Karlsruhe Institute of Technology

Institute for Applied Materials

Microstructure and mechanical properties of Zircaloy-4 claddings hydrogenated at temperatures typical for LOCA conditions

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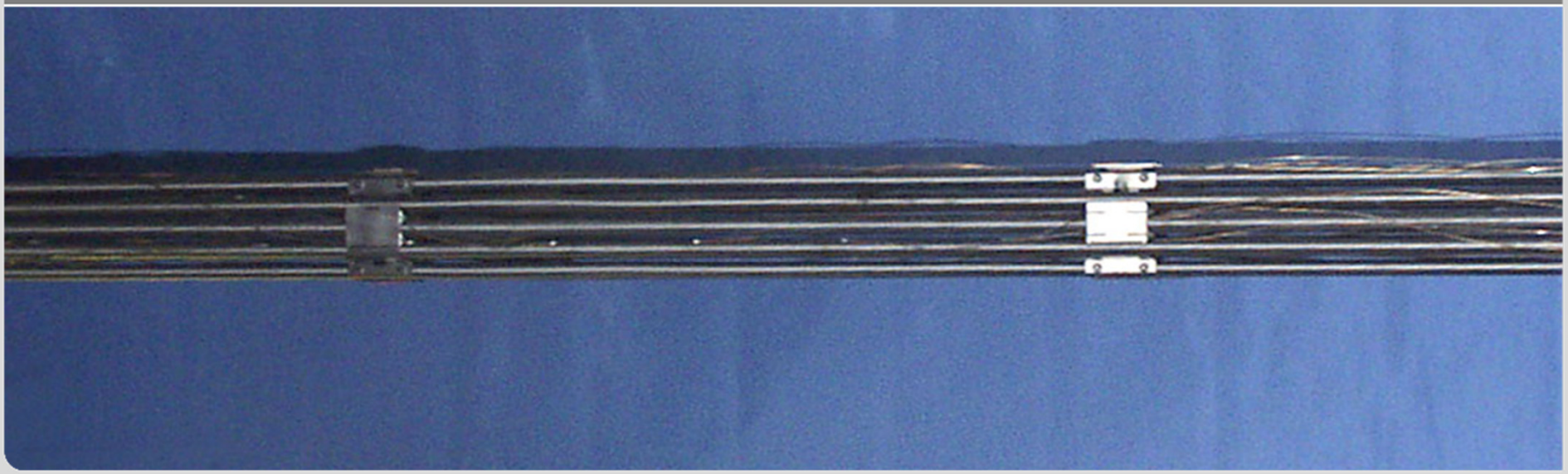
Institute for Applied Materials, IAM-WPT, Program NUKLEAR

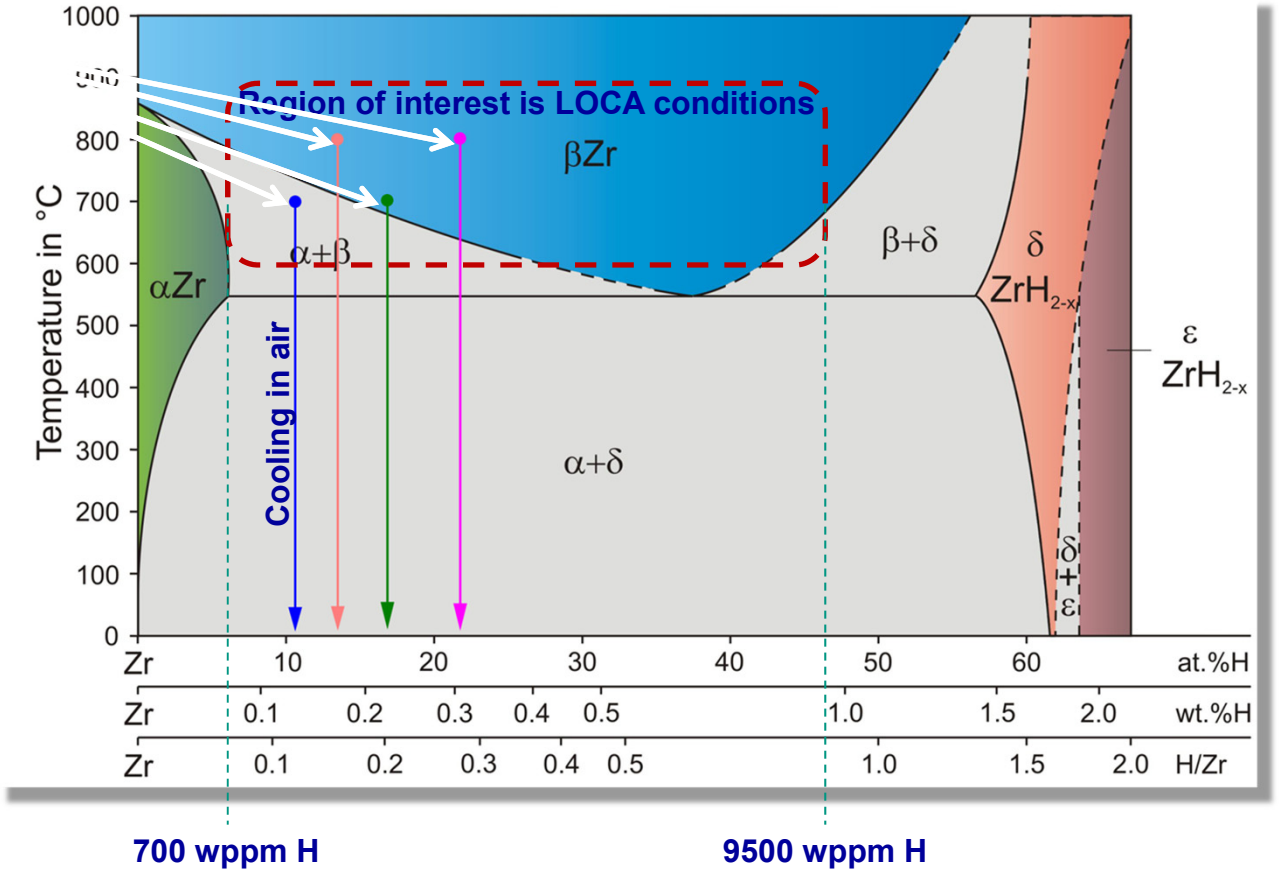


Objectives

- Structure assessment of annealed and hydrogenated specimens
- Fracture surface investigation
- Zirconium hydrides detection
- Progress in understanding the mechanism of embrittlement of Zirconium alloys
- Application to the results of QUENCH-LOCA test

Equilibrium phase diagram of Zr-H system*

selected examples of our tests



* According to E. Zuzek et al., Bull. Alloy Phase Diagr. (1990), 385

Material and methods of investigation

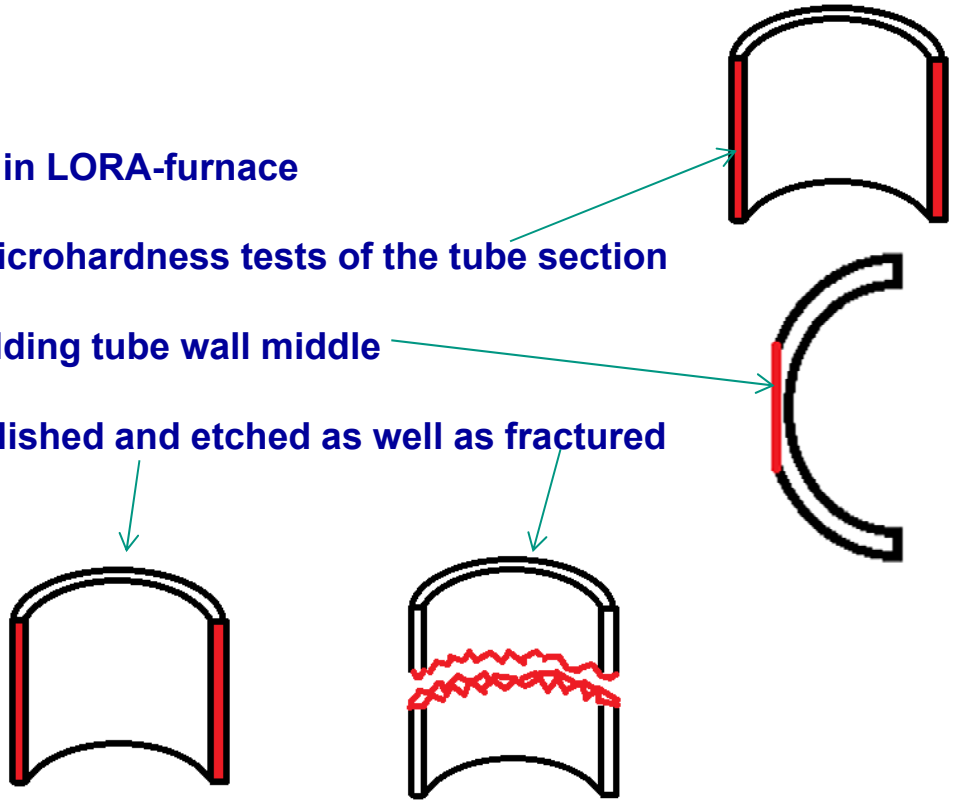
Material: Conventional Zircaloy-4 cladding tube

ICP-OES measurement of Zircaloy-4 chemical composition (by weight):

Sn: 1.33±0.02%, Fe: 0.23±0.002%, Cr: 0.12±0.0003%, O: 0.116±0.003%, Zr balance

Methods of investigation:

- Hydrogenation in Ar+H_2 gas mixture in LORA-furnace
- Metallographic investigations and microhardness tests of the tube section
- X-Ray diffraction analysis in the cladding tube wall middle
- Scanning electron microscopy of polished and etched as well as fractured surfaces



