linear heat rate affected maximum thickness, total cross-sectional area, and the median of cross-sectional shape factor. Fast neutron flux affected linear coverage, total cross-sectional area, linear number density and the median of cross-sectional shape factor. These characteristic parameters, except for the median of cross-sectional shape factor, also had correlations with irradiation time, but the rest of the characteristic parameters had no correlations with 3 operational parameters.

Maximum thickness depended on linear heat rate and showed a saturating tendency with burnup, namely

$$T_{max} \propto B^{0.7} \exp^{1.2 \times 10^4 t}, \quad (5)$$

or

$$T_{max} \propto e^{0.2 \times 10^4 t^{0.2}} \beta^{2 \times 10^4 t}. \quad (6)$$

Holzer & Stehle(4) have reported that maximum thickness was proportional to $B^{0.7}$ and showed a saturating tendency with burnup. Normalized data of the maximum thickness are plotted as a function of burnup in Fig. 4.

Maximum thickness was normalized by linear heat rate. The chain line represents the fitting curve with an exponential equation and solid lines show the upper and lower limits of 95 percentile probability and 95 percentile confidence interval.

Fig. 4 Maximum thickness as a function of burnup

There seemed to be a difference in thickness among the 3 lots, but their dependences on burnup had a similar tendency. Linear coverage of nodular corrosion showed increasing trends with fast neutron flux and irradiation time and no difference between lots was clear as shown in Fig. 5.
Linear coverage was normalized by fast neutron flux. The chain line represents the fitting curve with an exponential equation and solid lines show the upper and lower limits of 95 percentile probability and 95 percentile confidence interval.

**Fig. 5** Linear coverage as a function of fast neutron fluence

Regression equations were

\[ C \propto F^{0.523 \pm 0.05 \times 0.1} \phi^{-0.55 \pm 0.1}, \]  
\[ C \propto \phi^{0.523 \pm 0.2 \times 0.3}. \]

Linear number density increased, but had a saturation tendency with irradiation time or fast neutron fluence

\[ N \propto F^{0.52 \pm 0.3 \times 0.1}, \]  
\[ N \propto \phi^{0.52 \pm 0.4 \times 0.4}. \]

No apparent differences were also observed in linear number density among the 3 lots. Cross-sectional shape varied, depending on linear heat rate and fast neutron flux.

\[ R_{\text{med}} \propto \rho^{0.5 \pm 0.2 \times 0.5} \phi^{-0.5 \times 0.5}. \]

Furthermore, differences between lots were relatively clear. Total cross-sectional area depended on 3 operational parameters and had a saturation tendency with irradiation time.

\[ S_{\text{tot}} \propto t^{0.7 \pm 0.2} \rho^{0.1 \pm 0.2} \phi^{0.5 \pm 0.2}. \]

**IV. DISCUSSION**

These results may have included large uncertainties caused by large data scattering and by simplification of the operational parameters. Nevertheless, it was thought that they indicated the in-pile nodular corrosion behavior trends accurately.

The growth rate of nodular corrosion decreased during irradiation. The large decrease of increasing rate of total cross-sectional area implied a saturating tendency for cladding oxidation. The increasing rate value of 0.03 mm²/yr in the latter half meant that 0.06% of the cladding was oxidized per year and that, if total cross-sectional area was calculated in terms of average thickness, to assume a uniform thickness oxide, the growth rate of oxide was about 2.5 μm/yr. This result did not agree with the result from the out-pile corrosion test\(^4\), which showed that oxidation rate was proportional to time in a post-transition regime. This effect seemed to be related to microstructural change of Zircaloy-2 during neutron irradiation.

The microstructure of irradiated Zircaloy-2 was investigated using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). Samples for TEM observation were cut from neutron irradiated Zircaloy-2 cladding. Its fast neutron fluence was about \(7 \times 10^{25} \text{n/m}^2\) and burnup was about 35 GWd/t. Details of the preparation of TEM specimens will be reported elsewhere. From the above investigation, it was found that dissolution of alloying elements, such as Fe, Cr and Ni, occurred from intermetallic precipitates to Zircaloy-2 matrix, as shown in **Fig. 6**. Figure 6 shows a TEM image of irradiated Zircaloy-2 including two types of intermetallic precipitates, such as \(\text{Zr(Cr, Fe)}_2\) and \(\text{Zr}_4(\text{Ni, Fe})\). Arrows indicate the analyzed points using EDX and their results are also shown in Fig. 6. Alloying elements were detected in an irradiated Zircaloy-2 matrix, while they were not in an unirradiated one.

