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QUANTIFYING THE STRESS FIELD OF HYDRIDE PRECIPITATION BY μXRD TOMOGRAPHY

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ABSTRACT*: During the operation of a light water reactor, the cladding tube containing the fuel pellets, and which is made of a zirconium alloy, absorbs part of the hydrogen present in the reactor coolant. The hydrogen has been created at the hot cladding surface. When the hydrogen concentration surpasses the terminal solid solubility in the cladding, hydrides are formed. These hydrides could have severe impact on the mechanical properties of the fuel rod, and are thus safety relevant. The accommodation of the volumetric strain associated with the hydride precipitation is still an unclear issue. The strain field around hydrides is a key parameter, e.g. for hydrogen diffusion towards existing hydrides, hydrides growth and to model delayed hydride cracking (DHC) and hydrides reorientation, both of which being typical hydrogen-related degradation. In this study, we took advantage of the cutting edge development of the 3D micro-X-ray-diffraction tomography platform at the microXAS beamline (SLS, PSI) to visualize hydrides in zirconium alloy pillars with a diameter of approximately 35μm and a length of 100 μm, these dimensions being sufficient to prevent any stress release triggered by small size sample FIB milling. The use of a micro-beam combined with tomography measurements provides a XRD resolution scarcely achieved for the determination of respective strain fields. Up to now, four different samples taken from a Zircaloy-4 RX (recrystallized) plate hydrogenated to ~150 wppm H have been prepared and investigated, exploring various cooling rates during hydrides precipitation, potentially related to different scenarios in the cladding tube-end-of-cycle and compared to a reference H-free sample. Today, the complex 3D reconstruction based on the XRD data could not yet been completely achieved; thus, in this work, we present the project progress, from the specific sample preparation by Xe-plasma-FIB, to the first steps of the polycrystal Laue pattern processing leading eventually to the 3D reconstruction, via the description of the peculiar experimental set-up and data recording at* the *microXAS* beam line.

KEYWORDS*: hydrides, strain field, XRD tomography, Zircaloy-4*

I. INTRODUCTION

Hydrogen in zirconium alloy cladding tubes is one of the most important topics discussed nowadays in the nuclear scientific community in terms of safety (LOCA relevance), performance (for example reaching higher burn-up) and post-operation handling, transportation etc. In this study, we focus on the strain field induced by the precipitation of hydrogen in the cladding matrix. While the strain effect of hydrides in a more integral way has already been part of research (e.g. [1]), the 3D resolution of strain around – in an optimal way individual hydrides – is new. Strain measurements at this scale are generally a strong experimental challenge because the preparation of adapted, tiny samples suitable for in volume probing typically induces stress release. Moreover, computations show an only very localized small strain around hydride platelets (Figure 1). Another challenge is the reconstruction of the data to a 3D picture: due to the unusual pseudo-Laue diffraction indexation processing and the difficulty of the complex reconstruction, at this stage the present work can only deliver an update of the current progress.

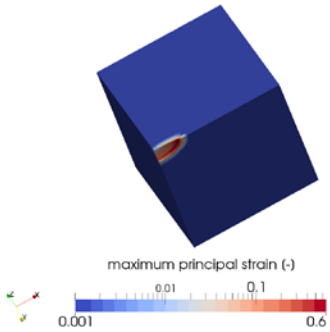

Fig. 1. Strain field computations for an inclusion of hydride of 1 x 4 x 8 μm^3 in a matrix of 40 x 40 x 40 μm^3.

The use of the advanced technique of micro-X-ray diffraction (XRD) tomography available at the microXAS beamline of SLS allows meeting these experimental challenges, first by probing samples large enough and then by using a sub-micrometric beam for resolved spatial resolution.

II. EXPERIMENTAL METHODS

I.A. Sample preparation

Four samples were prepared from a recrystallized Zircaloy-4 plate. Cut pieces were hydrogenated to 170 wppm at 400°C during 10h. Two cooling rates were applied: the "normal-cooling" at 10°C/hour, and the "slow-cooling" at 0.3°C/hour. The slow cooling conditions should lead to longer hydrides with a higher thermo-dynamical stability in respect to the embedding into the matrix.

