

Microstructural Changes of Fuel Claddings for Pressurized Water Reactors Fuel after Irradiation†

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Microstructural changes of spent fuel claddings discharged from pressurized water reactors were investigated by a radiation-shielded micro-X-ray diffraction system (μ -XRD). A zircaloy-4 cladding of UO_2 fuel and a zirlo cladding of burnable poison fuel (5.98 wt % gadolinia-urania) with 41 GWd/tU burn-up and a zircaloy-4 cladding of 58 GWd/tU UO_2 fuel were chosen as sample specimens to investigate the effects of burn-up on the irradiation behaviour of cladding. At 41 GWd/tU burn-up, the chemical interaction between a fuel pellet and cladding was not observed for both samples. The formation of ZrO_2 and ZrH_2 phases was observed in the outer surface of the zircaloy-4 cladding, while those phases were not observed for the zirlo cladding. It can be concluded that zirlo is more stable than zircaloy-4 at this burn-up. At 58 GWd/tU burn-up, the formation of a zirconium oxide (ZrOx) layer was observed at the inner surface of the zircaloy-4 cladding, which indicates that the cladding interacts with the fuel. On the outer surface of zircaloy-4 cladding, ZrO_2 and ZrH_2 phases were also observed.

Key Words: Spent fuel cladding, Zircaloy-4, Zirlo, Chemical interaction, Oxidation.

INTRODUCTION

At high burn-up conditions, fuel can come into contact with cladding due to fuel swelling, which results in a chemical interaction between the fuel and cladding (FCCI). There have been many studies on FCCI to investigate fuel rod behaviour¹⁻³. Because Zr is thermodynamically reactive with oxygen, this chemical interaction leads to the oxidation of the inner surface of the cladding. This in turn leads to a thinning of the cladding, which affects the safety of fuel pins. The extent of the reaction layer depends on the contact between UO_2 and its cladding. Because oxygen transportation from UO_2 to cladding is difficult to achieve, the oxidation of Zr cannot be observed without direct contact. In this study, to access the structural changes of the cladding by chemical interaction with UO_2 , the diffraction spectrum of a cladding's inner surface was measured for the different cladding materials and different fuel burn-ups. The corrosion of the fuel cladding under the primary circuits of pressurized water reactors and their dry storage is an important issue. Therefore, a cladding outer surface was also measured to investigate the oxidation behaviour of the cladding because this also leads to thinning of the cladding.

EXPERIMENTAL

Preparation of fuel cladding specimens: Three sample specimens were prepared from spent fuel rods discharged from a pressurized water reactor. Two specimens were couples of the UO_2 fuel/zircaloy-4 cladding, which were discharged from the NPP(Y-2). The burn-up of two fuels was 41 GWd/tU and 58 GWd/tU, as measured by the Nd-148 method (ASTM, E321-96)^{4,5}. The third fuel was a couple of burnable poison fuel (5.98 wt % Gd_2O_3 - UO_2)/zirlo cladding, which was discharged from the NPP(K-3). The average burn-up of the poisoned fuel specimen was 41 GWd/tU.

Axial slices of the fuel rods were cut at a 3 mm height. The slices of the spent fuels were embedded in epoxy resin and then polished at the post irradiation examination facility.

A radiation-shielded μ -XRD system (D₈ ADVANCED, BRUKER-AXS) was used to obtain the diffraction spectra^{6,7}. For an accurate and precise positioning of the samples, two linear stages (travel distance: 25 mm, minimum movement: 0.1 μm) and a rotation stage (rotation angle: 360°, minimum movement: 0.004°) were equipped with a microscope (magnification at 120 mm distance: 13x). Because the background signal of γ -radiation from a spent fuel specimen interrupts the diffracted signal from a sample and results in poor detection,

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the sample holder⁸ and detector were shielded with 5- to 10-mm thick tungsten sheets. The measurements were conducted with a scanning step of 0.04° (2θ) for 20 s per each count and a detector slit width of 0.6 mm. An X-ray diffraction spectrum was obtained by measuring one position of a specimen for approximately 2 h. The $\text{CuK}\alpha$ line filtered through an Ni foil and NaI (Tl) scintillation counter was used at 40 mA beam current and 40 kV beam generation power. The visual inspections of the fuel pellet involving the cladding were conducted using a radiation-shielded SEM (XL30, Philips) and the chemical compositions of the surface were analyzed by shielded EDS for uranium and zirconium content and a WDS system for oxygen content.

