Development of the Ultra-microhardness Technique for Post Irradiation Examination of Fuel Cladding Tubes

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Hardness measurements are potentially valuable for a quantitative discussion of embrittlement in the inner portions of fuel cladding tubes. The size of the indentation, however, is not negligible compared to the measuring region, even when a micro Vickers hardness tester is employed. This limits the measuring technique, and very little has been studied about degradation phenomena in the inner portion of the tubes.

A hardness measurement system, equipped with a depth-sensing indentation instrument, and the necessary post irradiation examination technique for specimens with high radioactivity were successfully developed and the following observations were obtained from the system's application example. The diffusion coefficient of oxygen obtained from the hardness of an unirradiated zirconium lined cladding with simulated oxidation in the fuel rod showed good agreement with literature data. The calculated diffusion coefficient from hardness in the inner portion of irradiated Zircaloy-2 fuel rods was almost the same value as that of unirradiated zirconium, which implied that neither neutron irradiation nor fission fragment bombardment enhanced the oxygen diffusion in the inner portion of cladding tube.

KEYWORDS: fuel cladding tube, mechanical properties, fuel rods, ultra-microhardness, hardness, hardening, inner surface, fission fragments, oxidation, diffusion, Zircaloy-2, neutron beams, irradiation, radiation effects

I. Introduction

The inner surfaces of fuel cladding tubes are exposed to high energy particles like fast neutron and fission fragments or to excessive amount of oxygen which are induced by the fission of UO₂ fuel pellets. These conditions may cause irradiation damage and/or irradiation-enhanced diffusion(1)-(3) in fuel cladding tubes, and will deteriorate the ductility of the inner portion of the cladding tubes. The embrittled surfaces are susceptible to micro cracks, which are enhanced by aggressive fission products like iodine or cadmium(4). This is one possible mechanism for cladding failure due to pellet cladding interaction under severe power ramp conditions(5). With an increase of fuel burnup, the amount of aggressive fission products and the bombardment of high energy particles on the inner surface of the tube increase. Then, to make high burnup fuel rods more reliable, it is necessary to clarify the mechanism and to quantify the degradation in the inner surface of fuel cladding tubes.

The oxygen distribution in the inner portion of fuel cladding tubes has been reported by Kleykamp(6). He found that oxygen diffused over about a 20μm depth based on analysis of PWR fuel cladding tubes irradiated at the burnup of 4.3%. The possibility has been reported that oxidation of the cladding inner portion would be accelerated by the effect of irradiation(7), however difficulties of a quantitative discussion for the mechanism have also been reported(8). Damage induced by recoil fission fragments implanted to the inner surface of the cladding has been simulated using high-energy ions bombardment and reported only changes of surface morphology by SEM, however, no information on the mechanical properties has not been reported(9).

Hardness measurements in the wall thickness direction are a promising approach to allow quantitative discussion. Even when a micro Vickers hardness tester is employed, the size of the indentation, however, is not negligibly small compared to the region of interest. This limits the measuring technique, so that degradation phenomena at the inner surface of irradiated cladding tube have not been studied very much.

The aims of the present study were to develop a hardness measurement system for small specimens with high radioactivity such as spent fuel cladding tubes, and to obtain a technique of post irradiation examination for the specimens.

II. Experiments

1. Materials

(1) Zirconium with Various Oxygen Concentrations

Different amounts of high purity zirconium dioxide

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were blended with high purity zirconium containing about 100 wt.ppm oxygen and the mixtures were melted in a high vacuum plasma furnace. After annealing at 1,023 K for 3 h, each ingot was machined into small pieces for hardness measurements, oxygen analysis by the inert gas fusion technique (LECO), and X-ray diffraction (XRD). The oxygen concentrations for each ingot were 0.12, 0.27, 0.58, 3.0, and 26 wt% with an error of 10% for each value. No peak of zirconium dioxide was detected in XRD analysis of each ingot after melting except one with 26 wt%.

