Hydrides and fracture of pure zirconium and Zircaloy-4 hydrogenated at temperatures typical for loss-of-coolant accident conditions

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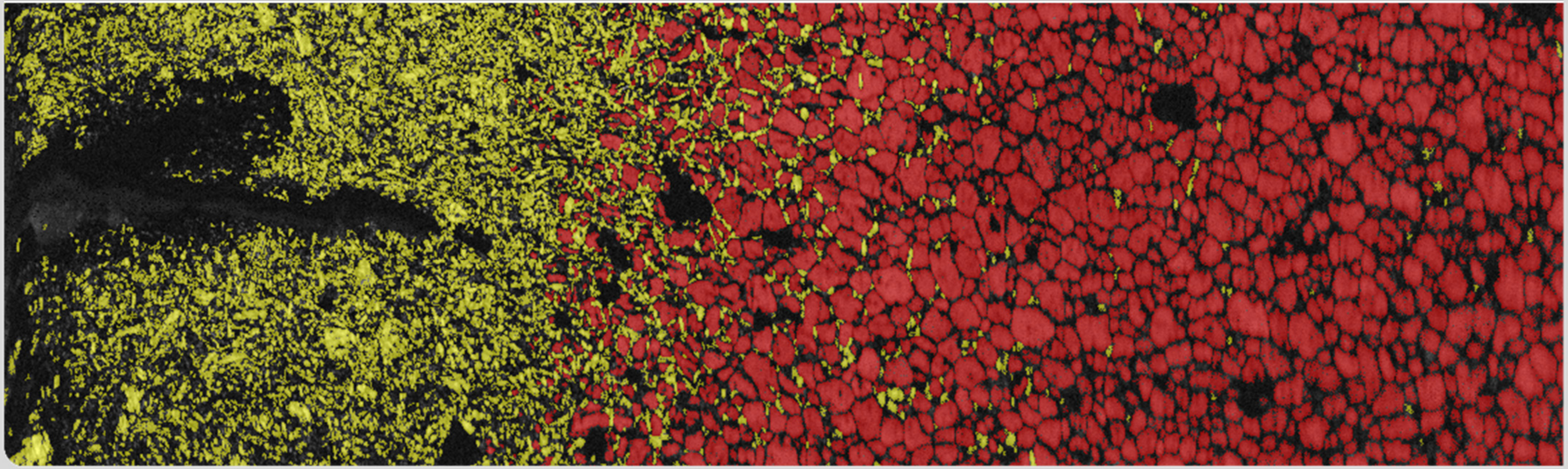
ICONE23, Chiba, Japan, 2015

Institute for Applied Materials (IAM), Program NUSAFE

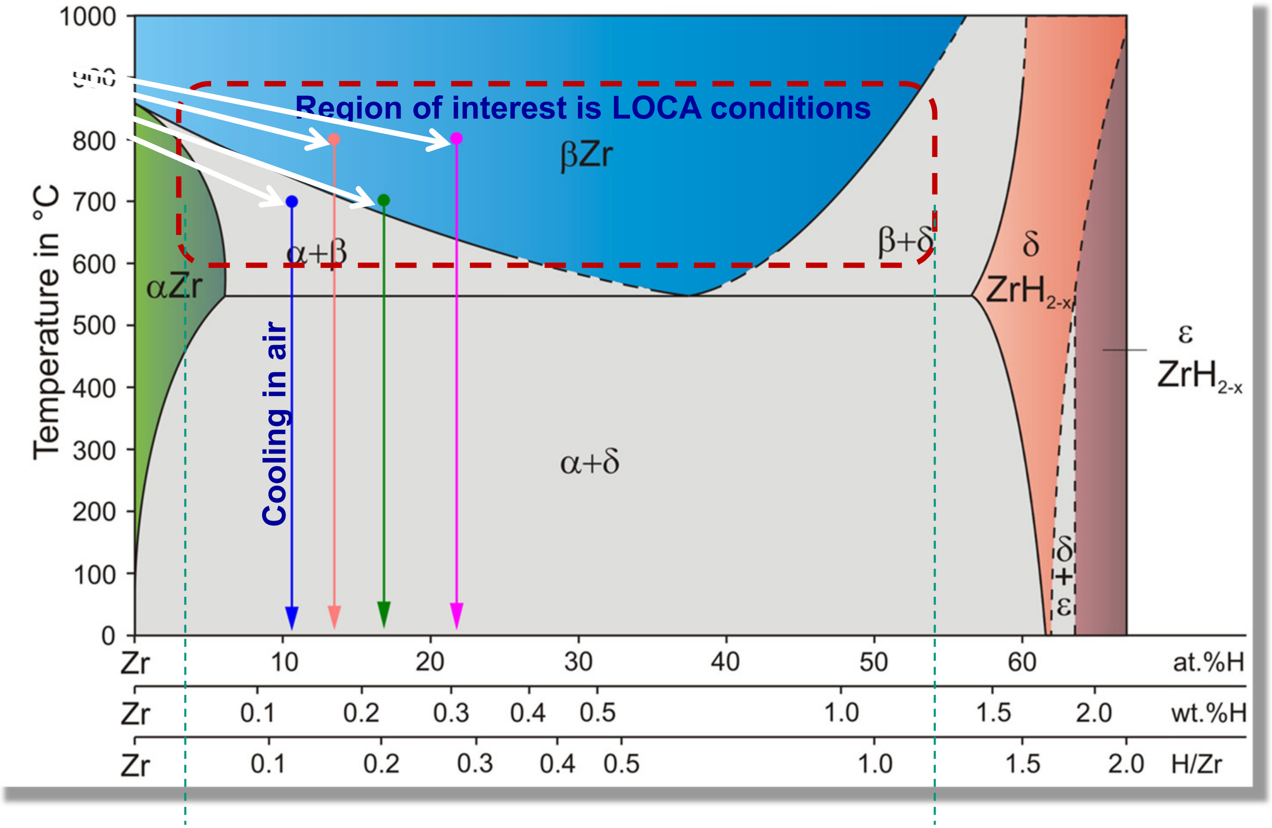


Objectives

- **Electron back scattered diffraction (EBSD) analysis of annealed and hydrogenated specimens**
- **Zirconium hydrides detection**
- **Fracture surface investigation**
- **Progress in understanding the mechanism of embrittlement of Zirconium and its alloys**
- **Application to the results of QUENCH-LOCA test**

Equilibrium phase diagram of Zr-H system*

selected examples of our tests



400 wppm H **12550 wppm H**

Embrittlement mechanism? Variety of hydride habit plane?
We need new tests!

