MOBILITY OF RADIONUCLIDES IN SNF IN VIEW OF EXTENDED DRY INTERIM STORAGE

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ABSTRACT

Integrity of the irradiated Zircaloy cladding after dry interim storage is essential e.g. for conditioning of the fuel assemblies for final disposal. The cladding is affected during reactor operation by various processes e.g. dissolution of hydrogen within the Zircaloy matrix. Swelling of the fuel pellets during irradiation eventually leads to the contact of the fuel pellets with the cladding. Precipitates of fission/activation products such as cesium, iodine, rubidium, tellurium, and chlorine present on the inner surface of the cladding or at the fuel-cladding interface possibly exhibit corrosive properties and thus affect the cladding integrity. Using various spectroscopic methods, the compositions of agglomerates found on the inner surface of a plenum cladding is analyzed in this study.

INTRODUCTION

After discharge of spent nuclear fuel (SNF) assemblies from a nuclear power reactor and subsequent cooling in a spent fuel pool for several years, the fuel assemblies are eventually sent for dry cask storage in the German waste management concept. Dual-purpose casks (CASTOR®, GNS) are used for transport and dry interim storage of SNF assemblies in 16 storage facilities available in Germany. Finally, the SNF is designated for direct disposal in a deep geological repository available by 2050 at the best [1].

However, considering the delay in the site selection process so far as well as the time needed for exploration, construction, and commissioning of a repository for high-level waste, start of waste emplacement is expected by the end of this century or beginning of next century [1].

Thus, a prolonged dry interim storage of SNF assemblies is inevitable. Moreover, dry interim storage of SNF assemblies was intended to last only a few decades, and hence licenses for storing of CASTOR® casks in the interim storage facilities expires already in the years 2034 to 2047. Thereafter, a thorough revaluation of all safety relevant aspects regarding the long-term behavior of the casks and their inventory is required.

Integrity of the irradiated Zircaloy cladding after 50 to 100 years of dry interim storage is essential e.g. for conditioning of the fuel assemblies for final disposal. However, the cladding is affected during reactor operation by various processes such as elongation of the fuel rods due to creep behavior and oxidation with the water coolant causing a reduction of the Zircaloy wall thickness, respectively. Further, dissolution and precipitation of hydrogen within the Zr-alloy matrix, during reactor operation, possibly leads to hydrogen embrittlement and delayed hydride cracking of the cladding. Swelling of the fuel pellets during irradiation due to fission products build-up eventually leads to the contact of the fuel pellets with the cladding. The so-called pellet/cladding interaction (PCI) induces tensile stress on the cladding, especially during power ramps. Precipitates of fission/activation products such as cesium, iodine, rubidium, tellurium, and chlorine present on the inner surface of the cladding or at the fuel-cladding interface possibly exhibit corrosive properties and thus affect the cladding integrity.

Using various spectroscopic methods, the compositions of agglomerates found on the inner surface of a plenum cladding is analyzed in this study.

MATERIALS AND METHODS

Zircaloy specimens were prepared from the plenum section of a spent UO_2 fuel rod segment. The fuel rod was irradiated during four cycles in the pressurized water reactor (PWR) Gösgen (Switzerland) and discharged in May 1989 after 1226 effective full power days. During reactor operation, an average burn-up of 50.4 GWd/t_{HM} as well as average linear power of 260 W/cm was achieved.

Subsamples were dry cut using an IsoMet® Low Speed Saw (11-1180, Buehler Ltd.) equipped with an IsoMet® diamond wafering blade (11-4254, Buehler Ltd.). Cutting was performed very slow (about one hour per sample) to prevent overheating of the material. Then, the subsamples were prepared for the various analytical techniques used in this study (see figure 1) Samples were prepared for investigating the inner surface as well as the cross section of the cladding tube.

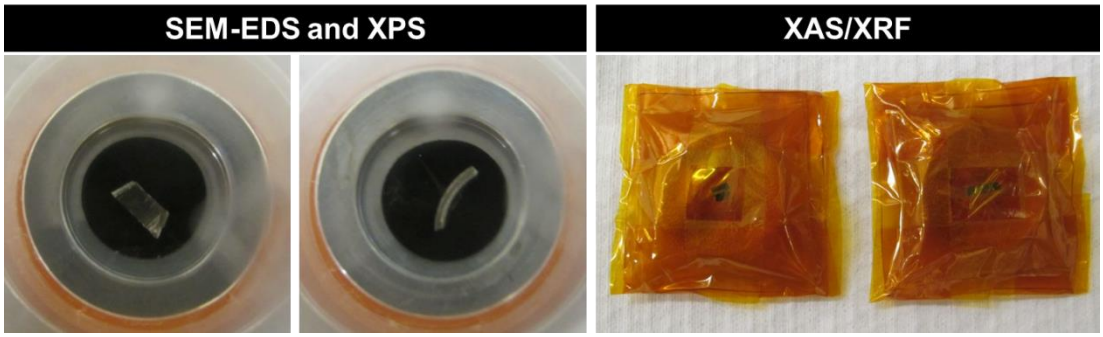

Figure 1: Pictures of irradiated plenum Zircaloy-4 subsamples prepared for analysis.