(2) Unirradiated Fuel Cladding Tubes

In order to simulate the inner surface condition of actual fuel rods with zirconium liner, oxidation at low partial pressure of oxygen is necessary since zirconium is easily over-oxidized by the oxygen in the atmosphere. Then the unirradiated fuel cladding tube with zirconium liner (liner thickness of 80 μm and an initial amount of oxygen of 580 wt.ppm) were sealed together with a mixture of copper and cuprous oxide in a quartz capsule, and heated at 723 K for 2,000 h. The chemical compositions for both oxygen-added zirconium and oxidized fuel cladding tubes are listed in Table 1.

(3) Irradiated Fuel Cladding Tubes

The inner surfaces of fuel cladding tubes will be different in hardness with axial positions of a rod, due to such neighboring effects as heat flux or fission fragment bombardment from fuel pellets. Specimens for hardness measurements were cut from three longitudinal positions (the bottom of the gas plenum region, and the top and mid pellet stack regions) of the Zircaloy-2 fuel rods irradiated up to five cycles in a commercial BWR.

The specimens positions of the gas plenum and the top pellet regions were very close; being separated by only 25 mm, but no fission fragments reached the gas plenum region because there are no fuel pellets in there. Fabrication and irradiation data of the rod used for the measurements are given in Table 2, and burn-ups and neutron fluences for each hardness specimen are summarized in Table 3.

2. Hardness Measurement Method

Although a depth-sensing hardness tester has been successfully applied to study mechanical properties of small unirradiated specimens or ion irradiated metal specimens(10)(11), no hardness measuring system has been reported so far which is specially designed for measurements in the inner portion of irradiated fuel cladding tubes with a high radioactivity. Such a system and its experimental technique would have to satisfy the following requirements; (1) loads, consequently the size of the indentation, have to be small enough to obtain a hardness distribution in a width as narrow as several tens of microns along the fuel cladding tube cross section, (2) remote and automatic operations in a γ-ray shielded glove box with negative pressure and with unavoidable faint vibration of air have to be possible.

We combined an ultra-low-load hardness tester (SHIMADZU DUH-50) and computer controlled specimen moving table (in Fig. 1) to develop a hardness measurement system in a γ-ray shielded glove box. This allows cladding tubes with high radioactivity to be examined. We developed the following measuring technique which has become a standard post irradiation examination in our hot laboratory. To sharpen the tip of the
indenter, a triangular-based pyramidal shaped indenter is employed instead of the conventional quadrangular pyramid one which is used for Vickers hardness measurements. The indenter is attached to a linear differential transducer with the sensitivity of 10 nm movements, and the variable load is applied by an electromagnet force with a resolution of around 20 μ. A typical test involves lowering the indenter towards the specimen surface at a constant speed. The moment of contact to the surface is detected by a sharp change in the indenter speed. After contact, load is increased to the desired value while keeping a constant force increment rate, to obtain the indenter compression load-penetration depth curve.

In this experiment, dynamic hardness is defined as the contact pressure under the indenter at the maximum force. The value is calculated as the applied load divided by the projected area of contact between the indenter and the specimen, as shown in

\[ H_D = \frac{KP}{h^2}, \]

where \( H_D \) is dynamic hardness, \( P \) is load in grams, and \( h \) is penetration depth in micrometers; \( K \) is a constant to calculate the area of contact from the penetration depth and it is determined by the angle at the tip of the triangular surface of the indenter.

In order to obtain the most suitable indenter angle, we carried out the following measurements. The tip end of the indenter was sharpened by reduction of the indenter angle. If the loading force is constant, the indenter with a smaller angle leads to a larger penetration depth and it has an advantage of eliminating any effect of the hardening depth caused by polishing. Smaller angles, at the same time, have disadvantage of cracking easily at the indenter tip. To find suitable angle, we employed three kinds of indenters with angles of 65°, 100° and 115° at the tip. The average hardness from ten measurements was obtained for standard specimens of micro

