

HYDRIDES RE-ORIENTATION AND METALLOGRAPHY ANALYSIS OF FIVE CYCLES IRRADIATED FUEL CLADDING SAMPLES

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ABSTRACT

For economical reasons the service time of nuclear fuel in LWRs as well as the power density is steadily increasing. These may lead to a higher hydrogen take up in the Zircaloy cladding. The mechanical properties of the cladding can degrade not only due to irradiation induced embrittlement, but also by precipitation of hydrides and by their (re-) orientation which plays an important role for fuel handling under dry storage conditions.

At Paul Scherrer Institut (PSI), the Laboratory for Nuclear Materials (LNM) and the Hot Laboratory Division (AHL) investigate these issues in close collaboration with industry and Swiss power plants.

Irradiated cladding tube sections with known hydrogen content were tested under elastic stress with different temperature and mechanical loading cycles to induce re-orientation of hydrides. The possibility of recovery of circumferential hydrides distribution through only heat treatment was also tested.

To determine the distribution and re-orientation of hydrides, metallography coupled with a specific analysis software was used. The analyses revealed differences in hydrides re-orientation depending on the thermo-mechanical treatment. Number and position of the radial hydrides can be considered as indication for potential failure under given conditions.

1. Introduction

Economic reasons ask for extended service time of nuclear fuel in LWRs as well as for increasing power density. Both leads to a reduction of spent fuel volume, means more free capacity in the intermediate storage and a smaller number of nuclear transports. On the other hand a longer dwell period leads to stronger materials degradation, for instance, to a higher hydrogen take up in the Zircaloy cladding. Thus, the mechanical properties of the cladding can degrade not only due to irradiation induced embrittlement, but also by precipitation of hydrides and by their (re-) orientation which plays an important role for fuel handling under dry storage conditions. The Laboratory for Nuclear Materials (LNM) and the Hot-Laboratory division (AHL) at Paul Scherrer Institut (PSI) investigate these issues in close collaboration with industry and Swiss power plants.

Among parameters that have been studied as of possible influence in hydrides reorientation are the testing temperature, the hydrogen content, the number of loading cycles, the orientation with respect to texture, and the initial thermal treatment. The irradiation state, along with hydrides distribution typical of spent fuel cladding, has not been studied so far.

While the threshold stresses are not influenced by the number of loading cycles, the fraction of reoriented hydrides is thus affected. Hydrides that have not been dissolved and possibly reoriented at the precedent loading step can be reoriented at the current loading step [1]. An initial heterogeneous orientation of hydrides in the sample is also expected to favor this behavior. For claddings of spent fuel from nuclear power plants the hydrides density is higher on the external side of the cladding tube since this area is colder than the internal side. Thus cycling can have an important effect on the reorientation behavior in irradiated cladding tubes. However, it has been shown that after three to four reorientation cycles, a saturated behavior occurs and the fraction of reoriented hydrides does not increase anymore.

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The irradiated cladding samples with known hydrogen content were tested under elastic stress with different temperature and mechanical loading cycles to induce re-orientation of hydrides. Further, a particular aspect tested here is the possibility of recovering the initial circumferential hydrides distribution through a heating-cooling cycle without loading. However, when hydrides are reoriented under loading, they tend to activate specific precipitation sites for reoriented hydrides. Under further heating-cooling cycles without mechanical loading, it is not known if such sites are still active and would favor hydrides reorientation or if the cladding will recover the circumferential hydrides distribution it originally had.

To determine the distribution and re-orientation of hydrides, metallography coupled with a specific analysis software was used. Number, length and position of the radial hydrides, in relation to mechanical state during testing, can be considered as an indicator for potential failure sites under the given conditions.