Spectroscopic studies with irradiated Zircaloy subsamples were performed by means of X-ray photoelectron spectroscopy (XPS) using a ULVAC-PHI VersaProbe II spectrometer to characterize composition and chemical bonding of elements at the outermost atomic layers of the surface. Additionally, a scanning electron microscope (FEI Quanta 650 FEG) coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) was used to increase the information depth and lateral resolution. Moreover, X-ray absorption spectroscopy (XAS), µ-XAS and X-ray fluorescence spectroscopy (µ-XRF) were performed with the irradiated material using the INE-beamline at the synchrotron radiation facility KARA (Karlsruhe Research Accelerator) of the Karlsruhe Institute of Technology.

RESULTS AND DISCUSSION

XPS investigations of the plenum show the presence of C, N, O, Rb, Cs, Ba and U, besides Zr of the cladding. Rb up to about 7 at% is the most abundant fission product detected at the inner surface of the cladding at the plenum section. SEM-EDS elemental maps of Fe, Rb, Zr, Cs, and U are compiled in figure 2 in combination with a backscattered electron image depicting material contrast. Bright areas at the backscattered electron image correspond to high *Z* elements. No contact with nuclear fuel was expected at the inner surface of the plenum section. However, individual fuel particles and particle agglomerations are observed at the oxidized cladding surface. The fuel particles are presumably remnants of filling UO_2 pellets into the fuel rod during fabrication. The elemental maps exhibit enhanced concentrations of Rb and Cs at the fuel particle agglomerate (see figure 2).

Analyses of individual particles were performed at accelerating voltage of 10 kV to minimize the excitation volume of characteristic X-rays (see figure 3). Particles of U-oxide (analysis areas #2, #5) and

of Fe-(Cs,Rb)U-oxide (analysis areas #1, #3, #4) were identified. The iron maybe originates from wear of the plenum stainless steel spring. Since Rb is detected by XPS at higher concentrations than U and Zr at some analysis areas, a part of the Rb in the plenum section is not bound to U-oxide or Zircaloy.

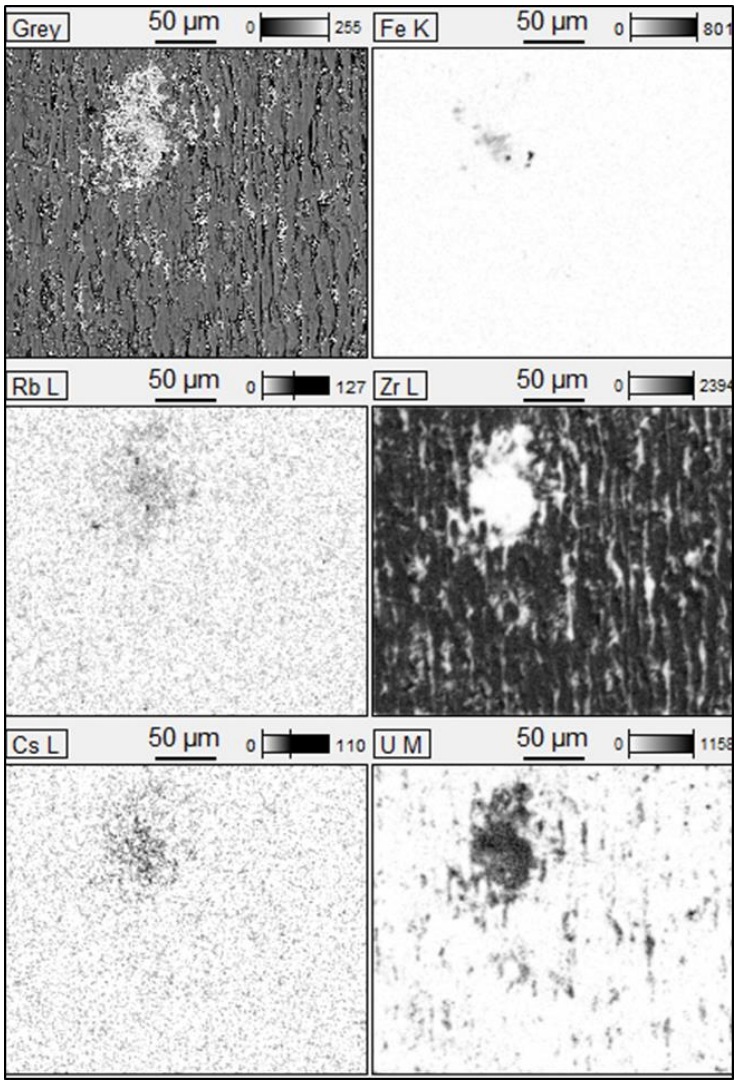

Figure 2: SEM backscattered electron image (grey) of the inner surface of the plenum section in combination with SEM-EDS elemental maps of Fe, Rb, Zr, Cs, U. Accelerating voltage 30 kV.