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Fuel</th>
<th>Axial position of fuel rod</th>
<th>Local burnup (GWd/t)</th>
<th>Temperature (K)</th>
<th>Neutron fluence ((E &gt; 1 \text{ MeV}) ) ((n/m^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>UO₂</td>
<td>Bottom of gas plenum</td>
<td>—</td>
<td>580</td>
<td>(1 \times 10^{25})</td>
</tr>
<tr>
<td>G1</td>
<td>*</td>
<td>&quot;</td>
<td>—</td>
<td>580</td>
<td>(1 \times 10^{25})</td>
</tr>
<tr>
<td>A2</td>
<td>UO₂</td>
<td>Top of fuel stack</td>
<td>7</td>
<td>610</td>
<td>(1.2 \times 10^{25})</td>
</tr>
<tr>
<td>G2</td>
<td>*</td>
<td>&quot;</td>
<td>7</td>
<td>610</td>
<td>(1.6 \times 10^{25})</td>
</tr>
<tr>
<td>A3</td>
<td>UO₂</td>
<td>Center of fuel stack</td>
<td>36</td>
<td>610</td>
<td>(6.6 \times 10^{25})</td>
</tr>
<tr>
<td>G3</td>
<td>*</td>
<td>&quot;</td>
<td>35</td>
<td>610</td>
<td>(5.7 \times 10^{25})</td>
</tr>
</tbody>
</table>

*: \text{UO₂ + 1.5\%Gd₂O₃},  \(^1\): Fabrication data: Table 2

Fig. 1 Schematic diagram of the hardness measurement system
Vickers hardness (MHV700 and MHV200) and for the zirconium and Zircaloy-2 portions of zirconium lined fuel cladding tube before and after etching by 5/45/50 vol% of HF/HNO₃/H₂O solution for 30 s. Figure 2 shows that the load dependence of hardness decreases with larger indenter angle. The coefficient of variation (calculated as the standard deviation of hardness divided by the mean value), shown in Fig. 3, becomes a minimum at the angle of 100°. From these results, the indenter with the angle of 100° was selected for the experiments. The increment rate of compressive force during loading on the specimen was surveyed and a value of 24 mg/s, which induced the minimum variation in hardness, was chosen for standard measurements. The mean value of hardness was an average of ten measurements.

III. Test Results

1. Zirconium with Various Oxygen Concentrations

Oxygen concentration dependence of the Vickers hardness for five zirconium specimens with different oxygen concentrations is shown in Fig. 4 together with previous data. The hardness values are in good agreement with literature data(12)-(15) except for the specimen with microcracks (the point enclosed in parentheses). Relationship between dynamic hardness and the oxygen concentration of zirconium specimen is shown in Fig. 5; one point enclosed in parentheses is excluded from the curve. A precise relationship between the dynamic hardness ($H_D$), which is convenient for measurements in a narrow width using a small indentation, and conventional Vickers hardness ($H_V$) is indispensable to convert $H_D$ to $H_V$. Combination of the data in Figs. 4 and 5 leads to Fig. 6 which shows a linear relationship between $H_D$ and $H_V$.

2. Unirradiated Zirconium Lined Cladding Tube

The hardness distribution of the inner portion of the zirconium-lined fuel cladding tube after simulated oxida-
tion in the fuel rod was obtained. Typical indentations are illustrated with lines indicating measuring path in Fig. 7. They depict the decrease in impression size, or increase in hardness, on approaching the tube surface.

An enlarged cross section of the specimen inner portion is shown together with the hardness distribution in Fig. 8. The inner portion of the oxidized zirconium liner tube can be divided into three regions, A, B, and C. Each region has the following properties: (1) Region A is a zirconium dioxide layer which appears gray in the optical micrograph. Large scatter in hardness is observed, probably resulting from the pores in the layer. (2) The thin white layer B with a thickness around 2.5 μm is observed between the oxidized layer and the zirconium layer C. Hardness has its maximum value at the border adjacent to the oxidized layer A, and decreases sharply with the depth. (3) In region C, up to around 9 μm from the surface, a clear trend of decreasing hardness is observed.