2. Test Equipment and Setup

2.1. $\alpha\beta\gamma$ -Box in the Hot Laboratory

The thermo-mechanical testing device consists of several parts: the outer γ -shielding, see Figure 1 (left), equipped with manipulators reaching into the inner α -box behind the shielding, the universal tensile testing machine and the furnace. The furnace is flanged to the inner box like a back-pack and is part of the α -containment. The pulling rods of the testing machine, which is outside the α -box, lead through metal bellows into the furnace. The bellows with the pulling rods compose the interface between testing chamber and tensile machine. The chamber can be flooded with inert gas (Ar, N) or a slight vacuum can be created. The pressure in the chamber – as also in the α -box – is controlled to maintain the pressure cascade between furnace chamber, α -box and surrounding lab. The off-gas is directed into the general hotlab off-gas duct. The furnace is typically operated at temperatures up to 450°C, whereas higher temperatures up to about 700°C are possible for short-term operation. The furnace chamber is water cooled. This is a prerequisite as the operation of a furnace in a closed box needs active heat removal. The cooling consists of 2 circuits: in case of the rear of the furnace chamber the flanges for the cooling water pipes are outside the α -box, the cooling water pipes for the furnace door lead through the α -containment. Therefore a special water leak control had to be installed inside the box. The universal testing machine is an Alliance RT/30 with a 30 kN load cell from MTS. Specimen holders and tools are own developments.



Figure 1: (left) $\alpha\beta\gamma$ -box with open door of the γ -shielding, α -box is behind the shielding and (right) Telatom-4 microscope at the metallography box.

Metallography work in the hotlab is carried out in a specific hotcell, see Figure 1 (right). The equipment comprises cutting machine, polishing machine, and the possibility to make chemical etching. The metallography samples are embedded under vacuum in a 2-component resin (Epofix / Struers). After hardening they are ground with pre-polishing disks (MD-Piano / Struers), starting with 80 followed by 220 grit and 1200 grit (see Figure 2). Finally, the samples are polished on a polishing towel from 15 μm down to 1 μm Diamond paste. The hydride precipitates in the fuel rod are then etched with a mixture of 95 ml HNO_3 (65%) and 5 ml HF (38%). The relatively short etching sequence (5 sec) is repeated until an optimal metallography picture is achieved. To prevent the metallography box from corrosion due to acid vapors a special box with gas exhaust system is used. Finally, the metallography pictures are taken using a Telatom-4 microscope from Leica presented on Figure 1 right.



Figure 2: (left) mould for embedding tube sample, the ring on the bottom is used to center the sample, (right) the grinding and polishing machine handled with manipulators.

2.2. Testing Reorientation Characteristics on Irradiated Cladding Tubes

Using the Cladding Tensile Deformation Test (CTDT) configuration of PSI [2], the samples were put in a specific sample holder, consisting of two half-cylinders, snuggling into the tube section, and which can be pulled apart so that a load is induced which is perpendicular to the tube length axis (see Figure 3). The samples and the half cylinders are lubricated to minimize friction between them. Otherwise, a non-uniform loading due to sticking of the sample to the half-cylinders could arise, compare [3].