Experimental procedure

Hydrogenation facility
LORA furnace

Specimen before hydrogenation

Hydrogen gas partial pressure was 0.1 bar

Specimen withdrawal in air after hydrogenation

Estimated cooling rate was 5 K/s

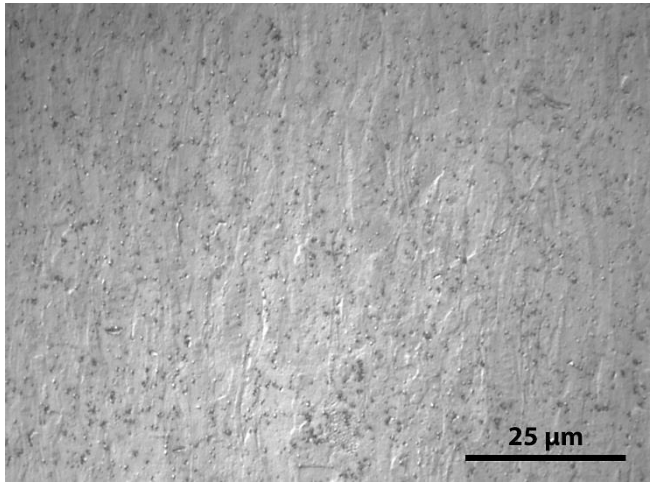
Cooled specimen after hydrogenation

H_2 duration was 2 to 12 minutes

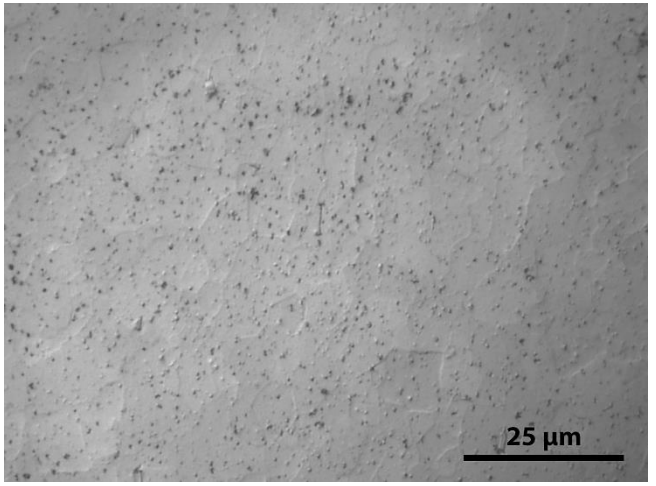
Results of metallographic observations

Optical metallography of annealed Zircaloy-4

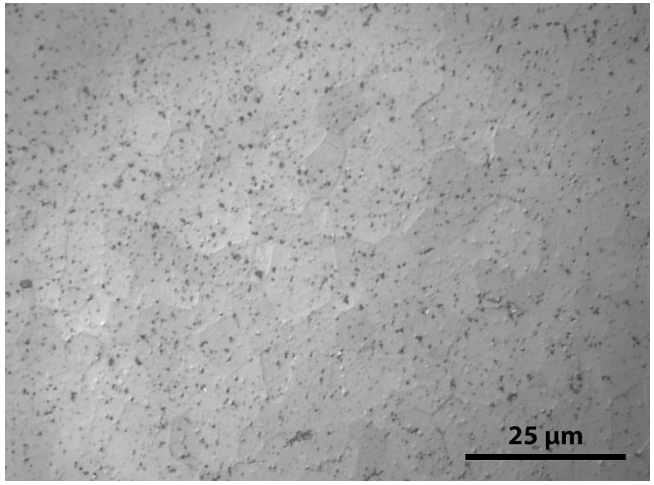
Annealing of Zircaloy-4 cladding at various temperatures during 8 minutes and fast cooling in air



As-received

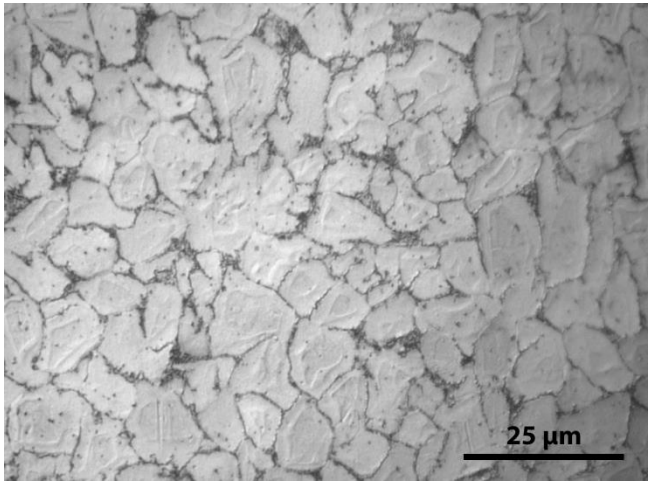


700 °C



800 °C

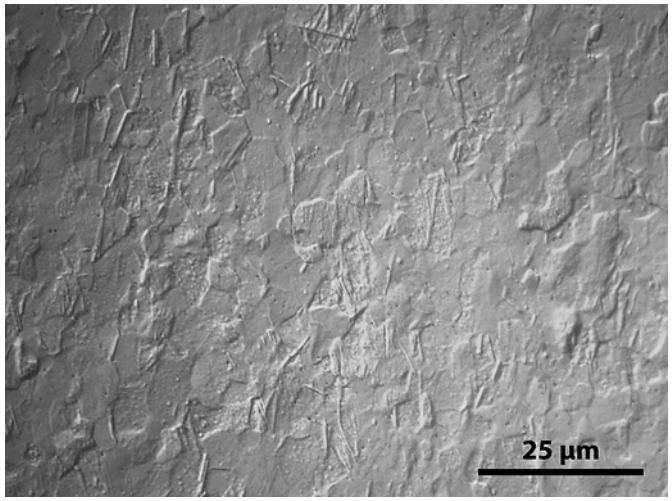
At 810 °C starts α → β phase transformation



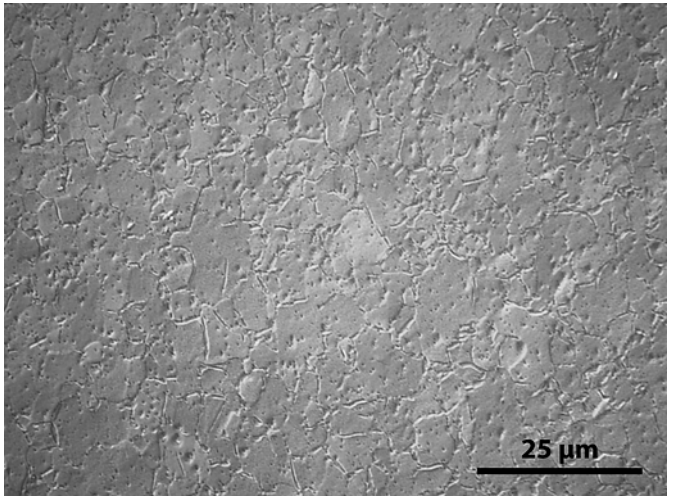
900 °C

Optical metallography of hydrogenated Zircaloy-4

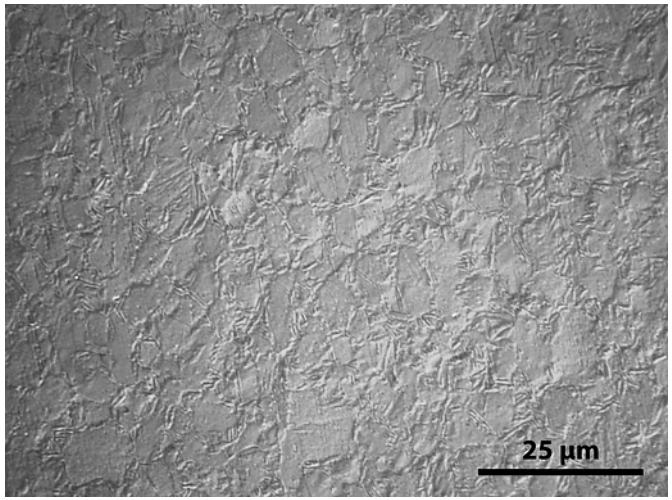
Hydrogenation of Zircaloy-4 cladding at 600 °C in Ar+H_2 mixture and fast cooling in air