The identified requirements to fulfill the study goals are: sample thick enough to avoid any stress release, ensuring the presence of hydrides platelets, suitable for tomographic measurements and preparation in a reasonable time. The best geometry is a pillar of 30-40 μm in diameter and 100 μm in length that were prepared thanks to the Xe plasma FIB of the ScopeM facility (ETH Zürich) (Figure 2). Two orientations of the hydride platelets were tested for a validity qualification of our method, that are platelets parallel to the long pillar axis, and perpendicular.

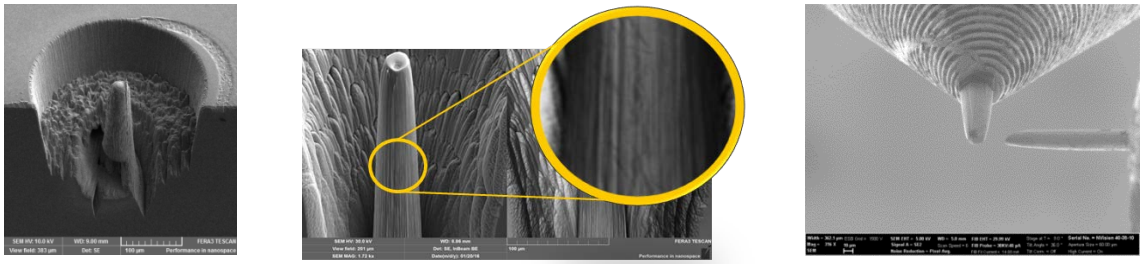

Fig. 2. SEM images of pillar preparation at the edge of a sample piece and hydrides (left and middle). Right: lift-out and transfer of the pillar on the Cu-pin sample holder suitable for the tomographic set-up, performed at the EMF platform (PSI).

I.B. Micro-XRD tomography measurements

Micro-XRD tomography measurements were performed at the microXAS beamline (Figure 3) of the SLS using a sub-micrometric beam of 0.9 x 0.9 μm^2 permitting the spatial resolution required to distinguish hydrides from Zr-grains of 4-5 μm size. X-ray diffraction patterns were acquired in the transmission mode along the entire lateral sample size, at several X positions (horizontal) equally spaced by 0.5 μm (necessary to obtain all crystal positions at one theta orientation), and over 90 azimuthal orientations equally spaced by 2° (Figure 3). The marCCD detector was chosen for its high pixel resolution to obtain the required accuracy on d-spacing though necessitating a longer acquisition time. In these conditions, a slice could be

measured in 10-12 hours. For each sample, 4-5 slices were recorded at various vertical positions probing regions with or surrounding hydrides grains.

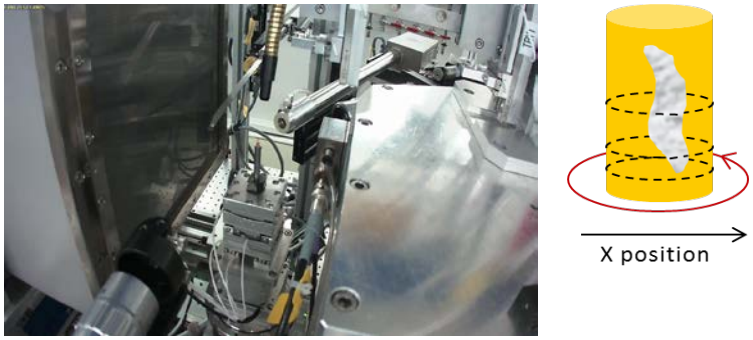

Figure 3: Experimental set-up at the microXas beamline (SLS) and sketch of the XRD tomography measurements.