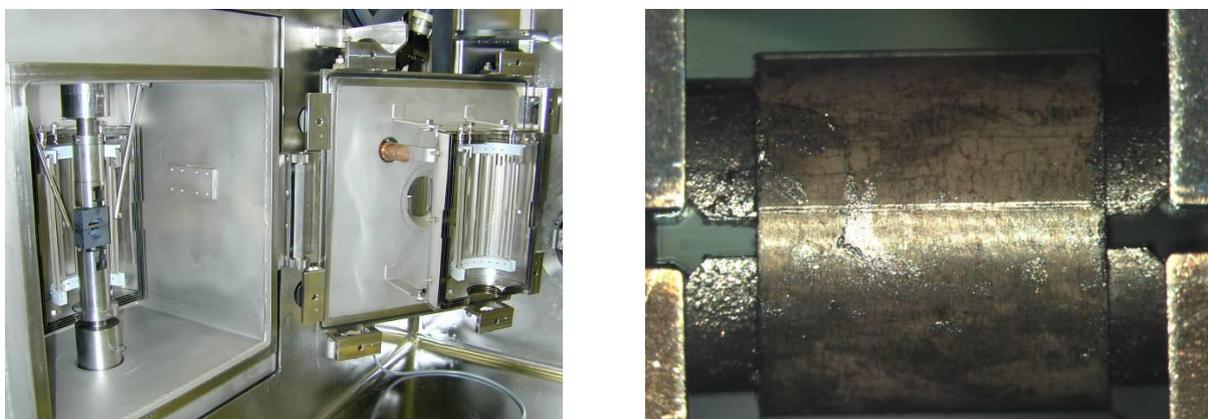


Figure 3: (left) opened furnace chamber and tensile testing setup in the shielded α box; (right) Cladding Tensile Deformation Test (CTDT) sample during reorientation test.

To study hydride reorientation, the approach, also described on Figure 4, is as follows: a test sample about 10 mm long, is first heated at a temperature T_{max} such that all hydrogen contained in the sample is in solid solution, then the sample is cooled down under a constant tensile load F_{max} to provoke hydrides reorientation. The cooling rate has been checked to be sufficiently slow to reach equilibrium [2]. After chemical etching, a micrographic analysis of the cross-section of the sample is done.

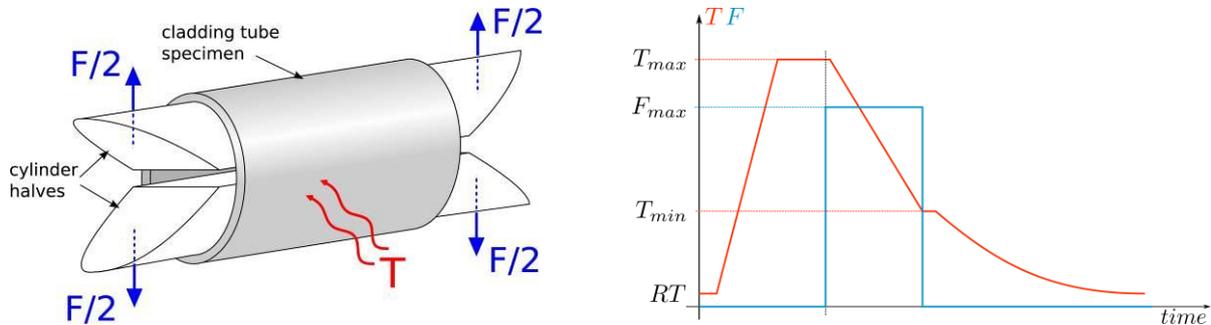


Figure 4: thermo-mechanical loading of the cladding tube sample and schematic evolution of a standard step of the thermo-mechanical loading during one cycle.

2.3. Irradiated Samples: Origin, Characteristics and Preparation

The irradiated specimens stem from the Swiss pressurized water reactor of Gösgen, KKG. The rods have seen five reactor cycles leading to a burn-up of around 72 GWd/tU. The cladding is a Zircaloy-4 based material with outer liner from Areva (DX-D4). The samples have been thoroughly examined after irradiation and fully characterized.

Table 1: characteristics and cutting sketch of the segments used for irradiated samples.

Segment	C	GE	I
	H measurement	reorientation tests	H measurement
Elongation	1001 mm	3040 – 3102.5 mm	3112 mm
H content total	134 ppm		446 ppm
metal	116 ppm	-	392 ppm
oxide	17.8 ppm		54 ppm
<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 20px;">segments</div> <div style="display: flex; align-items: center;"> <div style="width: 100px; height: 15px; background-color: #ccc; border: 1px solid black; margin-right: 5px;"></div> <div style="width: 200px; height: 15px; background-color: #ccc; border: 1px solid black; margin-right: 5px;"></div> <div style="width: 100px; height: 15px; background-color: #ccc; border: 1px solid black; margin-right: 5px;"></div> <div style="width: 100px; height: 15px; background-color: #ccc; border: 1px solid black; margin-right: 5px;"></div> </div> </div> <p style="text-align: center;">total length after service approx. 3890 mm</p>			

As can be seen from Table 1, the hydrogen content in the metal at a position close to the tested samples is approx. 400 ppm.