RESULTS AND DISCUSSION

Irradiation behaviour of the zircaloy-4 and zirlo claddings at 41 GWd/tU: During irradiation, a fuel pellet can swell and contact the cladding, leading to a chemical reaction between the fuel and cladding. The characteristics of the chemical reaction in this interface region should be understood because they affect the integrity of the cladding. For an identification of the reaction product in this interface region, the XRD spectrum was measured for the reaction area between a fuel and its cladding.

The XRD spectra of a zry-4 cladding contacted by 41 GWd/tU UO_2 ($\text{UO}_2/\text{zry-4}$) and zirlo cladding contacted by 41 GWd/tU poisoned UO_2 ($\text{Gd}_2\text{O}_3\text{-UO}_2/\text{zirlo}$) are shown in Figs. 1 and 2, respectively. Diffraction spectra were obtained from the inside to the outside of the cladding at 50-100- μm intervals. At the inner surface, zirconium oxide (ZrOx) was not observed in either sample. The observed UO_2 phase resulted from the fuel due to the beam width at the interface. It appears that the chemical interaction between the fuel and cladding did not occur for both zry-4 and zirlo claddings at 41 GWd/tU fuel burn-up.

At the outer surface, the $\text{UO}_2/\text{zry-4}$ couple showed ZrO_2 and ZrH_2 phases, although these diffraction patterns were not clearly identified due to weak intensity of the peaks and peak overlap. The very thin corroded layer and limited spatial resolution (*ca.* 50 μm) of our μ -XRD system appear to be responsible for the weak signals. Nevertheless, some estimation on the

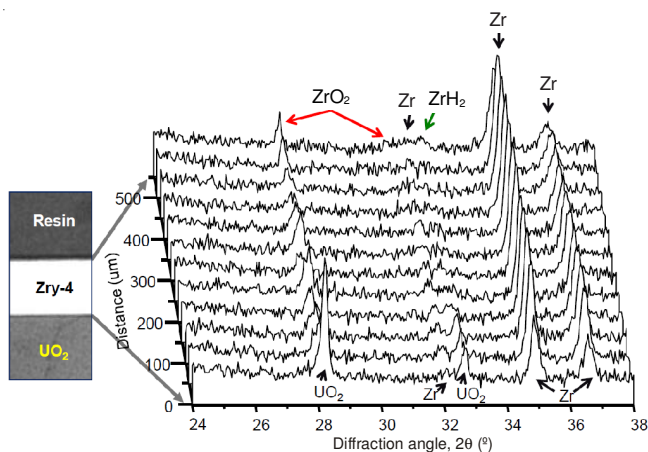


Fig. 1. XRD spectra of the zry-4 cladding contact with 41 GWd/tU UO_2 fuel discharged from NPP(Y-2)

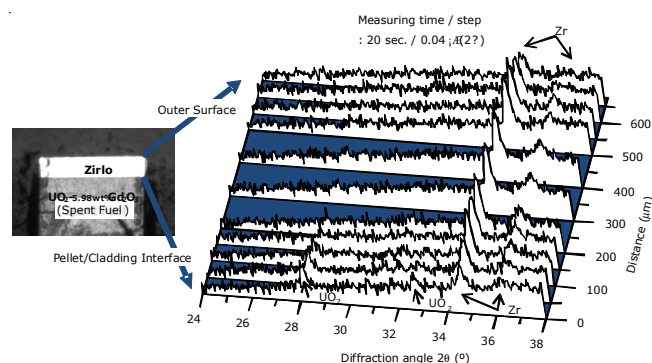


Fig. 2. XRD spectra from the inner surface to the outer surface of a zirlo cladding contacted with 41 GWd/tU poisoned fuel ($\text{UO}_2\text{-5.98 wt \% Gd}_2\text{O}_3$) discharged from NPP(K-3)

composition of the corrosion region may be possible. It has been reported that a corrosion layer of a cladding under the primary circuits of pressurized water reactors is produced by the diffusion of oxygen or hydrogen from the cooling water into the cladding during the operation of a nuclear reactor^{9,10}. Therefore, ZrO_2 and ZrH_2 phases in the outer layer of the cladding can be formed by the diffusion of oxygen and hydrogen from the cooling water. However, nothing was detected except zirconium in the outer surface layer of a zirlo cladding contacted by $\text{Gd}_2\text{O}_3\text{-UO}_2$ fuel. It can be estimated that the corrosion resistance of the zirlo cladding is better than the zry-4 cladding.