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

Materials and methods of investigation

Materials: **1) pure Zr 99.5%, Hf < 0.3%, (Fe+Cr+O+N+H) < 0.2%**

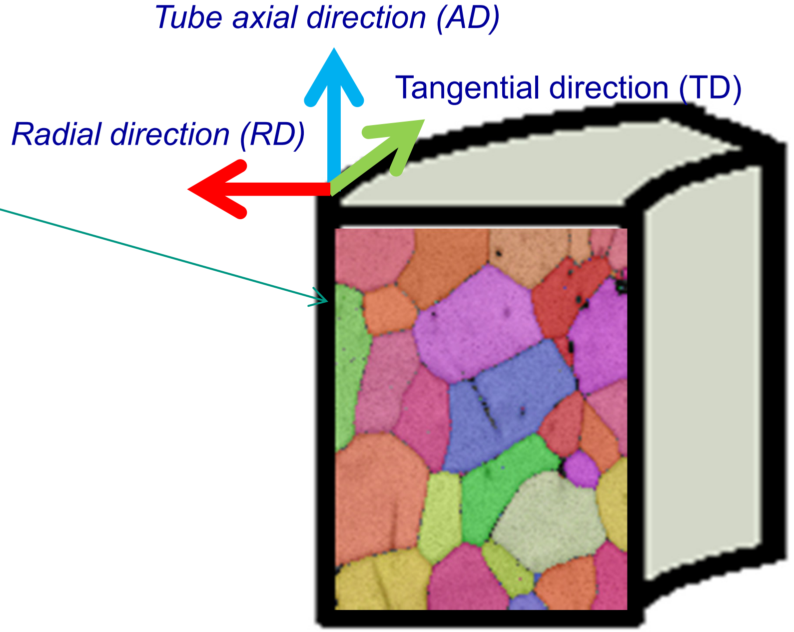
2) Conventional Zircaloy-4 cladding tube

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**
- **EBSD measurements of the cladding tube axial section**
- **Phase detection by means of QUANTAX microanalysis system combined with Esprit software (Bruker Nano GmbH, Germany)**
- **Scanning electron microscopy of fractured surface**



Cladding section:
scheme of EBSD measurements
of a cladding tube wall

Experimental procedure

Hydrogenation facility LORA furnace

Hydrogen gas partial pressure 0.1 bar

Specimen before hydrogenation

H_2 duration 2 to 12 minutes

Specimen withdrawal in air after hydrogenation

Estimated cooling rate 5 K/s

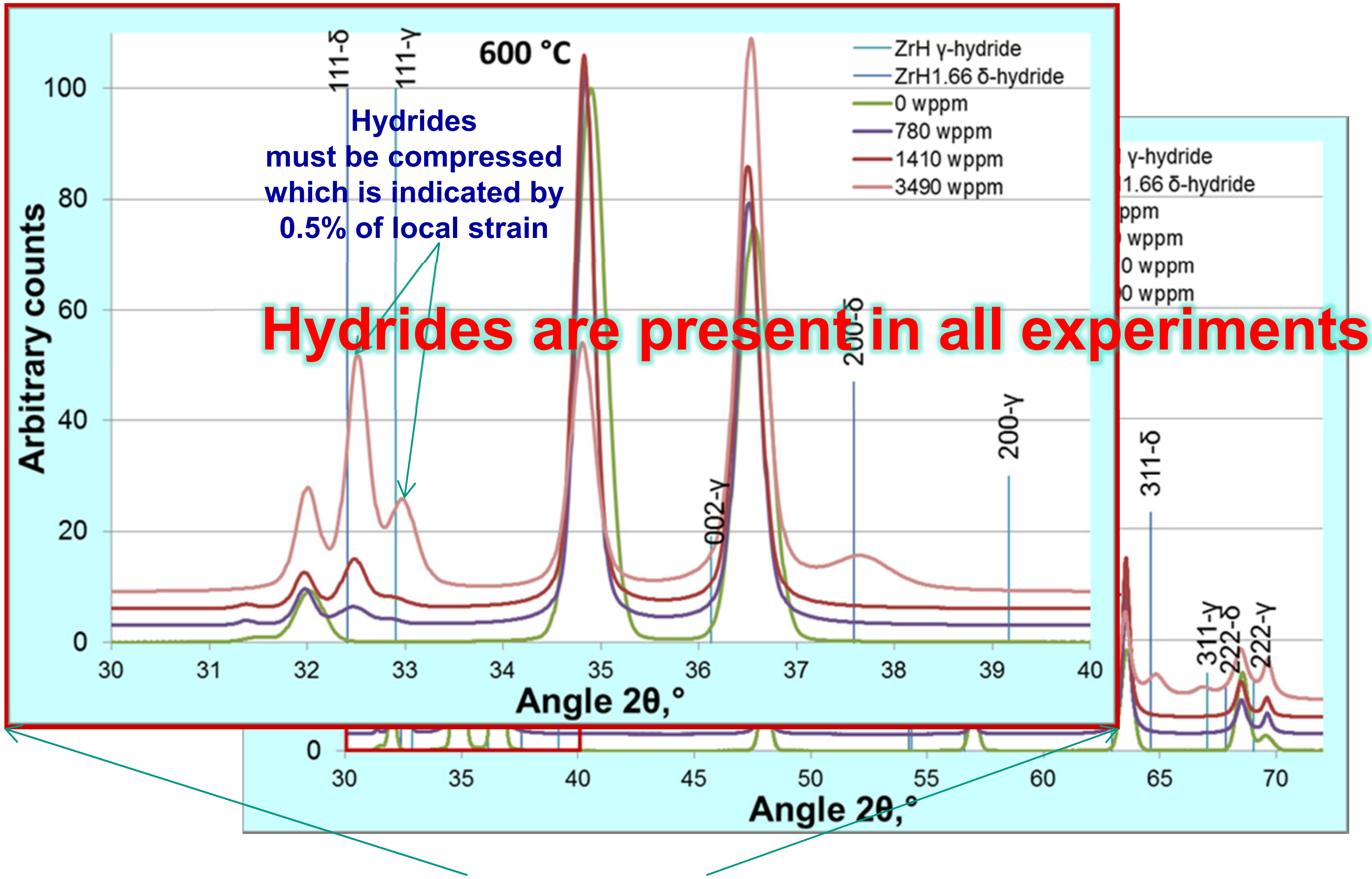
Cooled specimen after hydrogenation

Mass gain technique to calculate hydrogen content

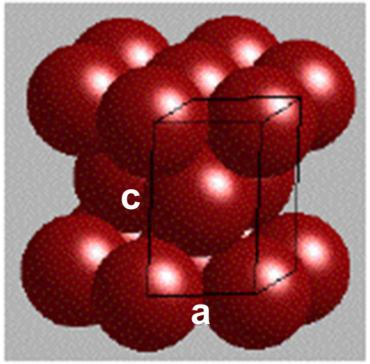
The previous results* on XRD-analysis and optical microscopy

*Published in *A. Pshenichnikov, J. Stuckert, M. Walter, Nucl. Eng. Des. 283 (2015) 33–39.*

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



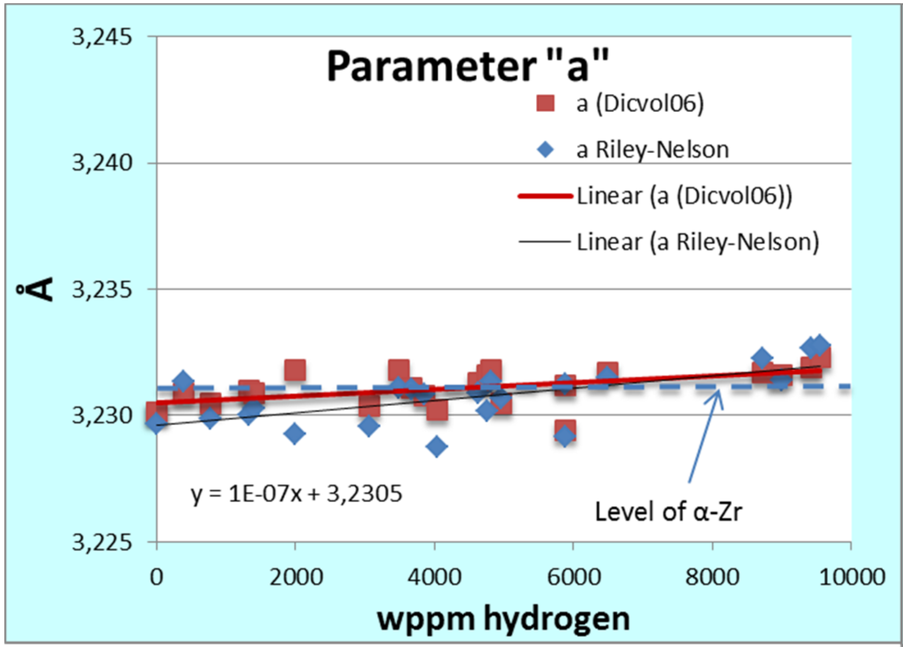
Change of lattice parameters "a" and "c" after hydrogenation of Zircaloy-4 samples