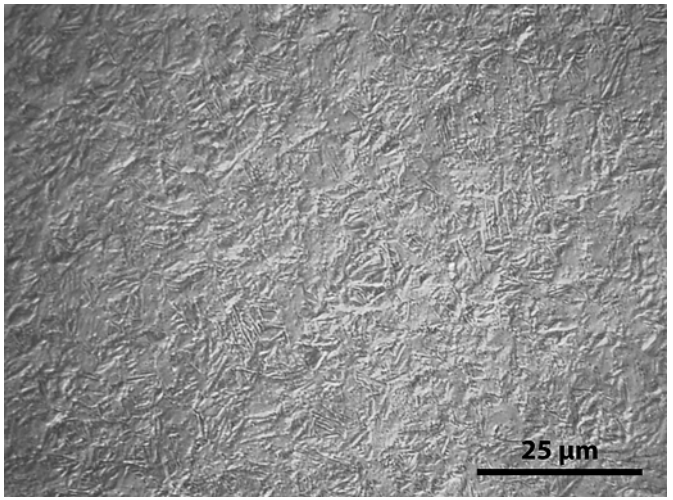
780 wppm H



1400 wppm H



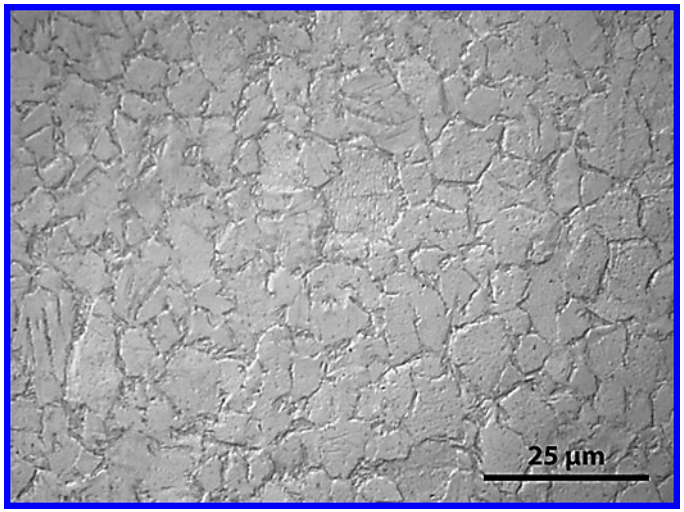
2000 wppm H



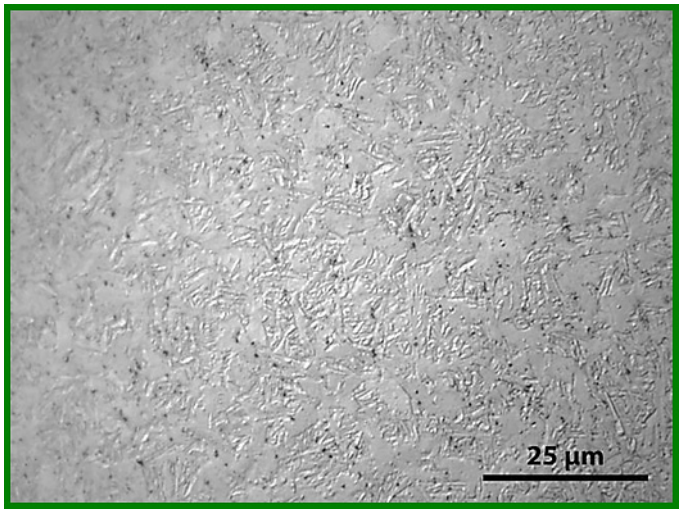
3490 wppm H

Optical metallography of hydrogenated Zircaloy-4

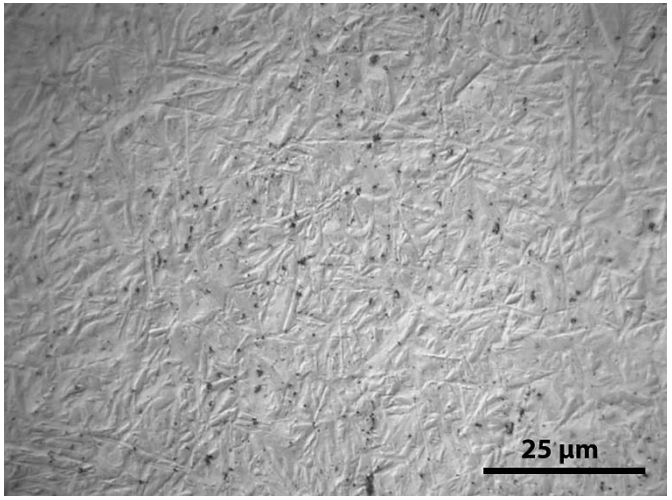
Hydrogenation of Zircaloy-4 cladding at 700 °C in Ar+H2 mixture and fast cooling in air



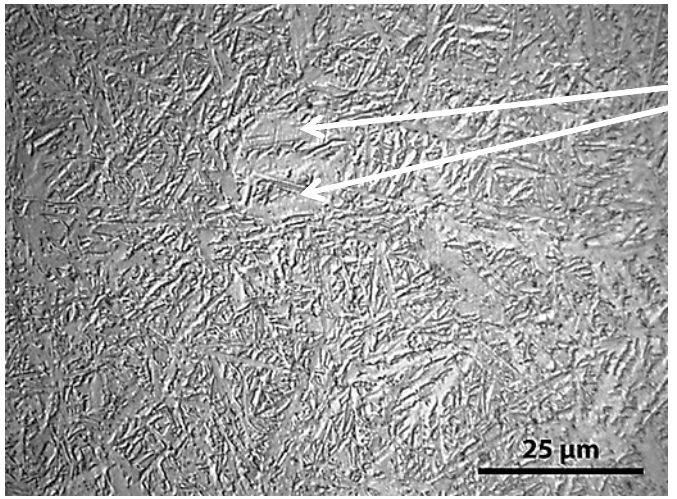
1330 wppm H



2250 wppm H



4000 wppm H

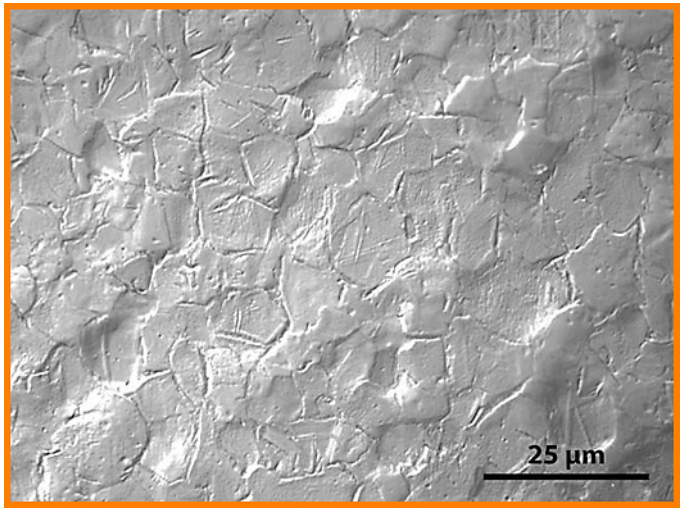


4760 wppm H

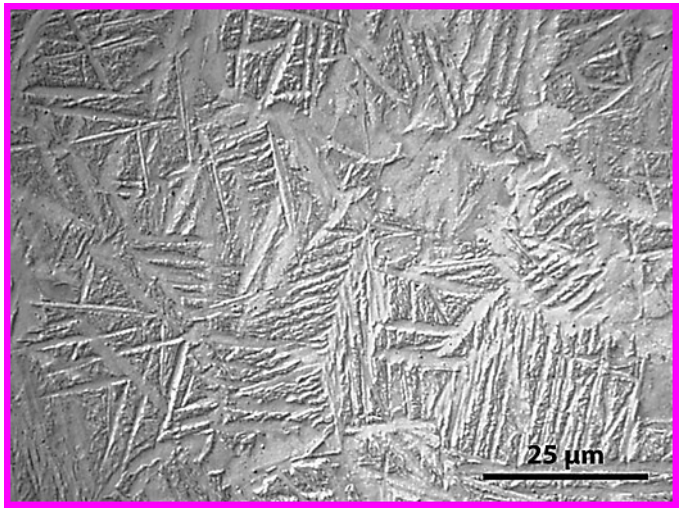
α - Zr „islands“

Optical metallography of hydrogenated Zircaloy-4

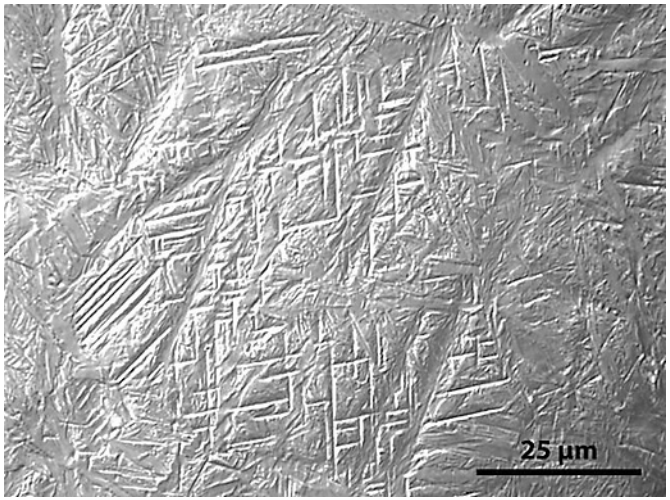
Hydrogenation of Zircaloy-4 cladding at 800 °C in Ar+H2 mixture and fast cooling in air