Irradiation behaviour of zircaloy-4 cladding at 58 GWd/tU fuel burn-up: For the $\text{UO}_2/\text{zry-4}$ couple of 58 GWd/tU fuel burn-up, zirconium oxide (ZrOx) was observed at the inner surface as shown in Fig. 3. However, the expected phase of zirconium oxide cannot be easily distinguished from those of UO_2 because the XRD patterns of those phases are nearly identical, as shown in Fig. 4. Thus, the elemental analysis was performed by EDS and WDS (Fig. 5) to clarify the composition of the reaction layer. A line scan analysis for the content of Zr, U and O was performed at 2.5- μm intervals around the interface. This measured region can be divided by three parts as follows: (a) cladding, (b) reaction layer and (c) the rim region of the fuel. Zirconium is the major element in the cladding (Fig. 5-a) and its content decreased slightly in the reaction layer (Fig. 5-b) and then decreased considerably in the rim region

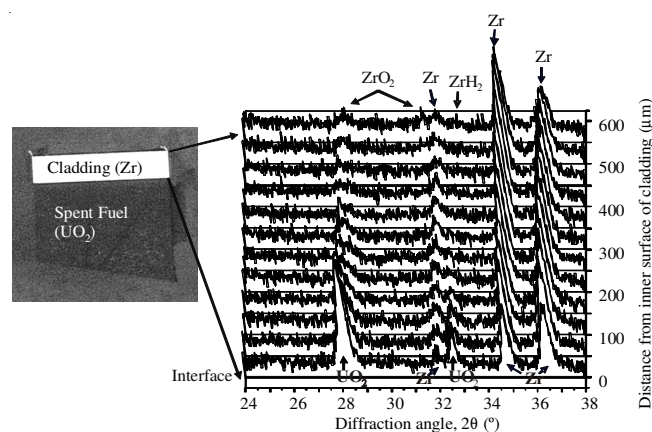


Fig. 3. XRD spectra measured from the inner surface to the outer surface of the zry-4 cladding contacted with 58 GWd/tU UO_2 fuel

of the fuel (Fig. 5-c). The uranium content decreased sharply at the interface between the rim region and reaction layer, which indicates that the uranium diffusion into the interaction layer was not significant. The O content decreased slightly in the reaction layer and then decreased sharply in the cladding. It is thus concluded that a ZrO_x ($x \leq 2$) was generated by an oxygen uptake of the cladding from the UO_2 pellet.

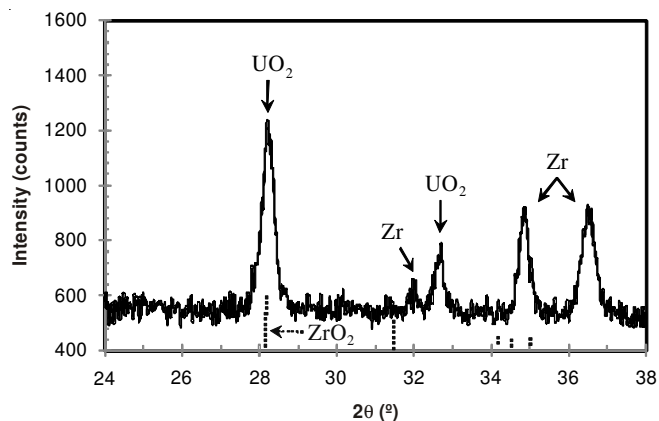


Fig. 4. XRD spectrum measured at the interaction layer between UO_2 fuel and zry-4 cladding. Dotted line: index of ZrO_2 phase from database

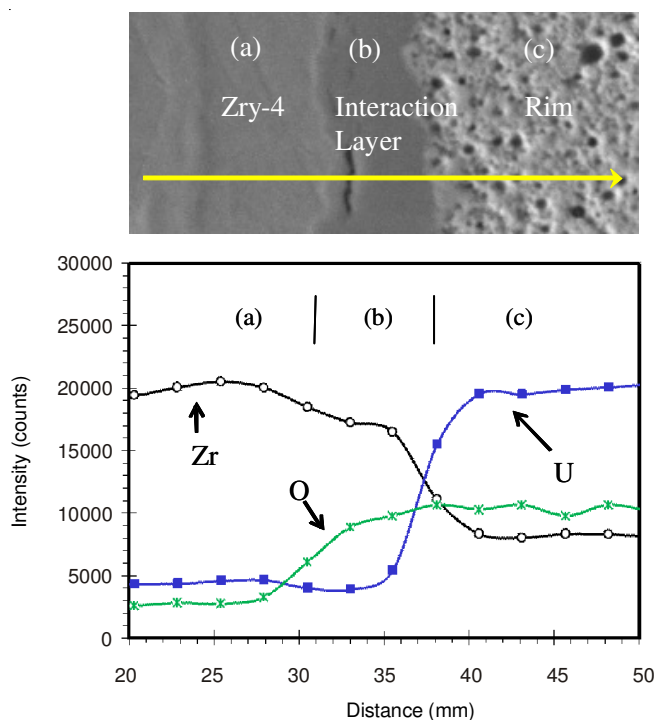


Fig. 5. Interaction between fuel and cladding: (top) SEM image, (bottom) the content of Zr and U measured by EDS and that of O measured by WDS