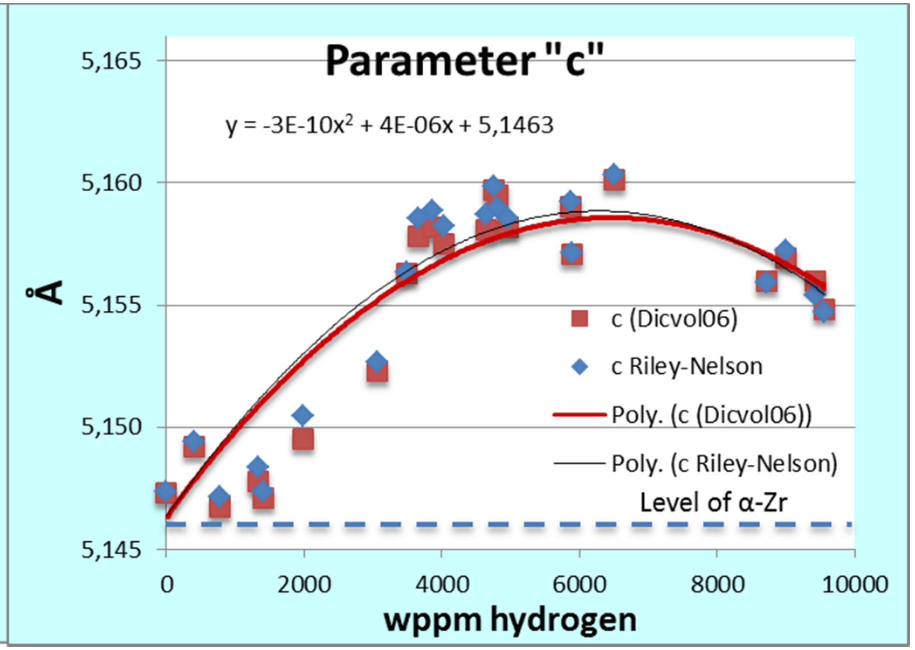


Calculation of lattice parameter was performed on the base of XRD data by means of two methods:

a) **red color is a dichotomy method implemented in DICVOL06 software (fast, convenient, instrumental error can be minimised automatically)**

b) **Blue color points and black line is a classical Riley-Nelson approximation method (slow, accurate, instrumental error independent)**



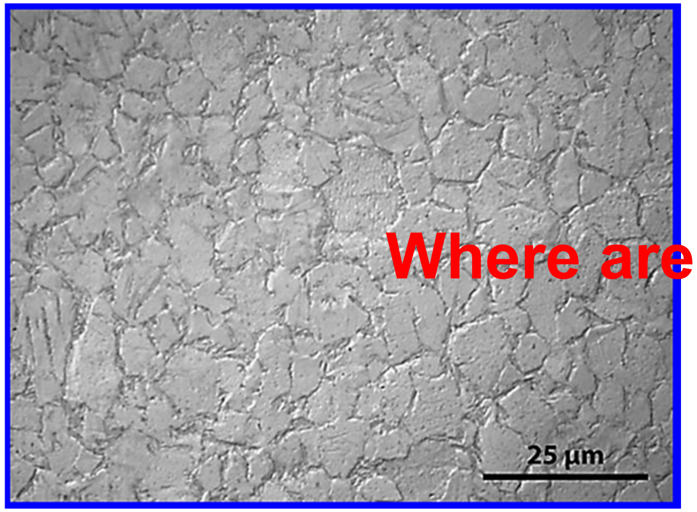


a – didn't change noticeably

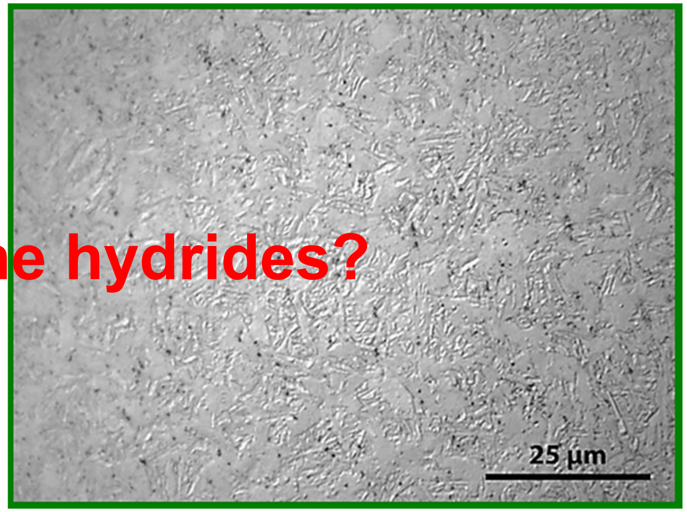
c – significantly increased after hydrogenation

Optical metallography of hydrogenated Zircaloy-4

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



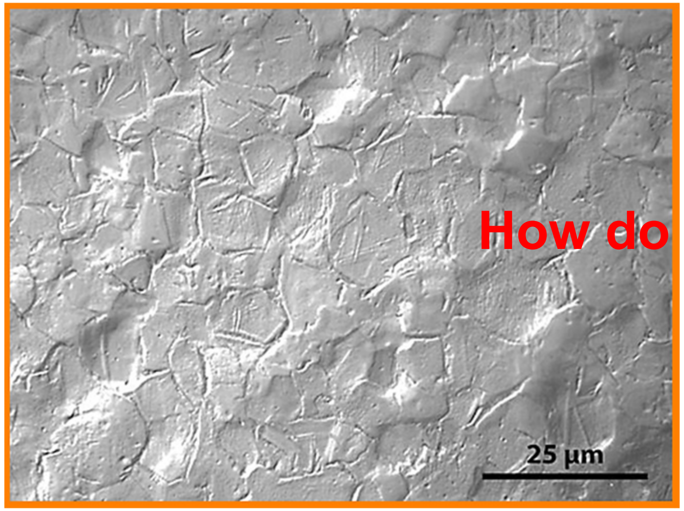
1330 wppm H



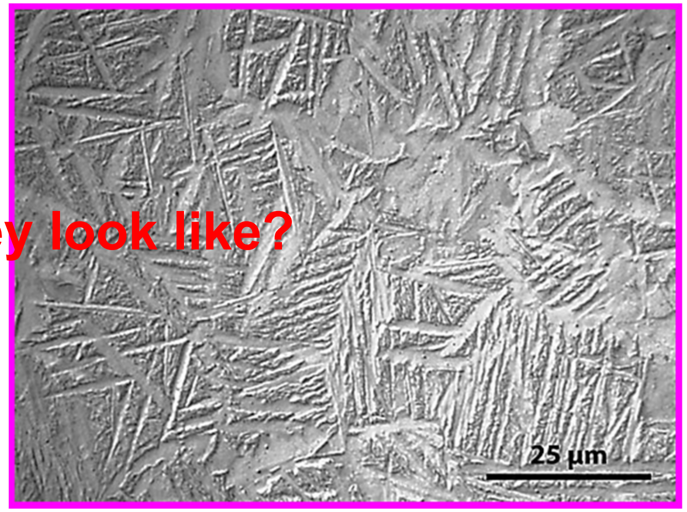
2250 wppm H

Where are the hydrides?