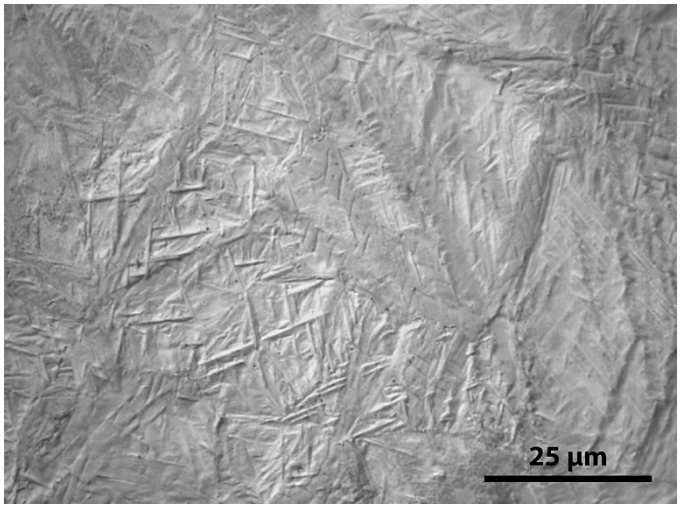
1790 wppm H



3060 wppm H



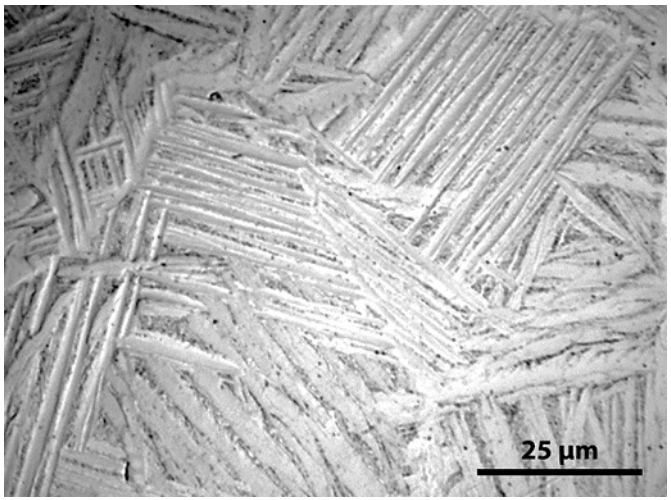
8600 wppm H



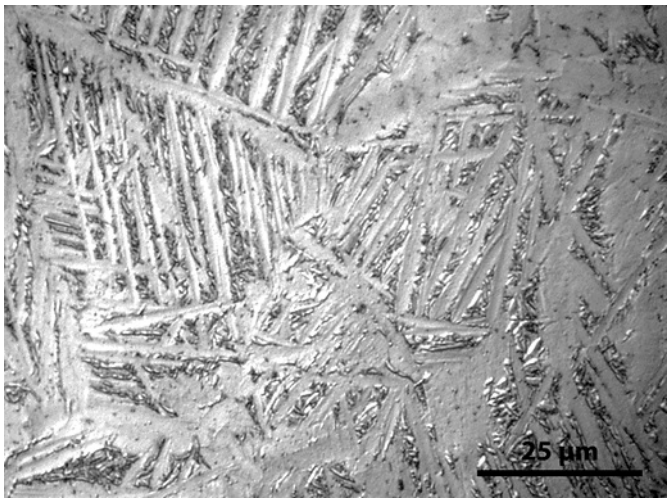
9550 wppm H

Optical metallography of hydrogenated Zircaloy-4

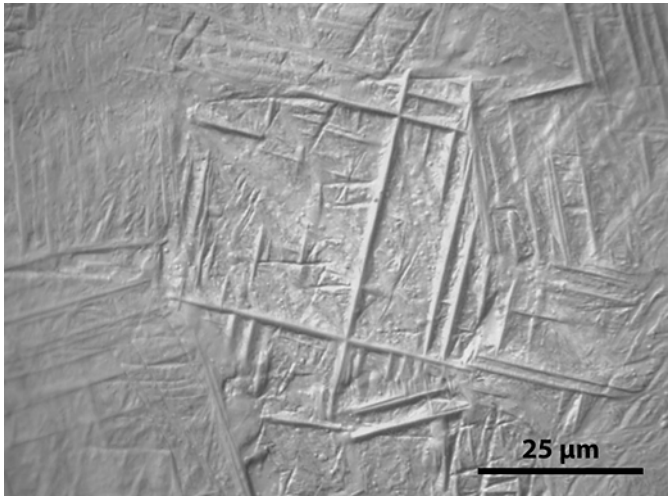
Hydrogenation of Zircaloy-4 cladding at 900 °C in Ar+H2 mixture and fast cooling in air



880 wppm H



1500 wppm H



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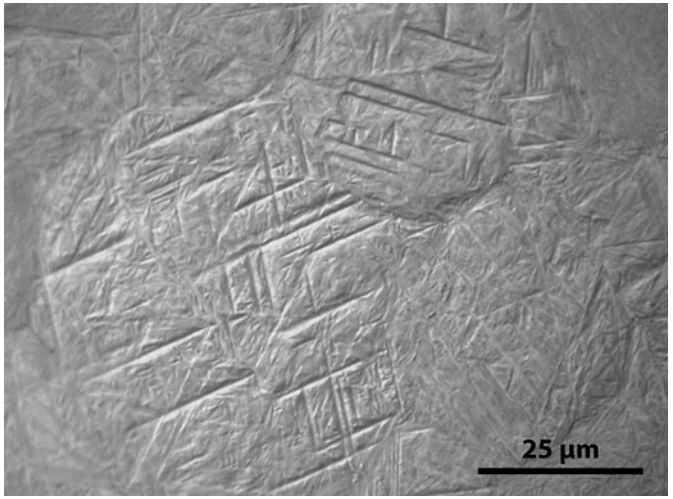
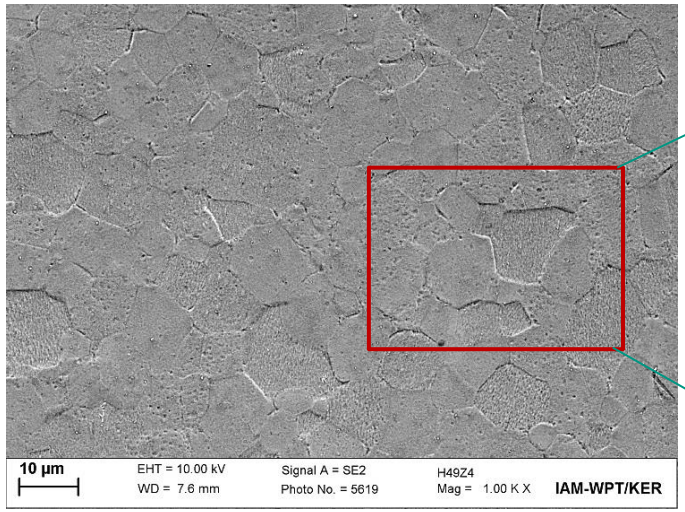


6700 wppm H

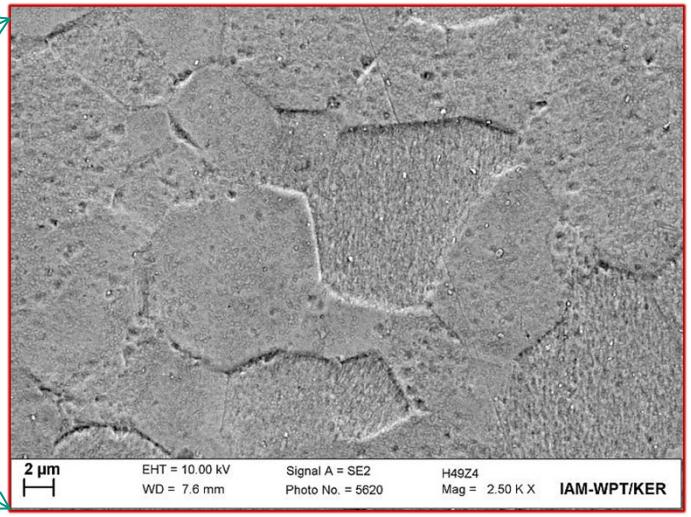
Scanning Electron Microscopy polished and etched specimens

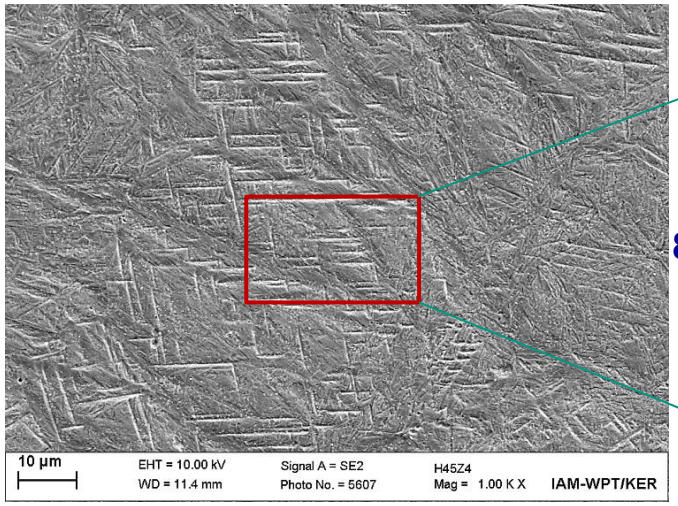
Scanning electron microscopy of annealed and hydrogenated Zircaloy-4

After polishing and etching

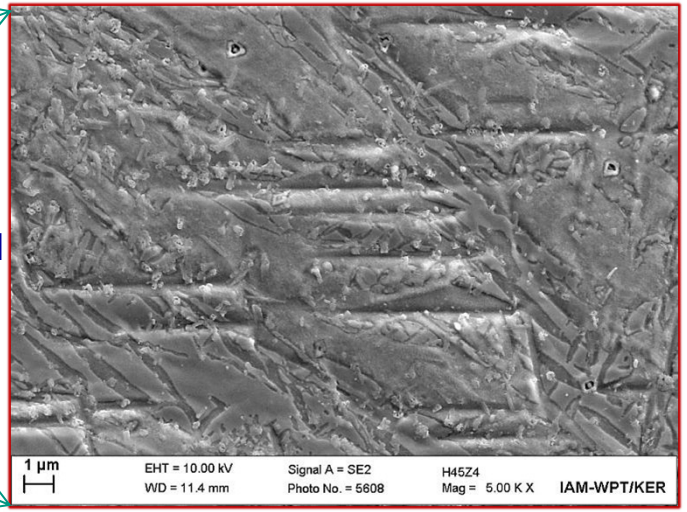


0 wppm H



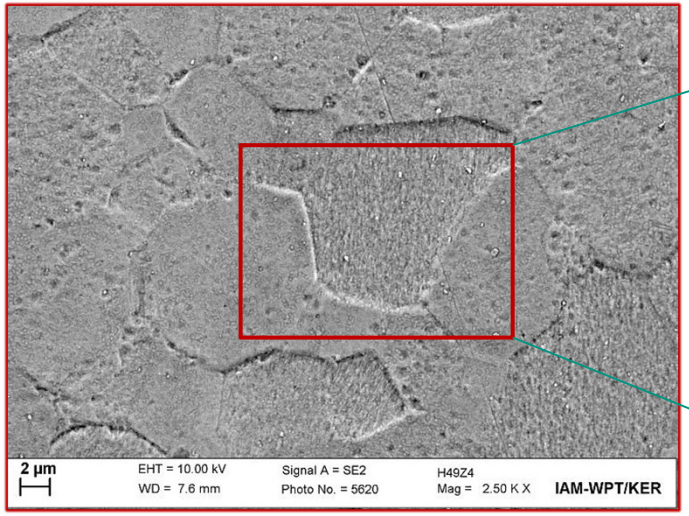


8600 wppm H

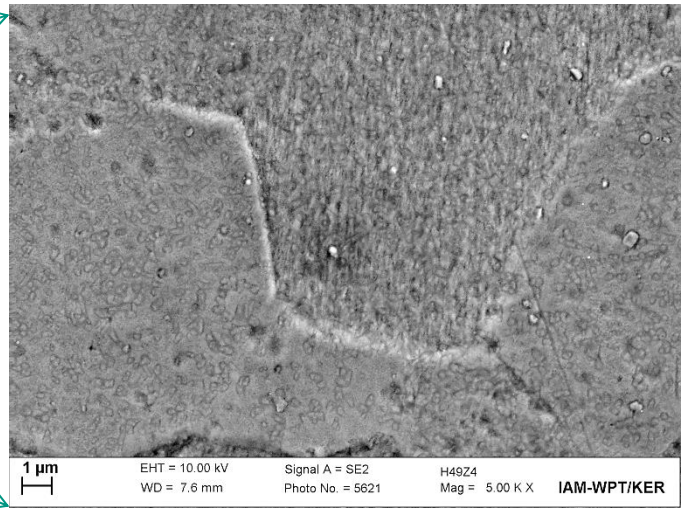


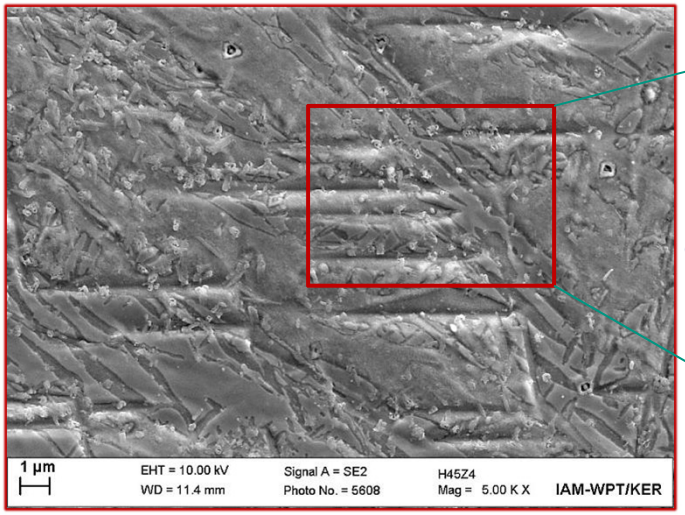
Scanning electron microscopy of annealed and hydrogenated Zircaloy-4