3. Irradiated Zircaloy-2 Tube
Dynamic hardnesses of six specimens cut from irradiated fuel rods were measured with a load of 1 g (9.8 x 10^{-3} N) to obtain clear indentation since indentation size for irradiated specimens was smaller than that for unirradiated one. Some areas in the inner surfaces of the specimens cut from fuel stack regions (A2, G2, A3, G3) were found to be covered by a fuel/cladding chemical bonding layer. In such specimens, an area where there was no reaction layer between the UO2 pellet and cladding material was searched for circumferentially and the measurement was made there. The dynamic hardness distribution is plotted in Fig. 9. Features of the hardness distribution at fuel stack positions (squares and triangles) include a sharp decrease in hardness up to around 2–3 μm from the surface and a very slight decrease with depth above 3 μm depth. It is clear from the comparison between the squares and triangles that neither the mag-

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**Fig. 5** The relationship between oxygen concentration of specimens and dynamic hardness

**Fig. 6** The relationship between Vickers and dynamic hardnesses for five specimens in this study

**Fig. 7** Typical example of indenter impressions in the inner portion of zirconium lined cladding tube
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The magnitude of the hardness nor its distribution are affected by addition of gadolinia to UO₂. The hardness at the bottom extreme position of the gas plenum region, which is not so far from the top of the fuel stack (as little as 25 mm) but receives no fission fragment bombardment, is shown by circles in Fig. 9. In the area less than 3.5 μm from the inner surface of the specimen at gas plenum region, hardness was not measured due to the occurrence of a shoulder slope during the specimen polishing. Such a slope did not occur for the specimens cut from fuel stack positions, though.

IV. Discussion

1. Diffusion Coefficient of Oxygen in Unirradiated Zirconium

Using the hardness-oxygen concentration relationship obtained in Fig. 5, we obtained the oxygen concentration at the depths from the surface of the oxidized zirconium liner tube, as Fig. 10, based on the substitution of oxygen concentration for hardness in Fig. 8. Oxygen concentration in Fig. 10 decreases rapidly from the maximum value of around 26 wt% to 1 wt% in the white layer (Region B in Fig. 8). With less than 1 wt% oxygen (Fig. 10), we see no change in color in metallographic section. The solid circles enclosed in parentheses in the outer surface oxide region should be excluded from the discussion, because hardness does not represent the correct oxygen concentration due to the porosity of the oxide.

After the hardness measurements, relative oxygen concentration of the specimen was obtained by Auger electron analyzer (PHI Model 404). The range from surface to 9 μm in which oxygen increments were detected is shown in Fig. 11, and it corresponds to the range of measured oxygen distribution from dynamic hardness as in Fig. 10.

The diffusion coefficient of oxygen in unirradiated zirconium is estimated on the basis of the oxygen concentration distribution in Fig. 10 and the following approximate solution of Fick's equation for a semi-infinite cylinder and constant surface conditions:

\[ \frac{C}{C_0} = 1 - erf \left( \frac{x}{2(Dt)^{0.5}} \right), \]
where \( C/C_0 \) is the relative value for the oxygen concentration at the surface. The \( \text{erf} \) is error function, \( x \) the depth, \( D \) the diffusion coefficient and \( t \) the time. When \( x \) equals \( 4(Dt)^{0.5} \), \( C/C_0 \) decreases to 0.005, which is for all practical purposes the detection limit of observation. Then, the value of \( 4(Dt)^{0.5} \) is regarded as the maximum depth of the observed hardness distribution or diffusion zone thickness in this study. Thus, \( D \) can be obtained when the diffusion zone thickness of the oxygen or the maximum depth of hardness distribution is measured.

Though, such conditions as diffusion of oxygen in both the oxide and metal, the volume change during oxidation, and the moving boundary should be considered for precise calculation. Here, for simplicity the two-phase diffusion can be neglected and the boundary surface position during diffusion is approximated to be in the oxide layer (between 1–3 \( \mu \)m from the oxide surface in Fig. 10) and the maximum depth of diffused oxygen be 9 \( \mu \)m. Thus, the diffusion zone thickness \( x \) in Eq. (2) is calculated to be in the range of around 6 to 8 \( \mu \)m. The specimen was heated for 2,000 h at 723 K. Then, a diffusion coefficient of \( 3.1 \times 10^{-19} \) to \( 5.6 \times 10^{-19} \) m\(^2\)/s is estimated based on the dynamic hardness distribution. Comparison of the diffusion coefficients with the previous data \((16)\) are made in Fig. 12. The diffusion coefficient of this work agrees well with the previous data obtained by strain-ageing, internal friction, oxide thickness measurements, or ion probe analyzer. This supports the validity of the hardness measurement method for discussing the diffusion.