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



1790 wppm H



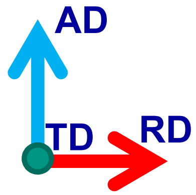
3060 wppm H

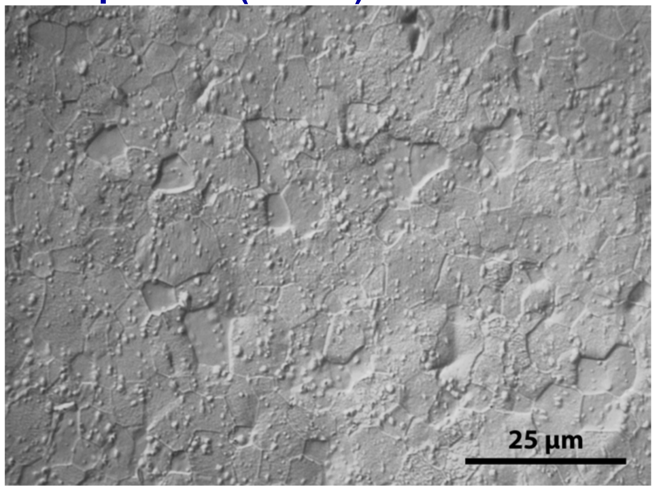
How do they look like?

New results on EBSD-analysis

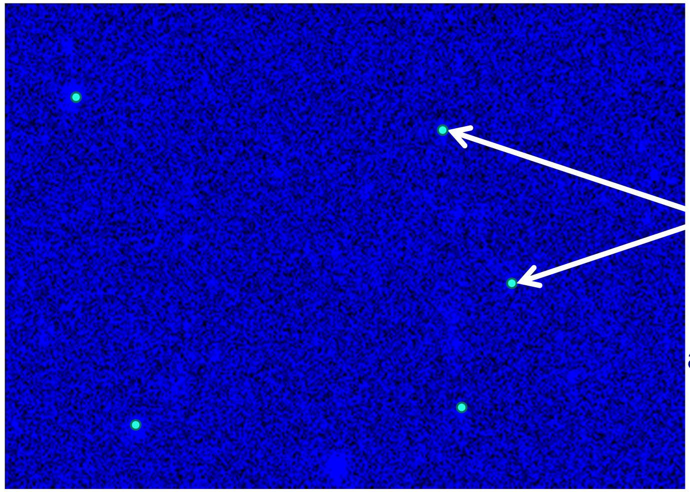
Zr as-received

Optical image of recrystallized pure Zr (99.5%) tube wall

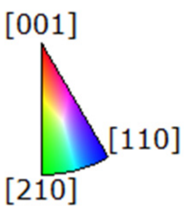


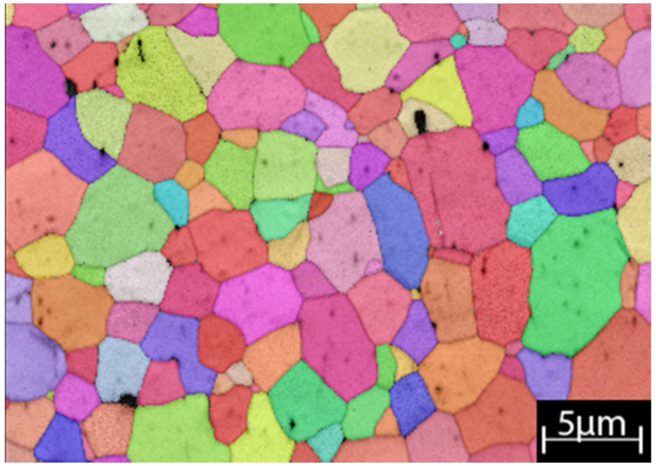


EBSD-pattern quality map



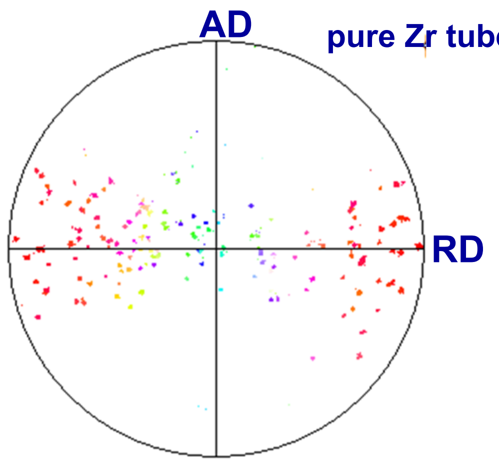
EDX-analysis of impurities distribution (Fe) near to grain boundaries and inside the grains