2.4. Specific Test Characteristics

Five samples of the rod described in Table 1 were tested for reorientation. An additional sample taken out from the segments was put aside to serve as reference. The characteristics of the different test procedures are listed in Table 2 and Table 3. The design of the test matrix was not driven by the wish to make a quantitative determination of the threshold stress for reorientation, therefore repeatability was not assessed. The tests include two main types of cycling: one with load applied during every cool down and the other without loading during the last cool down of the respective test. Comparison between those two test types should give hints for revealing a possible recovery of the initial circumferential hydrides distribution.

Table 2: characteristics of tested samples.

Sample #	Loading cycle type	Heating rate [°C.min ⁻¹]	Solid solution temperature T _{max} [°C]	Dwell time [min]	Cooling rate [°C.min ⁻¹]	Holding force F _{max} [N]
1	A	2	440	30	0.5	280
2	B	2	440	30	0.5	280
3	C	2	440	30	0.5	280
4	D	2	440	30	0.5	280
5	E	2	440	30	0.5	280

Table 3: loading cycles – purpose and description.

Loading cycle type	Purpose of the cycle	Cycle description
A	Reference reorientation behavior	
B	Effect of two cycles loading, comparison between cycle A and C.	
C	Recovery of circumferential reorientation after one cycle.	
D	“Saturated” reorientation behavior	
E	Recovery of circumferential orientation at saturation.	

2.5. Analysis Method

After thermo-mechanical loading, the samples were cross-cut and polished for metallography. Digital photographs were taken stepwise from the whole section, i.e. the complete 360°. The pictures were stitched and analyzed with respect to the orientation, location and length of the hydrides, with the help of a specific software which was developed at PSI [4]. This software was designed to carry automatic segmentation of pictures from hydrided samples and has been developed using C++ language. The algorithm used is as follow (see Figure 5):

- stitch macrographies to obtain a picture of the whole tube cross section;
- convert pictures in gray level by red channel selection;
- convert gray level into black and white using a cluster threshold algorithm;
- recognize circumferential hydrides:
 - mark connected black pixels in the circumferential direction;
 - make gamut selection on the marked pixels;
 - determine size and orientation characteristics, filter non satisfying particles;
- erase circumferential hydrides from the original picture;
- recognize radial hydrides:
 - mark connected black pixels in the radial direction;
 - make gamut selection on the marked pixels;
 - determine size and orientation characteristics, filter non satisfying particles.

It is important to mention that the outer liner of the material has not been considered.