III. PRELIMINARY RESULTS

Figure 4 displays two XRD patterns representative of the reference H-free sample and the normal-cooling sample. Strained grains are clearly identified in the normal-cooling sample pattern by elongated spots, whereas the H-free sample pattern exhibits an almost ideal grain Laue pattern. The diffraction streaks already indicate a strong disturbance of the crystallinity by strains and / or dislocations. Figure 4 also shows an integrated 1D pattern of an average of 600 patterns. Peaks related to hydrides could be successfully indexed. They tally to the δ-polymorph of hydride as expected in such conditions of temperature and cooling.

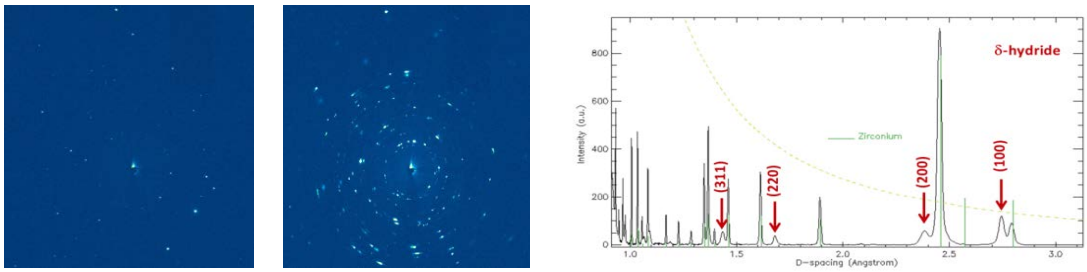

Fig.4. Left and middle: Representative 2D patterns of the reference H-free sample and normal cooling sample showing strained grain typical features, respectively. Right, indexed integrated 1D pattern.

Further analysis is in progress. Residual strains will be extracted for each individual Zr-grain from the deviation of lattice parameters from the reference stress-free specimen containing no hydrides. This requires the development of an analysis method indexing polycrystal micro-Laue diffraction patterns recorded with a monochromatic beam. There is no standard method to our knowledge for the analysis for micro scanning XRD tomography of polycrystalline materials (with grain sizes a few times bigger than the beam spot size) using monochromatic radiation. The development of a computational method based on similarities on spot shape and position assuming they belong to a same unique grain has been started, similarly as described for white beam analysis in Ref.[2]. This approach allows resolving spatial grain position as well as their size and shape. Ultimately, the goal of the ongoing analysis is to obtain also the spatially resolved stress and correlate it with the spatially resolved hydride distribution.

IV. SUMMARY AND CONCLUSIONS

We present here an update of an original experimental method to obtain spatially resolved strain fields in zirconium alloy grains surrounding hydrides. Data are still being processed. The residual lattice strain profile with a sub-micrometric resolution will be deduced from the measured deviations of the Zircaloy lattice parameters. Tomographic XRD measurements and subsequent 3D reconstruction analysis will eventually resolve hydrides (size, shape, orientation and strain)

as well as provide its surrounding strain field in a sample hydrogenated and cooled under various conditions. This study shall help to better understand the interplay between hydrides and the cladding matrix. The presented method has the potential to help further clarifying the following aspects

- the local conditions for hydrides precipitation,
- the diffusion of hydrogen in a strained matrix due to already existing hydrides,
- hydrides formation in a pre-damaged matrix,
- the 'memory effect' where hydrides re-precipitate at prior hydrides sites, or
- hydrides reorientation.

The outcome of the work may have relevance for spent fuel handling, intermediate dry storage and transportation.

ACKNOWLEDGMENTS

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REFERENCES

1. Blackmur, M. S. *et al.* Strain evolution during hydride precipitation in Zircaloy-4 observed with synchrotron X-ray diffraction. *J. Nucl. Mater.* **474,** 45–61 (2016).
2. Ferreira Sanchez, D. *et al.* X-ray micro Laue diffraction tomography analysis of a solid oxide fuel cell. *J. Appl. Crystallogr.* **48,** 357–364 (2015).