Grain orientation distribution in RD

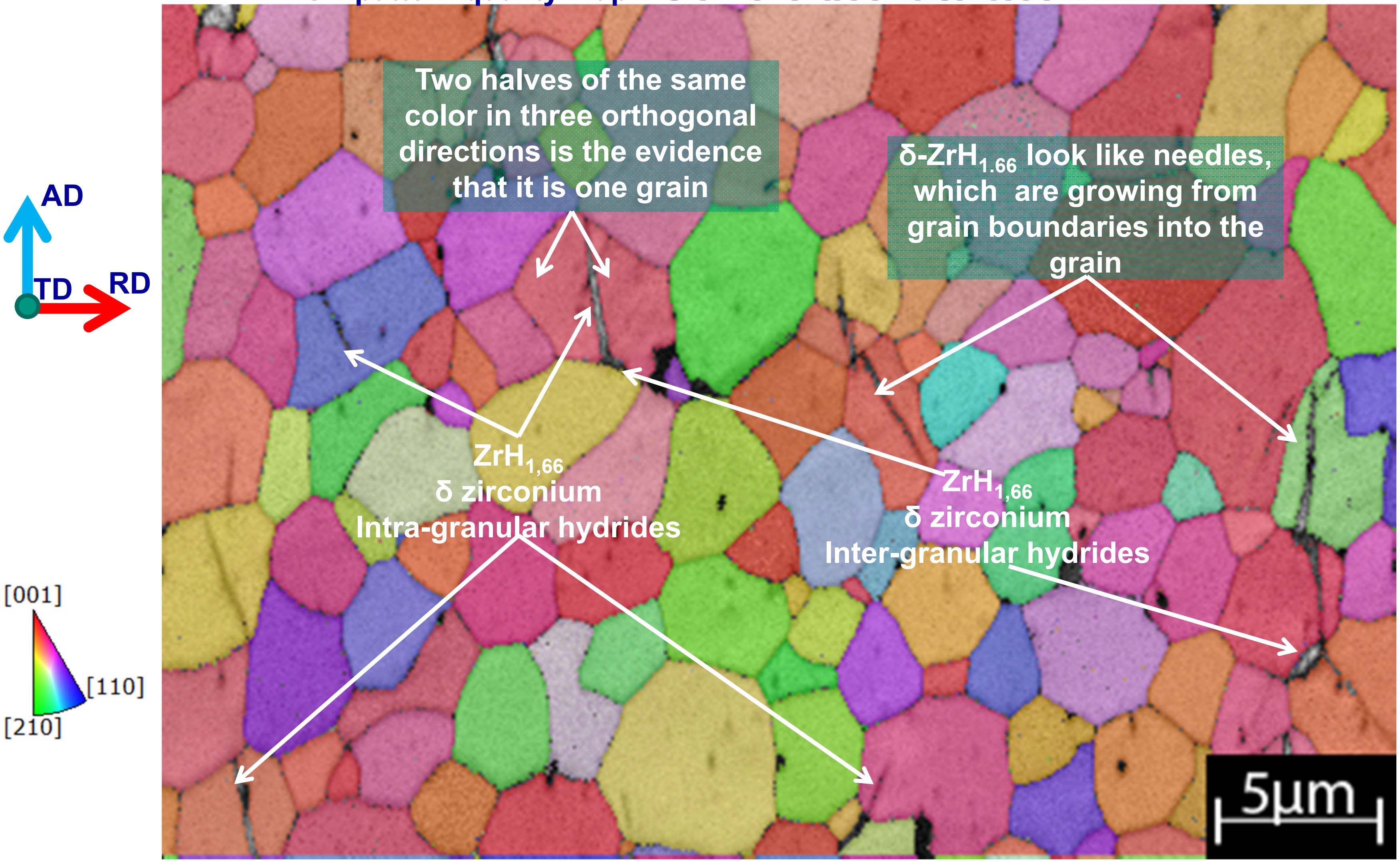
pure Zr tube has usual fiber texture



Microtexture $\{001\}_{\alpha\text{-}Zr}$ (basal plane)

Zr hydrogenated at 600 °C 400 wppm H

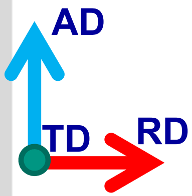
EBSD pattern quality map **Grain orientation distribution in RD**

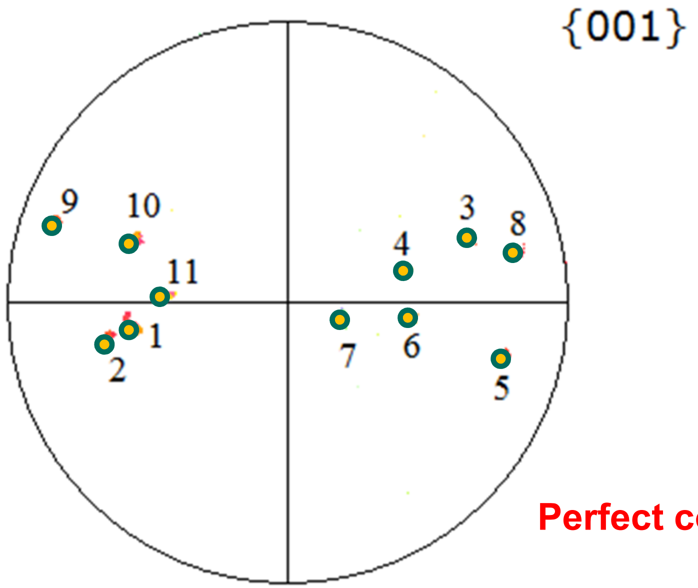


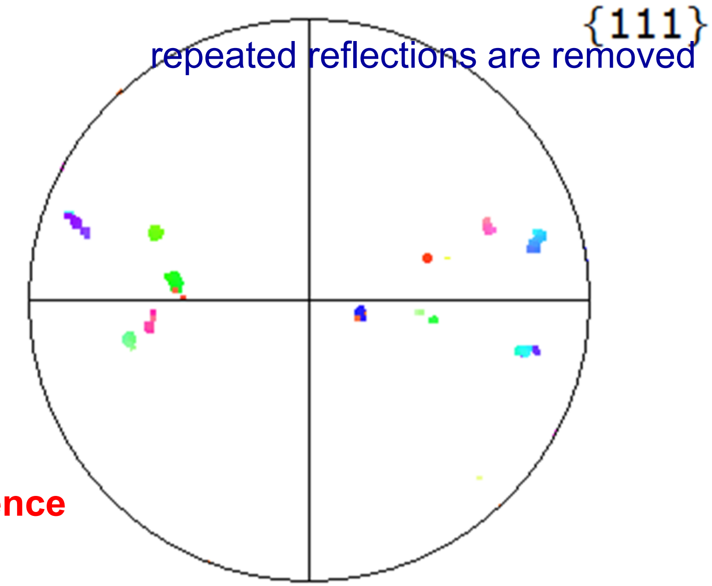
99.3% Zr, 0.7% $ZrH_{1.66}$, γ-ZrH – not detected (on the basis of image analysis)

Zr hydrogenated at 600 °C 400 wppm H

Microtexture analysis







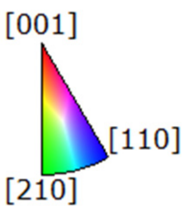
repeated reflections are removed

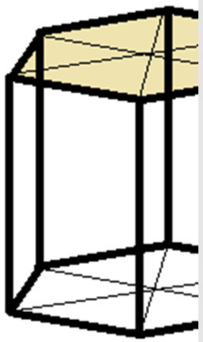
Perfect coincidence

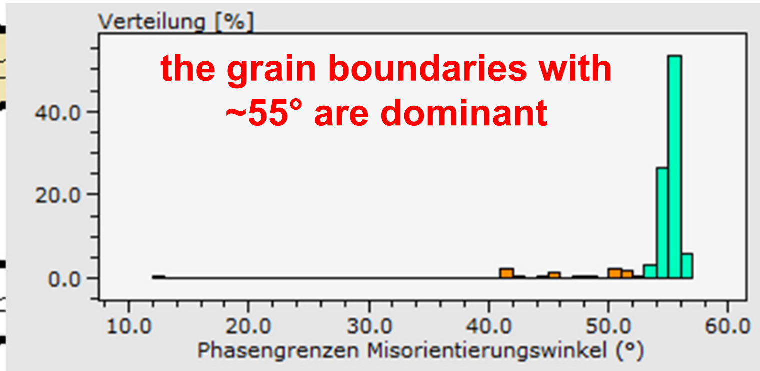
basal plane normal of α-Zr lattice

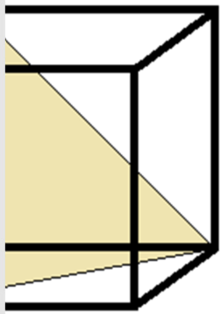
$\{001\}_{\alpha\text{-Zr}} || \{111\}_{\delta\text{-ZrH1.66}}$