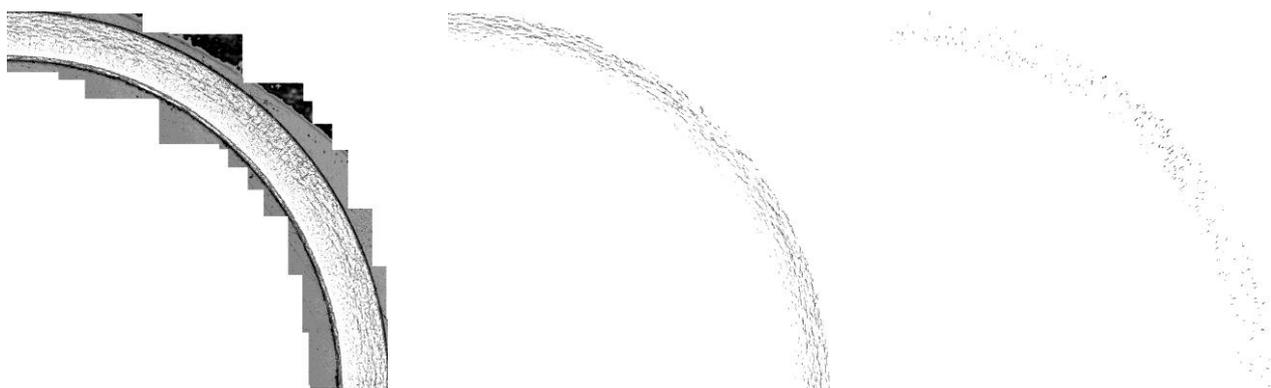


Figure 5: steps of the hydrides recognition software (left) stitching of the micrographies together, (middle) recognition of circumferential hydrides and (right) recognition of the radial hydrides. Only upper right quarter is depicted here.

3. Results

The cumulated lengths of all hydrides are shown in Figure 6. Unexpectedly, the total quantity of hydrides obviously differs for the different samples. The reason why there is a different cumulated hydride length is unknown. As the liner has not been considered in the analyses, it can be speculated that the lacking hydrogen is bound in it. However, a quick verification of this hypothesis revealed no clear indication for being true.

Principally there are 2 possibilities for the varying hydrides accumulation results in the different samples: (a) some of the hydrogen is not bound in hydrides and is not detected with metallography or (b) there are indeed different hydrogen contents. Which possibility is true can only be verified with further investigations.

Interestingly, the results for the tests with a pure thermal cycle at the end show the highest overall accumulation of hydrides.

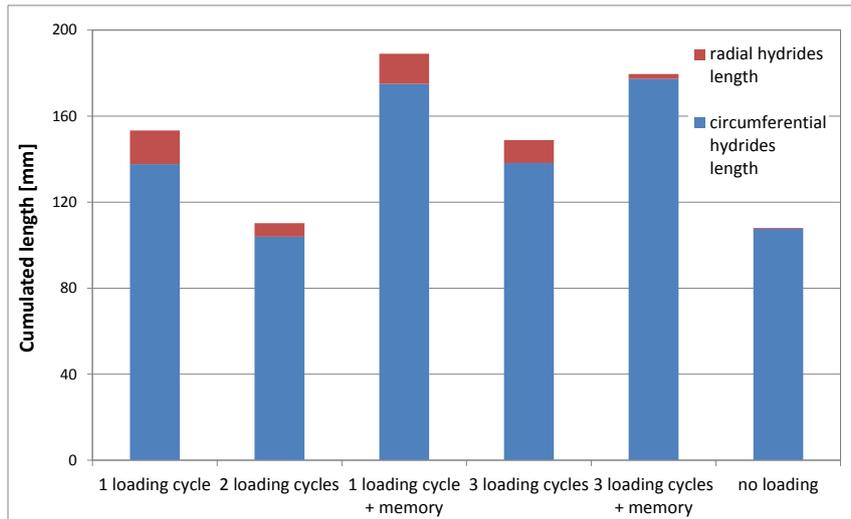


Figure 6: cumulated length of radial and circumferential hydrides for the different conditions.