After polishing and etching

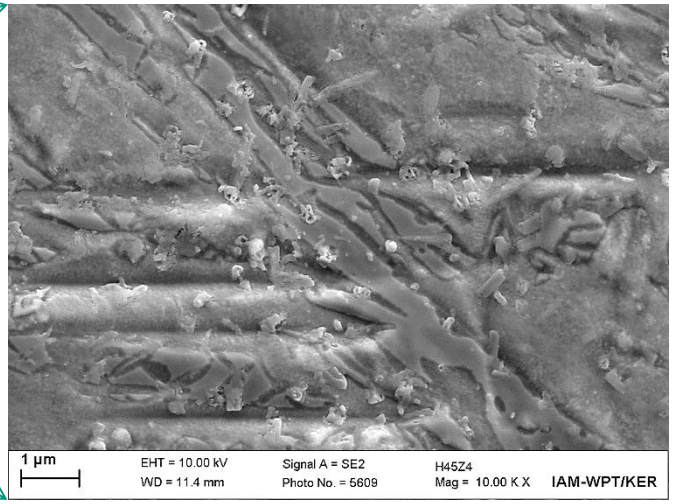


0 wppm H



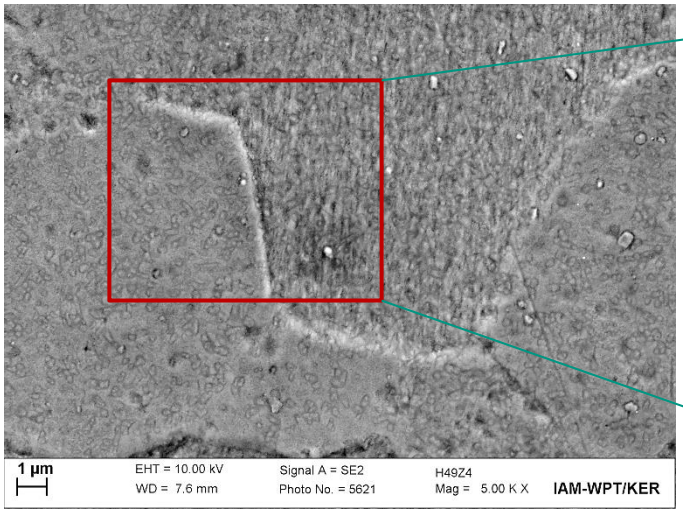


8600 wppm H

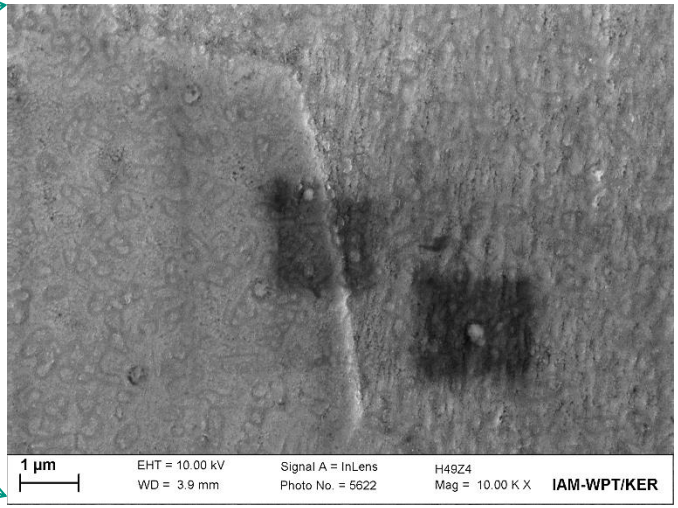


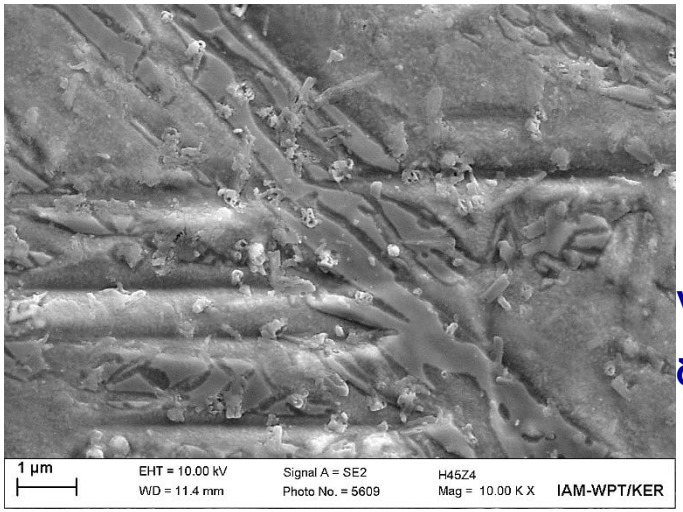
Scanning electron microscopy of annealed and hydrogenated Zircaloy-4

After polishing and etching



0 wppm H





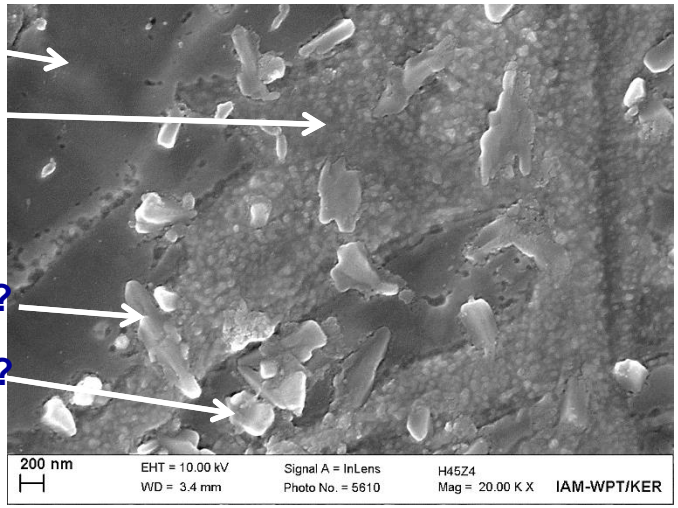
α-Zr(O)?

α-Zr (prior β phase)?

8600 wppm H

γ- Zr hydrides?

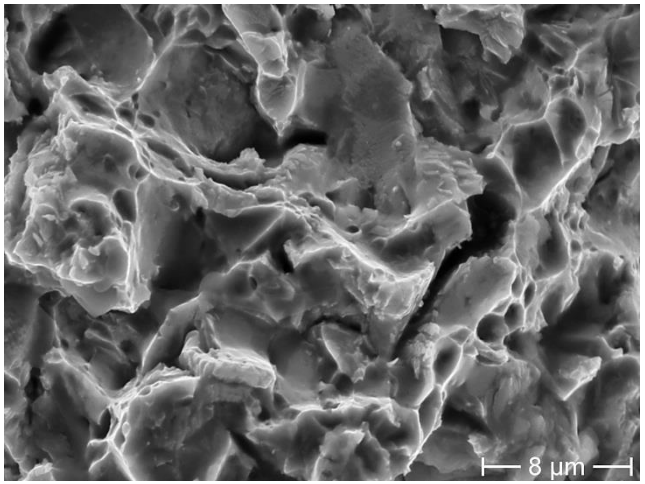
δ- Zr hydrides?