normal to cube diagonal of δ-$ZrH_{1.66}$ lattice









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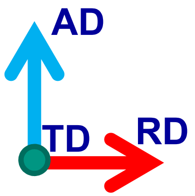
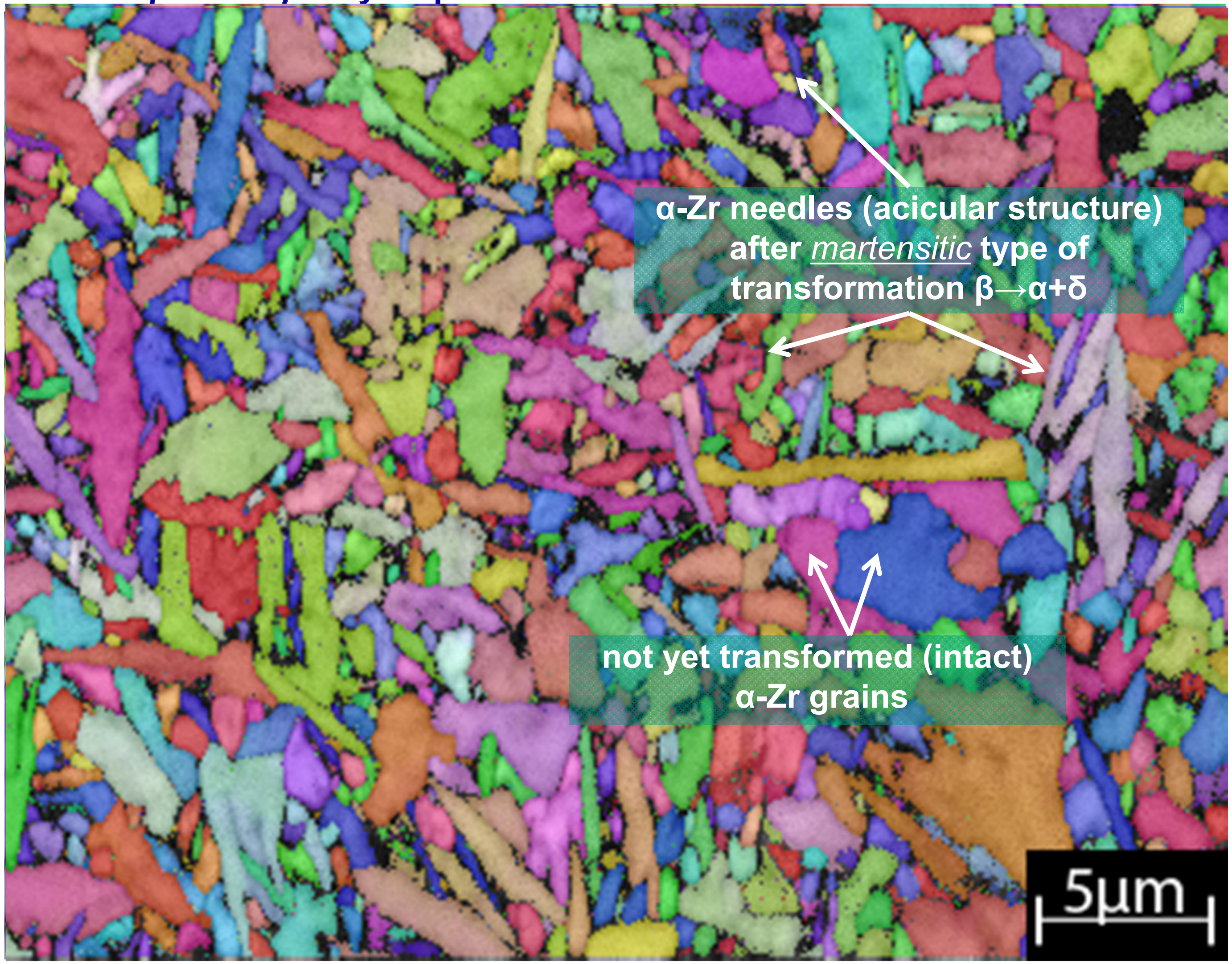
Zr hydrogenated at 600 °C 2290 wppm H

EBSD pattern quality map **Grain orientation distribution in RD**

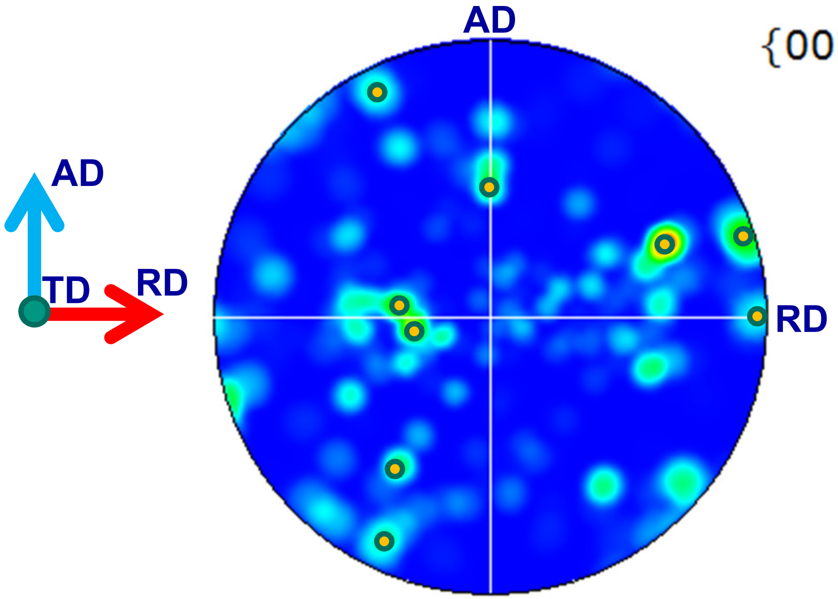


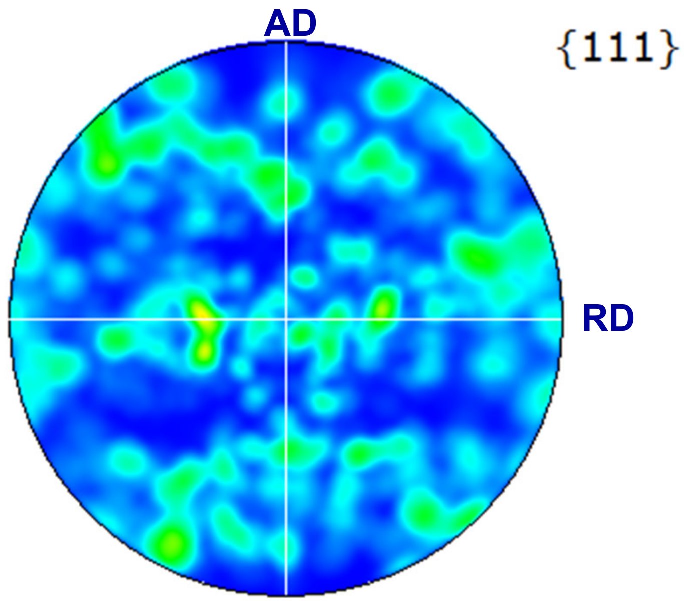


72.6% Zr, 26.5% δ-$ZrH_{1.66}$, 0.8% γ-ZrH (on the basis of image analysis)