**Fig. 10** Estimated oxygen concentration from dynamic hardness for zirconium lined cladding tube with simulated oxidation of fuel rod

**Fig. 11** Relative oxygen concentration obtained by Auger analysis for zirconium lined cladding tube with simulated oxidation of fuel rod

**Fig. 12** Comparison of diffusion coefficient of oxygen between the values obtained in this work and for \( \alpha-Zr \) in Ref. (16)
coefficient of oxygen in fuel cladding tubes.

2. Diffusion Coefficient of Oxygen in the Inner Portion of Cladding Tubes

The hardness distribution within 4 \( \mu m \) from the tube inner surface at the fuel stack positions in Fig. 9 is magnified and shown on the upper right of Fig. 13. All data from the two types of fuel rods are plotted by the same symbol, since the difference in hardness distribution at fuel stack positions for UO\(_2\) fuel and gadolinia added UO\(_2\) fuel rods was negligible in Fig. 9. The main cause of the hardness increase is thought to be the oxygen dissolution hardening of Zircaloy as in the case of unirradiated zirconium liner (Figs. 10 and 11).

We assume that the position at which hardness rises from the base line corresponds to the diffusion zone thickness of the oxygen and \( x \) equals \( 4(Dt)^{0.5} \) at this position. Then we estimate the diffusion coefficient of oxygen in the inner portion of fuel cladding tubes and compare it to that obtained from unirradiated \( \alpha-Zr \)\(^{16}\). An error of 0.5 \( \mu m \) in the maximum depth is inevitable, since the hardness measurement cannot be made at the inner surface within 0.5 \( \mu m \). Then as shown in Fig. 13, we can see that the diffusion coefficient is in the range from \( 1.1 \times 10^{-21} \) to \( 1.9 \times 10^{-21} \) m\(^2\)/s when the value of \( 4(Dt)^{0.5} \) corresponds to 1.5-2.0 \( \mu m \) and irradiation time in the BWR is 1,490 days.

On the other hand, if the diffusion coefficient of oxygen in Zircaloy-2 is independent as such in-reactor conditions as neutron irradiation or fission fragment bombardment, the value is simply calculated from the temperature dependence of the oxygen diffusion coefficient in unirradiated zirconium\(^{16}\). Although the temperature changes with the linear heat rates of fuel rods during in-reactor service, it seems reasonable to take temperatures at the tube inner surface region as being within 330°C to 350°C for typical BWR fuel rods\(^{17}\). The comparison of oxygen diffusion coefficients between the calculated and the experimentally obtained values is also made in Fig. 12, and there is good agreement. The diffusion coefficient of fission products in UO\(_2\) fuel has been reported to be two or three orders of magnitude larger than that for out-of-reactor tests\(^{18}\). Considering experimental result and that the stopping range of fission fragments of UO\(_2\), around 10 \( \mu m \)\(^{19}\), is deeper than the maximum depth of the hardness distribution, we can see in the case of oxygen in fuel cladding tubes that neither neutron irradiation nor bombardment of fission fragments affects the diffusion coefficient.

V. Conclusions

(1) A hardness measurement system, equipped with a depth-sensing indentation instrument and the post irradiation examination technique for irradiated fuel cladding tubes were successfully developed.

(2) The results of unirradiated zirconium-lined cladding after simulated oxidation in the fuel rod showed that the minimum oxygen concentration at the white layer, observed by an optical micrograph, was around 1 wt\%, and that the diffusion coefficient obtained from hardness measurements was in good agreement with previous data obtained by many methods as strain-aging, internal friction, oxide thickness measurements, or ion probe analyzer.

(3) From the hardness distribution in the inner portion of Zircaloy-2 fuel rod irradiated up to five cycles in a
BWR, it was concluded that neither neutron irradiation nor bombardment of fission fragments affected the oxygen diffusion coefficient in the inner portion of cladding tube.

---REFERENCES---