U L3 bulk XAS and µ-XAS measurements for elements identified in µ-XRF distribution maps with a lateral resolution of better than 20 µm were performed for both samples in fluorescence detection mode. Excitation energies were kept below the Zr K-edge (17.998 keV) to avoid saturation of the Vortex fluorescence detector. Uranium was detected as most abundant element (besides Zr which was not excited) omnipresent on the inner cladding surface – mostly concentrated in hot spots of a few tens of µm diameter (see figure 4). As mentioned above, it is assumed, that most of the uranium was originally deposited by abrasion during manufacturing of the fuel rods. The µ-XRF scan of the cladding cross section in figure 4 (bottom) exposes a marked uranium layer of about 25 µm thickness following the curvature of the inner surface. Besides uranium, a multitude of elements was detectable on the inner cladding surface, some of them probably deposited as volatile fission products (e.g. Rb, Ba, Ti), while

some (Fe, Cu, Ni) were detected as metallic particles, probably originating from the stainless steel plenum spring.

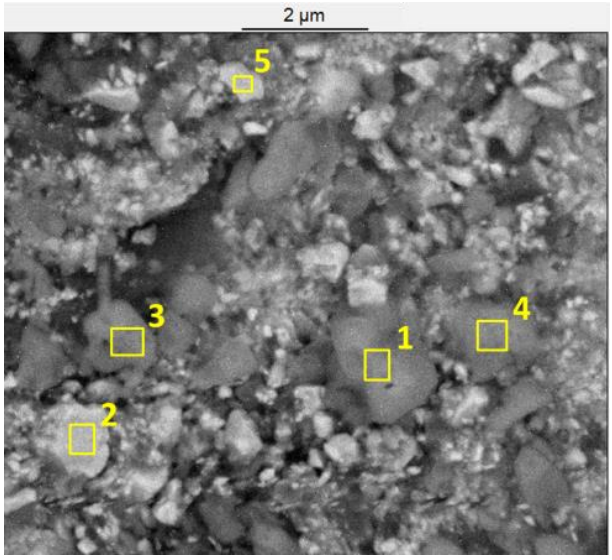

Figure 3: Backscattered electron image of an area at the inner surface of the plenum covered by particles. Areas of SEM-EDS analyses are indicated by numbered boxes. Accelerating voltage: 10 kV.

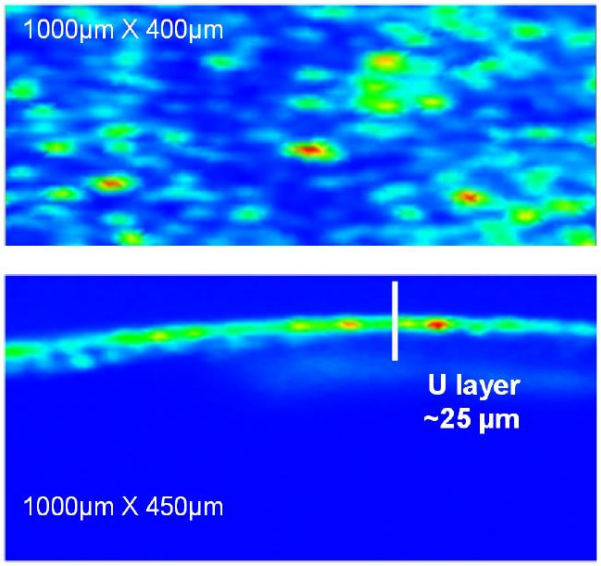

Figure 4: U Lα fluorescence images of (top) the inner cladding surface and (bottom) the cross section.

SUMMARY AND OUTLOOK

The volatile fission products Rb and Cs are analyzed on the inner surface of the plenum of a spent UO_2 fuel rod segment by using various spectroscopic techniques. Moreover, uranium remnants from fuel rod fabrication were found in the plenum. Most of the cesium and rubidium present in the plenum is due to migration of Cs and Rb, released from fuel pellets during reactor operation, and precipitating at the

relatively cold plenum compared to the warmer fuel pellet pile. Fission of uranium remnants present in the plenum are an additional source of Cs and Rb. The spectroscopic observations are in good agreement with experimental inventory determinations of the same plenum cladding reported elsewhere [2].

The results and findings of this study is prerequisite work for investigations on fuel cladding chemical interactions involving Zircaloy-4 cladding in contact with spent UO_2 and MOX fuel pellets.

REFERENCES

[1] "Abschlussbericht der Kommission Lagerung hoch radioaktiver Abfallstoffe," Berlin, Germany, K-Drs. 268, 2016.

[2] M. Herm, R. Dagan, E. González-Robles, N. Müller, and V. Metz, "Comparison of calculated and measured radionuclide inventory of a Zircaloy-4 cladding tube plenum section," *MRS Advances,* pp. 1031-1037, 2018.