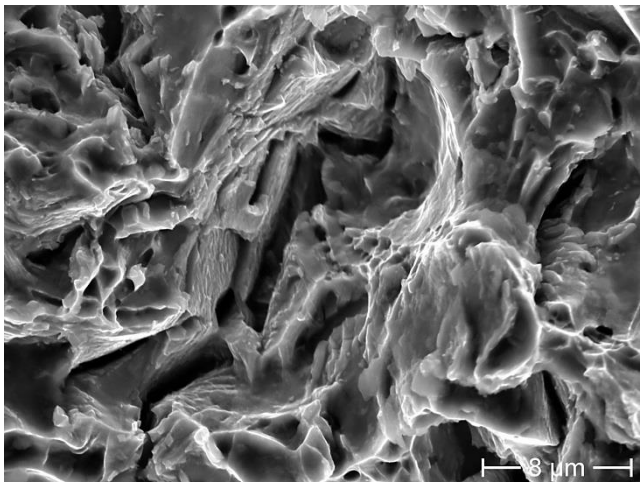
Scanning Electron Microscopy fracture surface

Scanning electron microscopy of fracture surfaces of hydrogenated Zircaloy-4

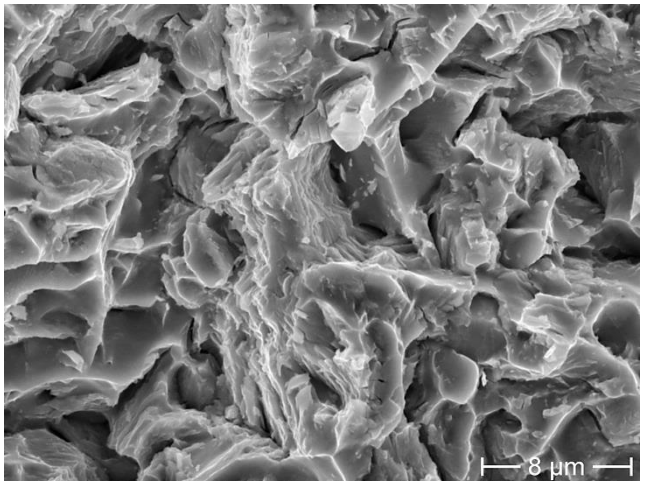
700 °C



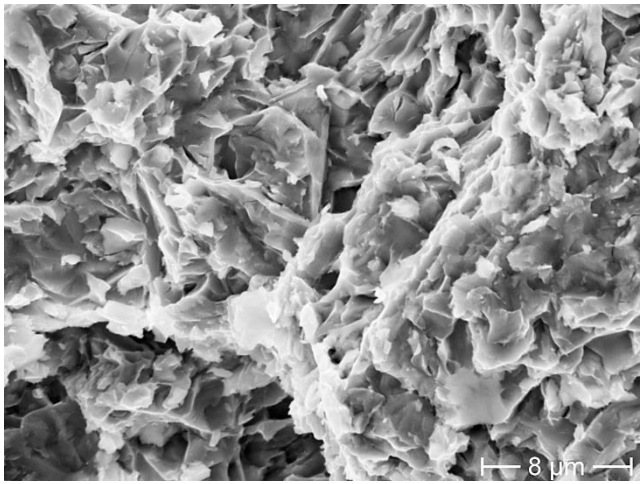
720 wppm H



1860 wppm H



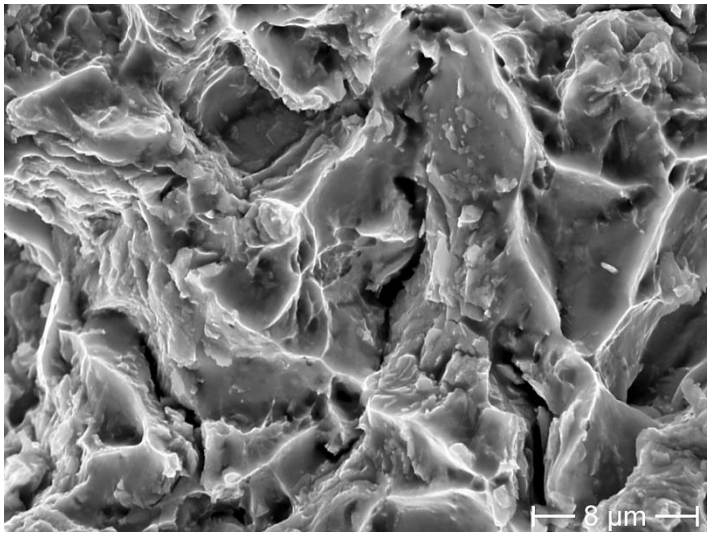
2790 wppm H



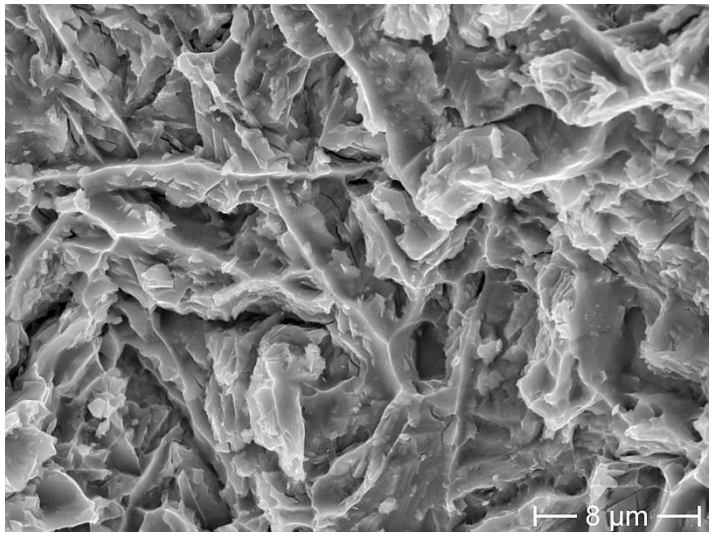
4850 wppm H

Scanning electron microscopy of fracture surfaces of hydrogenated Zircaloy-4

800 °C



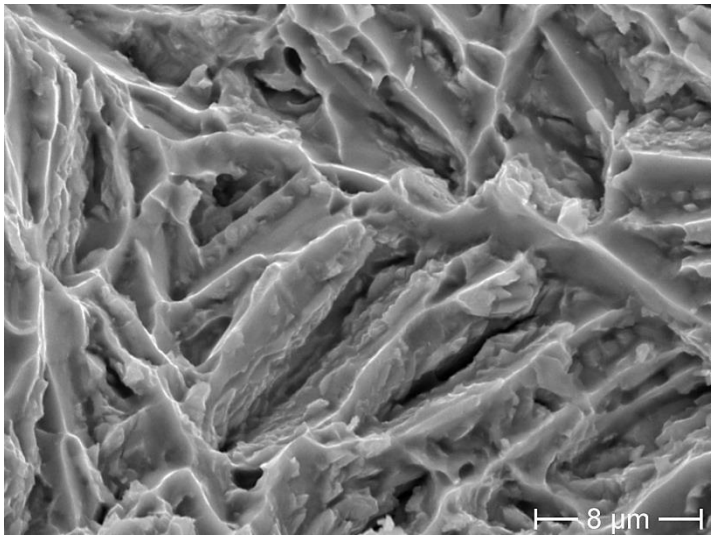
1110 wppm H

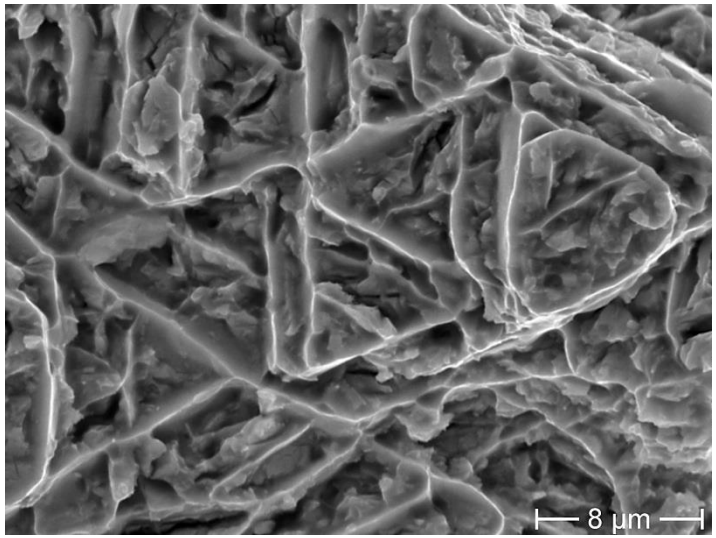


3070 wppm H

Scanning electron microscopy of fracture surfaces of hydrogenated Zircaloy-4

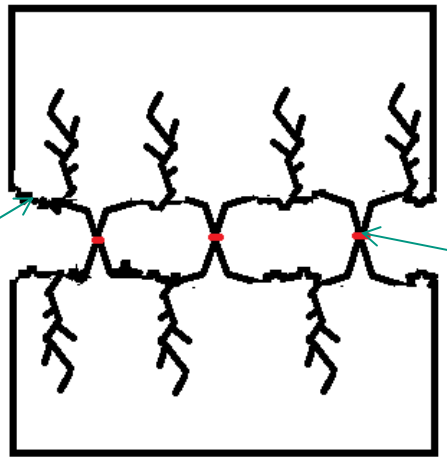
900 °C





1170 wppm H

1640 wppm H



Brittle fracture

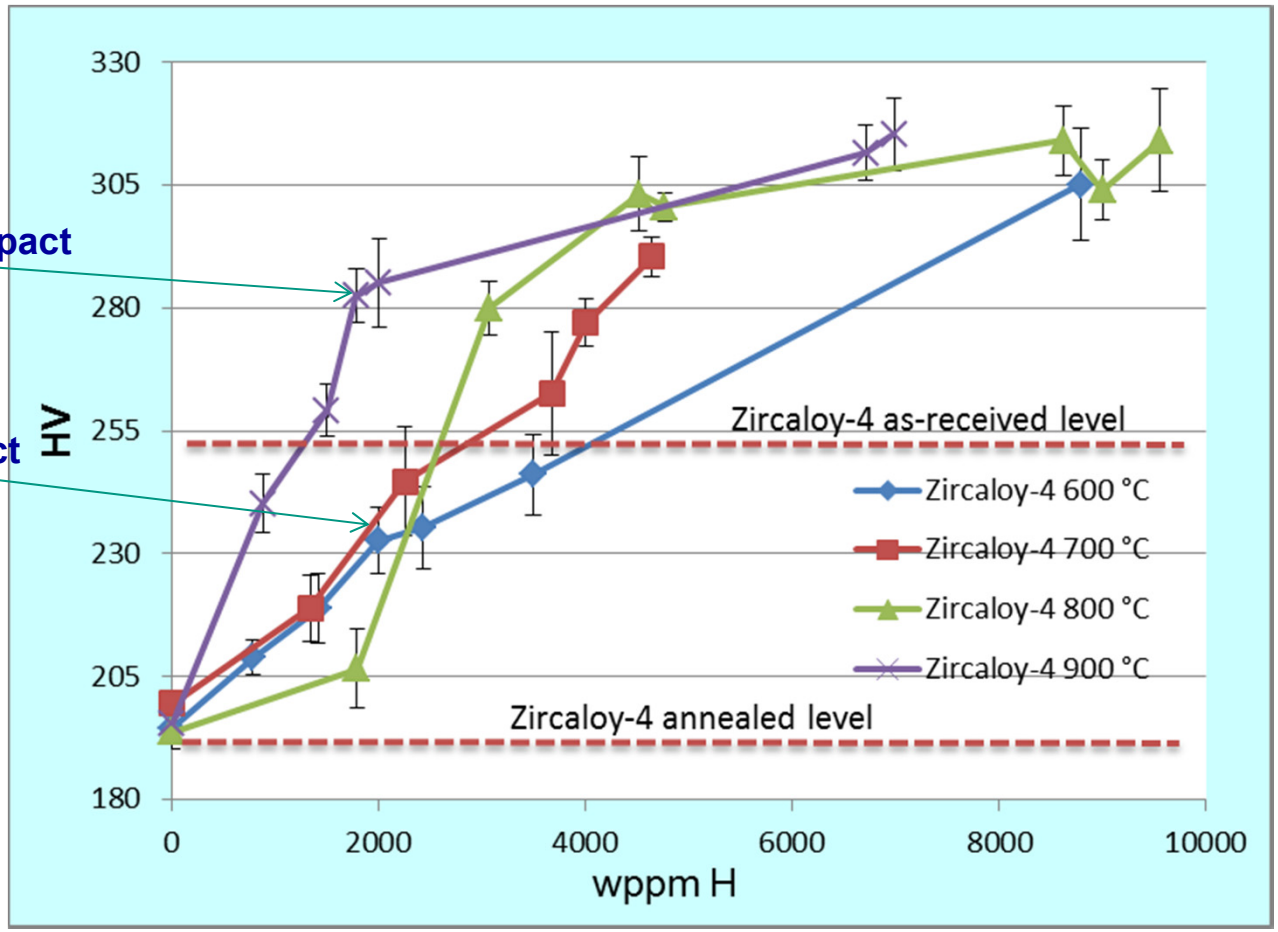
Ductile fracture on needles of α-Zr(O)