Zr hydrogenated at 600 °C 2290 wppm H

Microtexture analysis

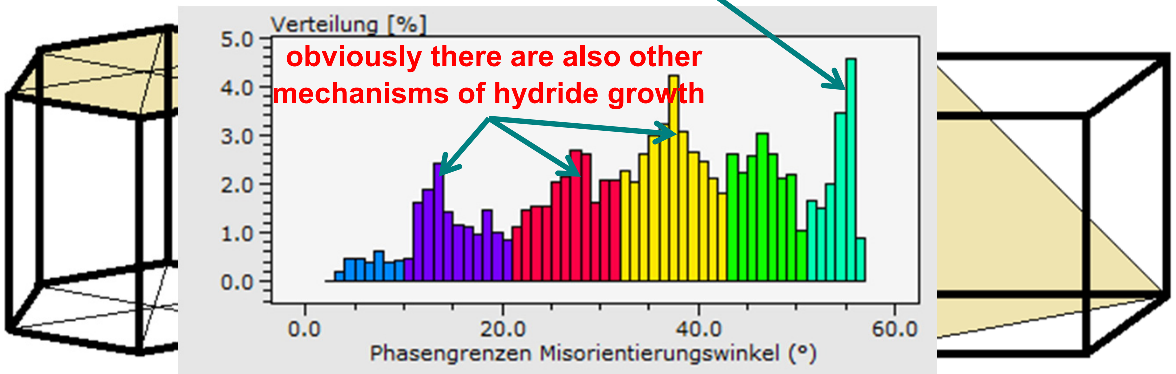




basal plane normal of α-Zr lattice

$\{001\}_{\alpha\text{-}Zr} || \{111\}_{\delta\text{-}ZrH1,66}$ partially

normal to cube diagonal of δ-$ZrH_{1.66}$ lattice



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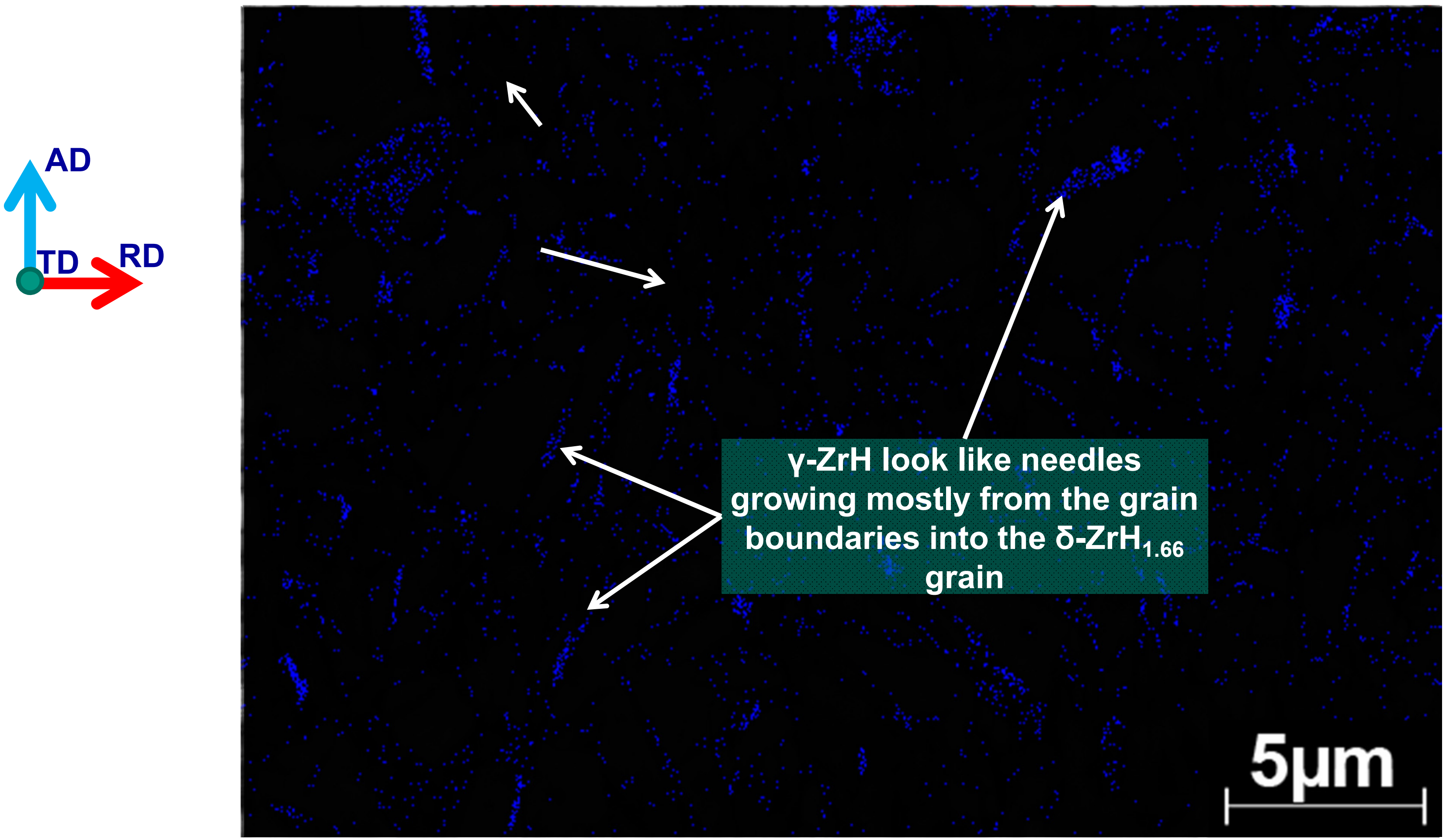
Zr hydrogenated at 600 °C 5400 wppm H

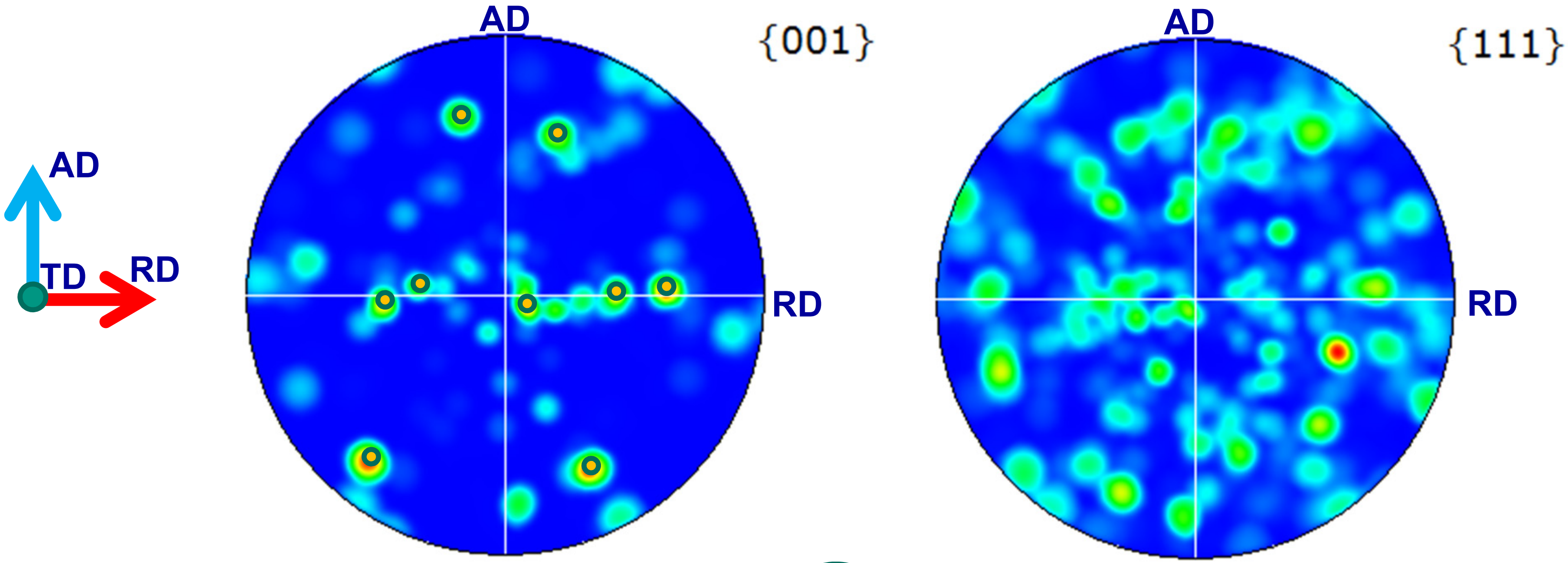
EBSD pattern quality map + Phase map



27.1% Zr, 70.6% δ-$ZrH_{1.66}$, 2.35% γ-ZrH (on the basis of image analysis)