The distribution of Fe was nearly homogeneous between two precipitates, but Cr and Ni concentrations decreased with increasing distance from precipitates. In particular, the dispersion distance of Cr was small. Yang *et al.*\(^5\) and Griffiths *et al.*\(^7\) also observed this dissolution of alloying elements after fast neutron irradiation. This distribution change of alloying elements might affect the growth rate of nodular corrosion.
The relationship of linear number density with irradiation time and fast neutron flux suggested that its nucleation could be slightly influenced by fast neutron flux. Fast neutron irradiation causes the above-mentioned dissolution of alloying elements, which would have a potential influence on the nucleation of nodular corrosion, too. Cheng & Adamson reported that all nodular corrosion was nucleated at approximately the same time and the solute elements depletion area was the nucleation site of nodules. It was found that medians of thickness, circumferential length, and cross-sectional area did not depend on burnup or irradiation time. This implied that new small nodules appeared during neutron irradiation.

Cheng & Adamson proposed a model for nodular corrosion nucleation and growth. Their model was based on the different protective properties for a corrosive environment between the near-stoichiometric ZrO$_2$ and the substoichiometric ZrO$_{2-x}$. If alloying elements were incorporated into zirconium oxide, ZrO$_{2-x}$ would be produced which would maintain stability in a corrosive environment, but if oxide grew on localized areas where depletion of solute elements existed, ZrO$_2$ would be produced which would not be protective. This non-protective oxide became granular oxide and then, nodular corrosion.

Their model did not mention the decrease of growth rate of nodules and the nucleation of new small nodules during irradiation. Figure 7 shows a schematic diagram of a proposed nucleation and growth model of nodules. This model was based on Cheng & Adamson's model. A depletion zone of alloying elements was assumed to be a nucleation site of the non-protective oxide and nodule. Because of the dissolution of the alloying elements from precipitates into the matrix during neutron irradiation, homogenization of the alloying elements distribution occurred and the depletion zone of alloying elements disappeared. Then, protective ZrO$_{2-x}$ would be produced and the growth rate of nodular corrosion would decrease. The net effect of neutron irradiation on the microstructure of Zircaloy was to homogenize the distribution of alloying elements, but locally it could be considered that a new, small depletion zone of solute

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**Fig. 6** Concentration distributions of alloying elements near two types of precipitates in neutron irradiated Zircaloy-2

*Fast neutron fluence was $7 \times 10^{20}$ n/m$^2$.*

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**Fig. 7** Schematic diagram of nucleation and growth model of nodular corrosion
elements was produced because of precipitation of solute elements, and then new, small nodules appeared.

Linear heat rate correlated with maximum thickness, total cross-sectional area, and median of cross-sectional shape factor. These results showed that linear heat rate accelerated the growth of nodules toward the thickness direction. The dependence of the nodule thickness on linear heat rate implied that the cladding temperature increase and the temperature gradient in the cladding by heat flux could be factors affecting the thickness. It could be considered that high cladding temperature enhanced the reaction rate of zirconium oxidation and precipitation of dissolved alloying elements. The latter effect would mean that the neutron irradiation effect on alloying elements distribution was small at high temperature.

Relatively distinct differences between lots were observed for cross-sectional shape of nodules. Cross-sectional shape of nodules in lot A was nearly circular, but in lot C it was more flattened, as shown in Fig. 1. This result suggested that the shape of nodules could be affected by a material factor. This material factor was unclear, but distribution and size of intermetallic precipitates would appear as most likely to affect the nodule shape. The oxides at the spacer contact position had a longer circumferential length and larger cross-sectional area than the others, so that their cross-sectional shape looked like the uniform oxide. It could be considered that galvanic corrosion reaction occurred due to the contact of two different metals, namely Zircaloy and Inconel, and a nearly uniform oxide was produced.

V. CONCLUSION

Nodular corrosion was characterized in terms of the morphology and distribution of nodules. The effects of irradiation time, linear heat rate, and fast neutron flux upon initiation and growth of nodular corrosion were investigated using metallography of fuel claddings irradiated in a commercial BWR for 2 and 4 cycles, and the following results were obtained:

1. The growth rate of nodules decreased with irradiation time.
3. New small nodules nucleated during neutron irradiation and the increasing rate of the number of nodules was decreased.
4. Linear heat rate encouraged the growth of nodules toward the thickness direction.
5. The cross-sectional shape of nodules depended on a material factor.
6. Relatively uniform oxide was produced at the spacer contact position.

ACKNOWLEDGMENT

The author would like to thank Mr. S. Koizumi of Toshiba and Mr. K. Ogata of NFD for useful advice and discussions.

REFERENCES