Microhardness tests

Microhardness of annealed and hydrogenated Zircaloy-4

hydrogen + T impact at 900 °C

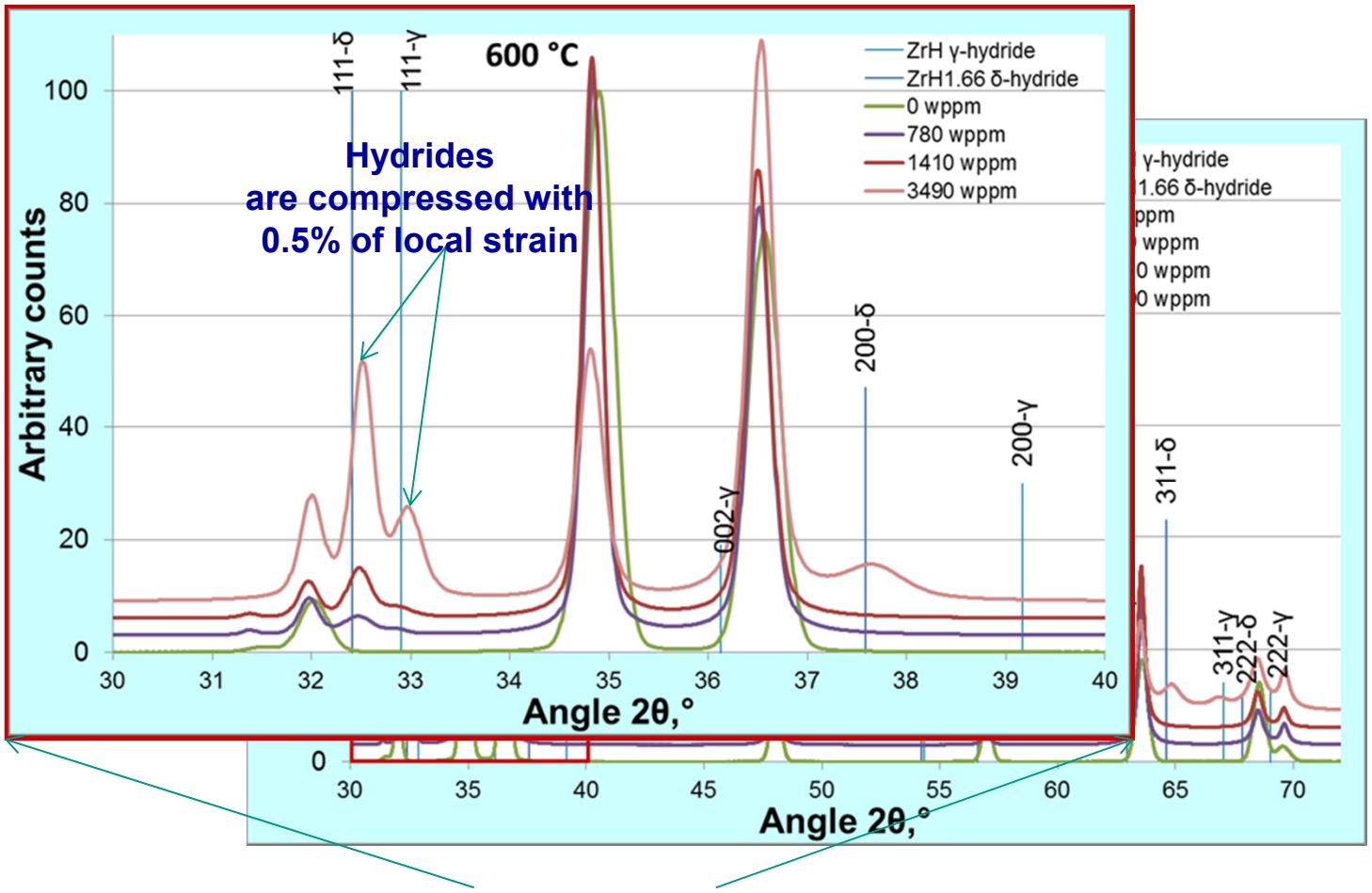
hydrogen impact at 600 °C



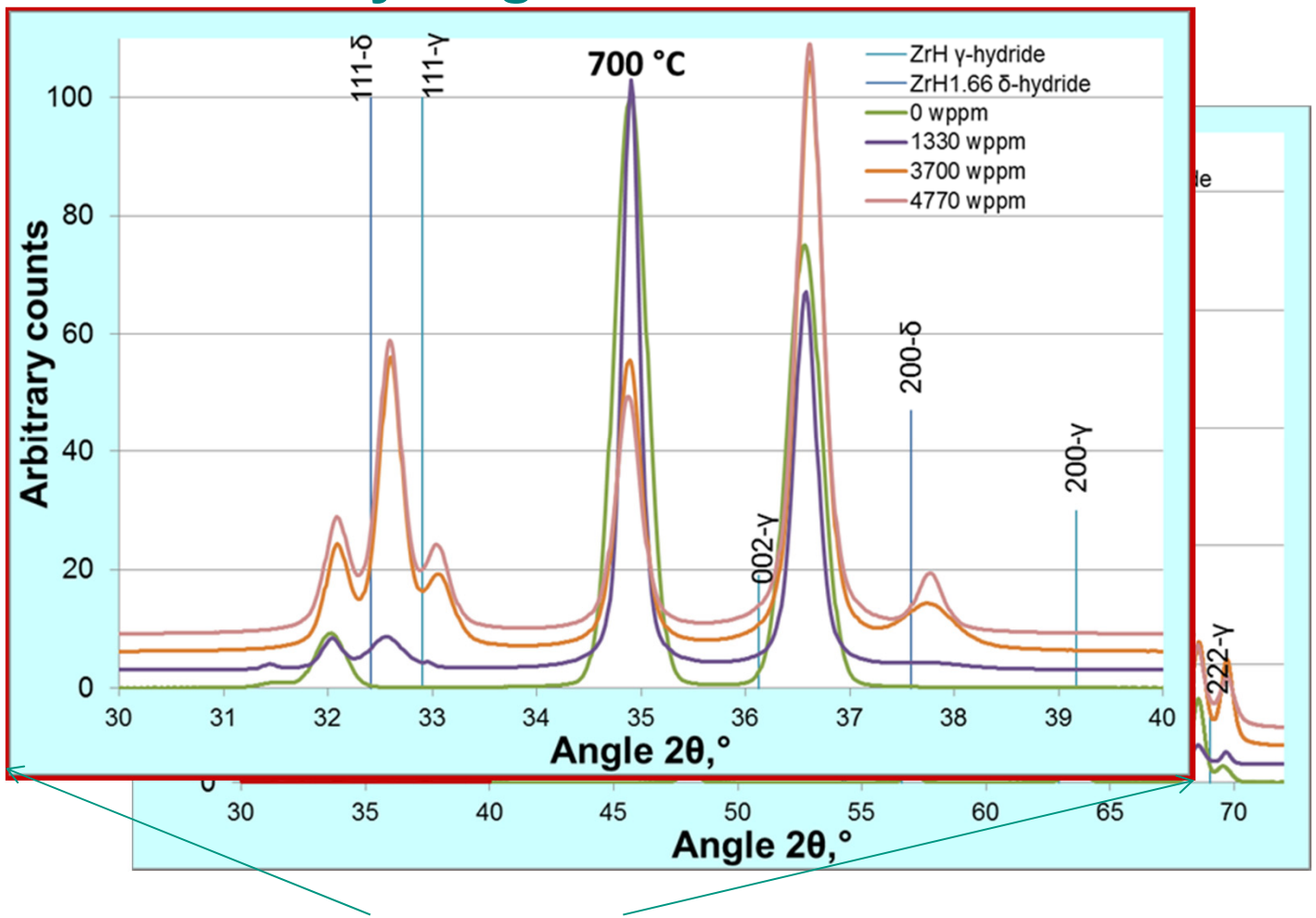
The diagonal length of resulting indented square was about 10 µm.