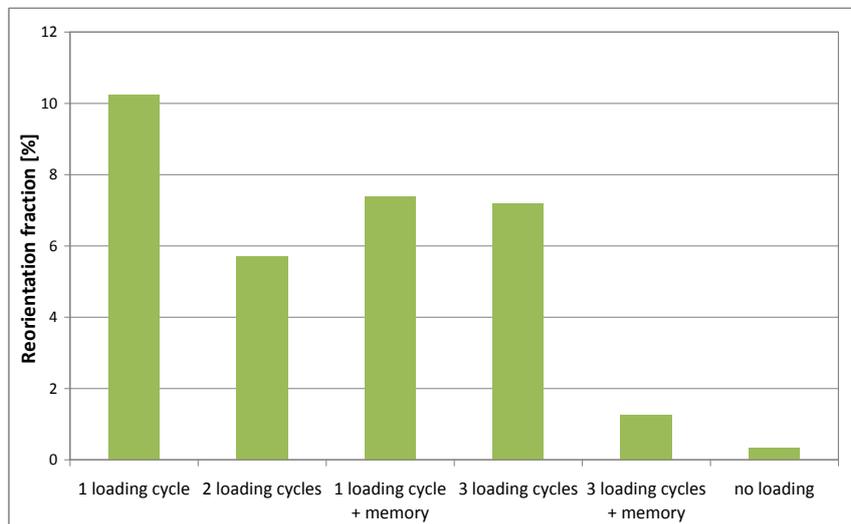


Figure 7: reorientation fraction for the different types of loading.

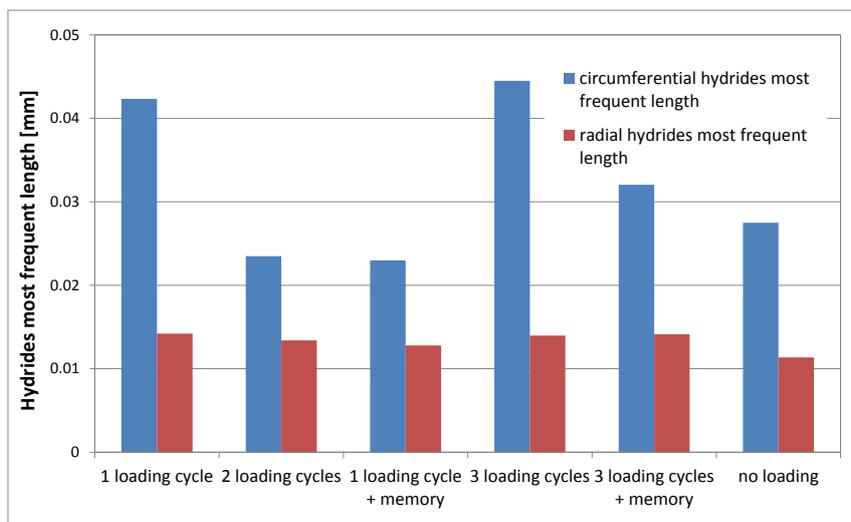


Figure 8: hydrides most frequent length as a function of the loading type.

The overall reorientation fraction obtained during these tests is presented on Figure 7. For the sample which did not undergo any mechanical testing, almost no radial hydrides were observed. Evolution of reorientation fraction with respect of number of loading cycles is rather unexpected when comparing with usual results where the reorientation fraction increases as a reason of the number of cycles. However, the comparison of Figure 7 with Figure 6 leads to the observation that with decreasing cumulated hydrides lengths the fraction of radial hydrides decreases, for both, the loadings with and without thermal cycle at the end, respectively.

In concrete:

- (a) order of decreasing accumulated hydrides lengths: 1 cycle → 3 cycles → 2 cycles
 order of decreasing reorientation fraction: 1 cycle → 3 cycles → 2 cycles
- (b) order of decreasing accumulated hydrides lengths: 1 cycle + thermal cycle → 3 cycles + thermal cycle
 order of decreasing reorientation fraction: 1 cycle + thermal cycle → 3 cycles + thermal cycle