In the outer surface of the cladding, the formation of ZrO_2 and ZrH_2 phases by the diffusion of oxygen and hydrogen from the cooling water was observed. However, the diffraction patterns of the ZrO_2 and ZrH_2 phases were not clearly identified due to the weak intensity of the peaks and peak overlap. The reasons for the weak signal are the very thin corroded layer and limited spatial resolution (*ca.* 50 μm) of our μ -XRD system. Therefore, the elemental analysis was performed by

EDS and WDS (Fig. 6) to clarify the composition of the corroded layer. The outer layer was shown to be zirconium oxide (Fig. 6-bottom). In the SEM image of the cladding (Fig. 6-top), the dark grey region represents the corrosion layer of the cladding caused by the oxygen uptake from cooling water. The thickness of the corroded layer was approximately 16 μm .

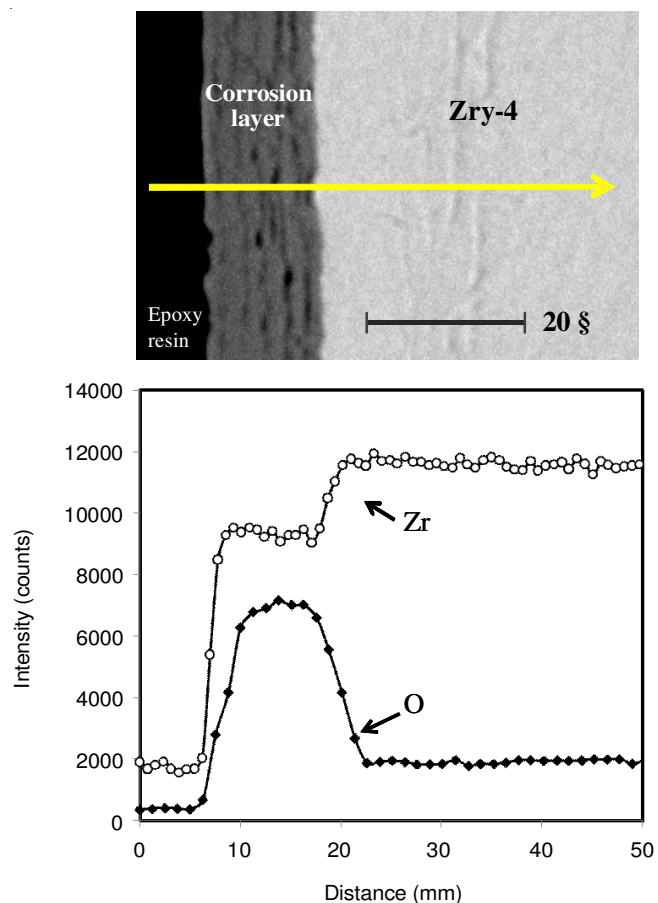


Fig. 6. Variations of Zr and O content from the outer corrosion layer to the inner zry-4 analyzed by EDS and WDS, respectively

Conclusion

The changes of claddings after irradiation were measured by μ -XRD. At lower burn-up (41 GWd/tU), the fuel and its cladding did not interact with each other, regardless of the cladding material (zry-4 or zirlo). However, the ZrO_2 and ZrH_2 phases in the outer layer of the zry-4 cladding were observed, but nothing was detected except zirconium in the outer layer of a zirlo cladding. We concluded that the corrosion resistance of zirlo cladding is superior to that of zry-4 cladding.

At higher burn-up (58 GWd/tU), the zirconium oxide (ZrO_x) layer was observed at the interface between the UO_2 fuel and zry-4 cladding, which suggests that oxygen diffused from the fuel into the cladding. In the outer surface of the zry-4 cladding, the formation of ZrO_2 and ZrH_2 phases by the oxygen uptake from the cooling water was observed. The thickness of the corroded layer was approximately 16 μm . Continued research on the fuels with burn-up over 58 GWd/tU is in progress and the results may provide a clearer picture regarding FCCI and structural change.

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