X-Ray diffraction analysis

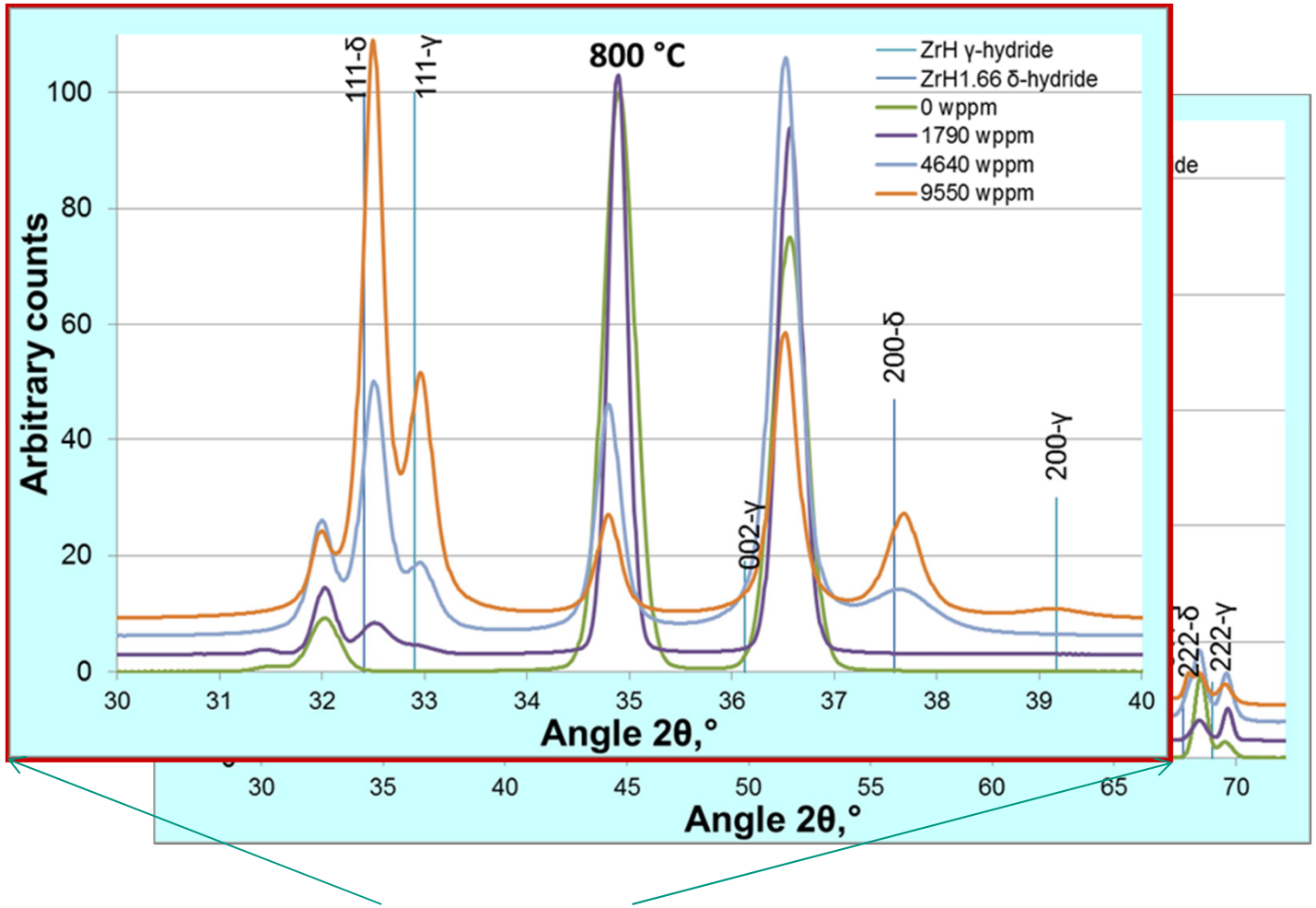
X-Ray profiles of Zircaloy-4 samples hydrogenated at 600 °C



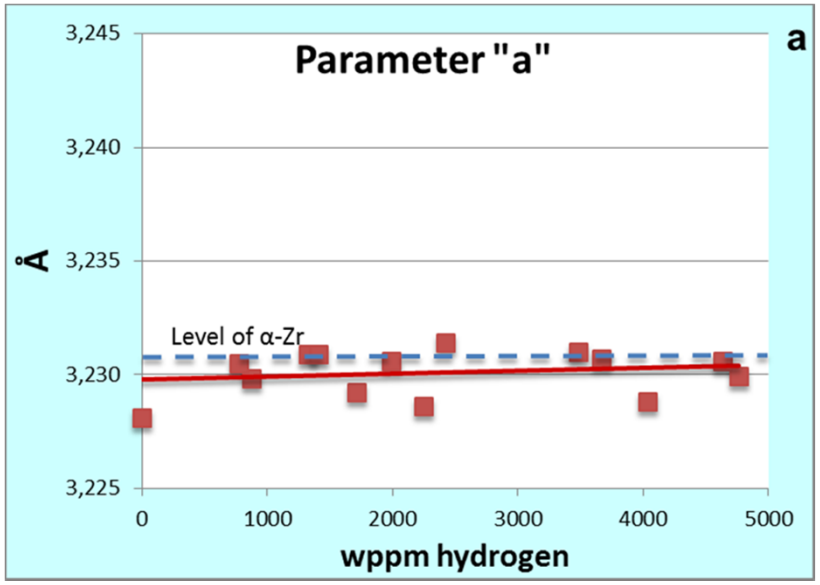
X-Ray profiles of Zircaloy-4 samples hydrogenated at 700 °C

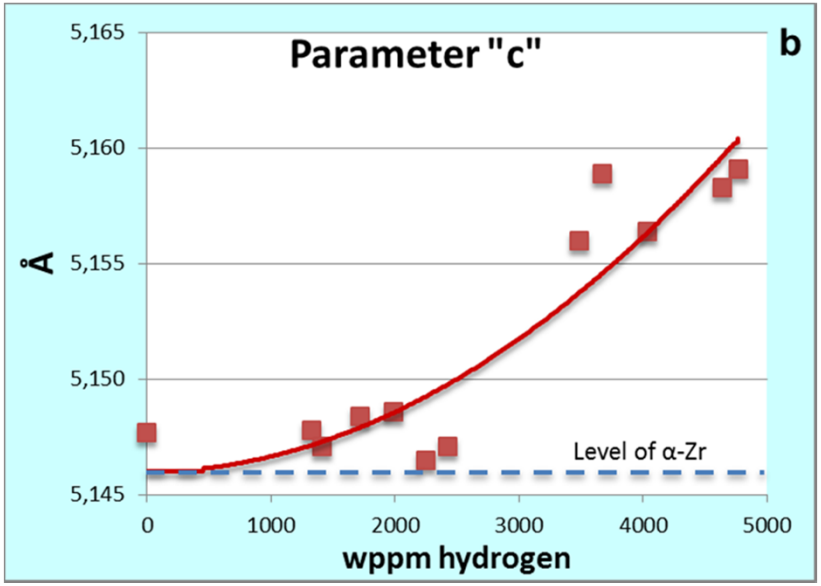


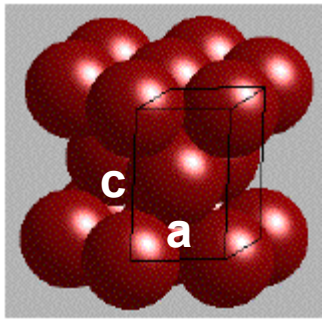
X-Ray profiles of Zircaloy-4 samples hydrogenated at 800 °C



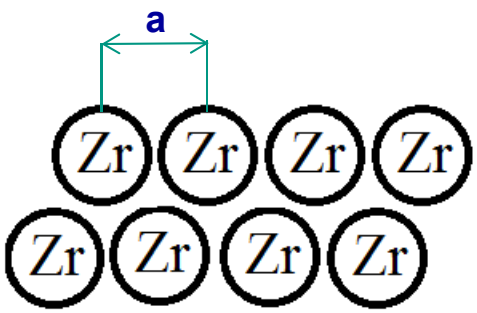
Change of lattice parameters after hydrogenation of Zircaloy-4 samples



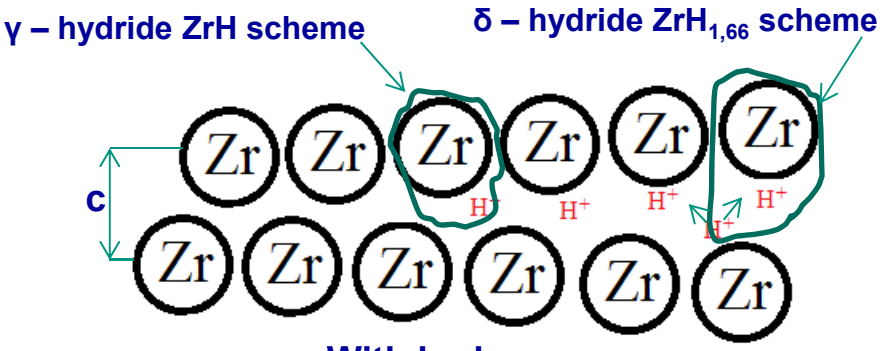




3D model of HCP-lattice



2D projection of HCP-lattice without hydrogen



With hydrogen

Scheme of decohesion mechanism, accompanied by hydride formation

Conclusion

- No “macroscopic” hydrides were detected by means of optical microscopy, only high magnification SEM observations reveal presumable submicroscale hydrides.
- Microhardness tests showed a relationship between hydrogen content hardening, annealing softening and hardening due to $\beta \rightarrow \alpha$ transformation during cooling phase.
- The XRD-analysis showed the presence of γ-, δ-phases of zirconium hydrides in all of performed experiments. With the increase of hydrogen content the hydride peak intensity was also increased. Simultaneously the hydrogen should be partially dissolved in the lattice which is indicated by increase of the lattice parameter “c”.
- Because carried out observations have proved only the presence of hydrides and gave not enough information on the hydride structure and distribution, further detailed EBSD and TEM investigations should be performed in order to determine the location, morphology and orientation of nano-scaled hydrides and to separate hydrides from other structural features.
- The performed experiments can explain the absence of macroscopic hydrides in QUENCH-LOCA experiments. The increased brittleness of some zirconium claddings after QUENCH-LOCA tests could be caused by nano-scaled hydrides which are distributed in the bulk of material. The fact of the growth of the lattice parameter “c” allows to suggest that the decohesion mechanism accompanied by hydride formation could be responsible for cladding destruction.

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Thank you for your attention!

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