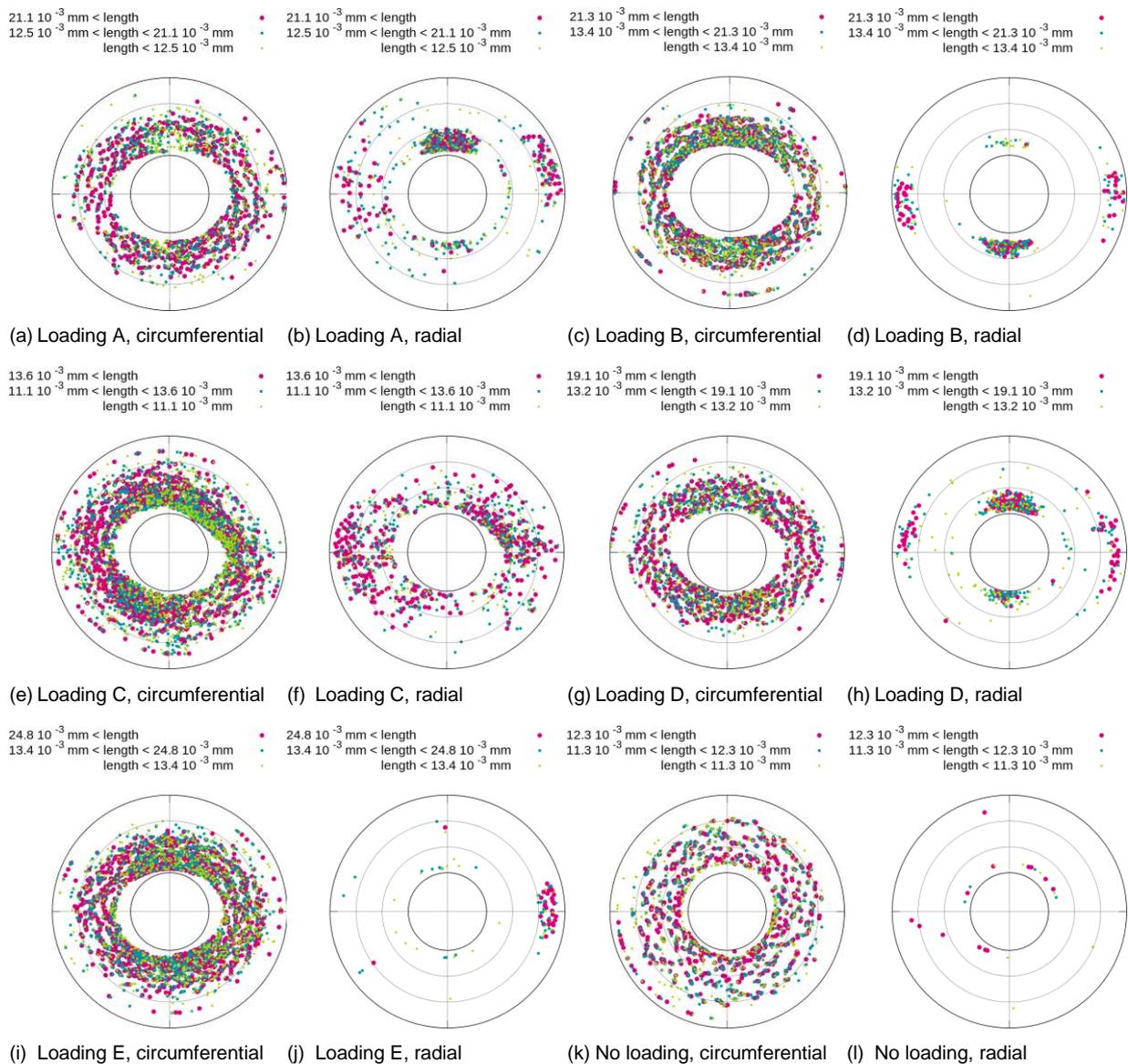


Figure 9: location of hydrides in circumferential and radial orientations as a function of the loading type. Tensile direction is horizontal. Radial scale is magnified.

Good news is that a thermal cycled at the end of the reorientation tests appears to lower the fraction of reoriented hydrides: in the 1 loading cycle case by 27% and in the 3 loading cycles case by 82%, respectively. While the most frequent hydride length for the different loading types varies significantly for the circumferential hydrides, Figure 8 shows that in this respect there is practically no change for radial hydrides.

The location of hydrides is depicted on Figure 9. As can be expected, radial hydrides can be found mostly in the areas that were submitted to a tensile stress during the test. The use of a memory cycle after one loading cycle results in a more homogeneous distribution of the radial hydrides in the cladding tube section.

The pictures in Figure 10 underline the un-complete understanding of the potentially different hydrides contents in the samples. One could tend to make the statement that hydrides which are lacking in the non-liner material should be located in the liner. But: in Figure 10 the left picture (reference sample without any cycle) reveals lower hydrides densities in both the cladding and in the liner material compared to the middle and right picture (both from the 1 cycle sample); there is no cladding/liner reciprocity. The pictures in the middle and on the right side are both from the same sample, but exhibiting different areas with higher stresses at the inner and outer side of the cladding. The zones of different stresses arise due to the loading set-up. The two pictures on the middle and the right side are representative for the observation that

- (1) higher stresses at the outer side do not only create radial hydrides close to the liner as well as in the liner, but also a general higher density of hydrides in the liner; whereas
- (2) higher stresses at the inner side of the cladding promote radial hydrides at this place, and the liner shows a lower density of hydrides; the central vein of the liner on the right picture is almost hydrides free.

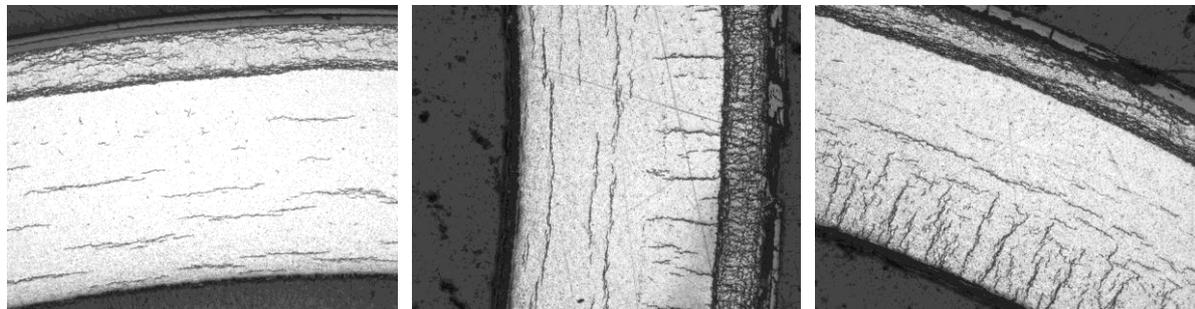


Figure 10: Hydrides densities – no loading cycle (left), 1 loading cycle with stress concentration at outer side of cladding (middle) and same sample with 1 loading cycle with stress concentration at inner side of the cladding

4. Conclusions

This paper addresses the testing of irradiated cladding tube samples of Zry-4 type with outer liner with respect to hydrides reorientation. 5 samples were submitted to various types of loading to assess the effect of thermo-mechanical and thermal loading on the fraction of reoriented hydrides.

The described results do not allow complete conclusions, because of indications that the hydrogen content of the test samples varied. It is speculated that the origin of the variations may also be linked with the outer liner of the cladding which has not been considered in the quantitative analyses. For instance, it is probably a consequence of that situation that the overall fraction of reoriented hydrides as a function of the number of loading cycles did not rise as would have been expected from previous tests on irradiated Zry-2. Therefore further investigation efforts are necessary.

However, an important effect could consistently be found: Cladding samples that were submitted to an only thermal loading after thermo-mechanical loading showed a lower reorientation fraction. This means that stress-less temperature cycles after unloading conditions with potential hydrides re-orientation seem not to present an additional risk factor, but may rather have a beneficial effect. However, the limit conditions –hydrogen concentration, hydrides distribution, temperature evolution and again the role of the liner– for such an effect would need further clarifications.

5. Acknowledgement

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6. References

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