Zr hydrogenated at 600 °C 5400 wppm H

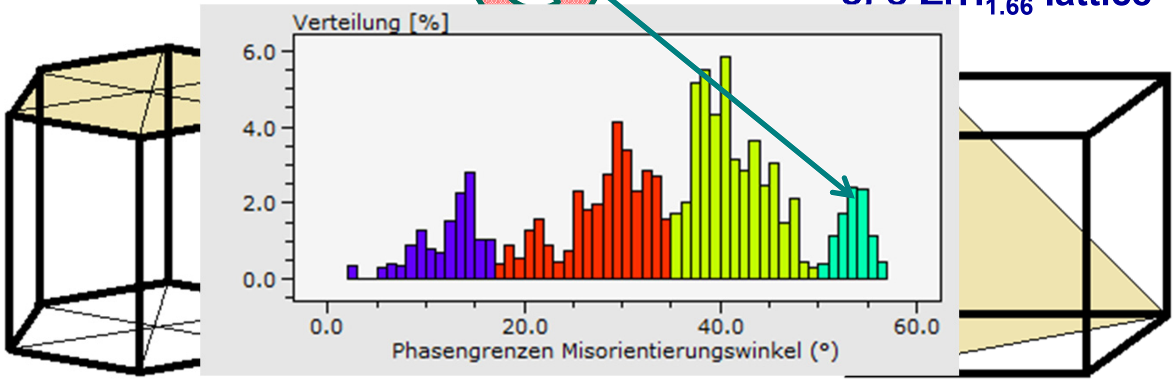
Microtexture analysis



basal plane normal of α-Zr lattice

$\{001\}_{\alpha\text{-}Zr} \| \{111\}_{\delta\text{-}ZrH1.66}$

normal to cube diagonal of δ-$ZrH_{1.66}$ lattice



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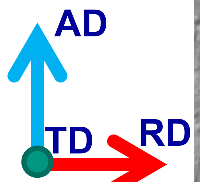
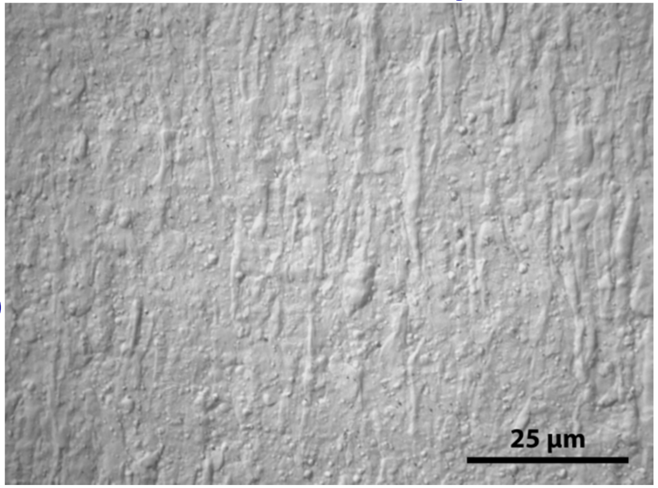
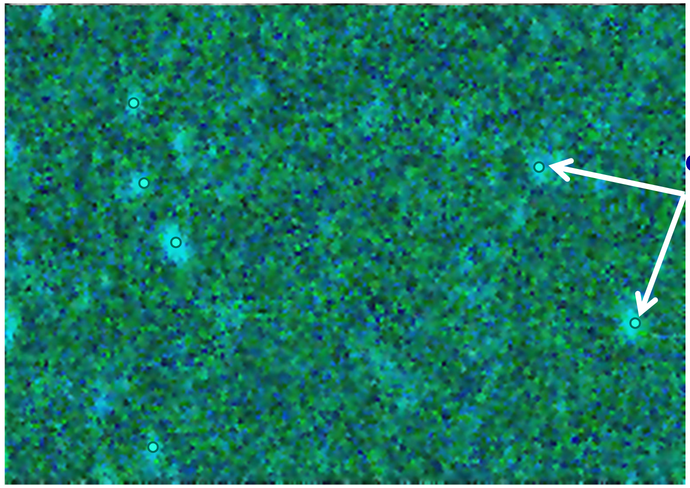
Zircaloy-4 as-received

Optical image of deformation textures in Zircaloy-4

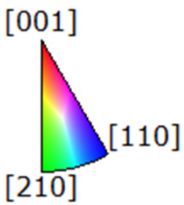


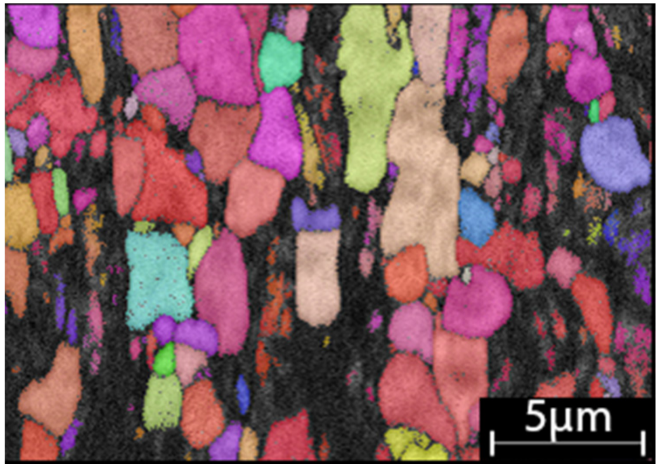


EBSD pattern quality map

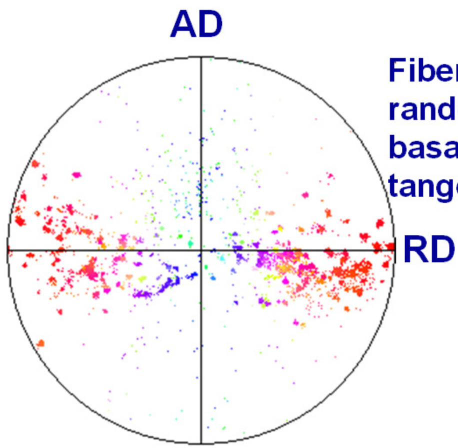


EDX-analysis of intermetallic particles distribution (Fe + Cr) mostly near to grain boundaries





Grain orientation distribution in RD



Fiber texture with a random distribution of basal poles in the radial-tangential plane*

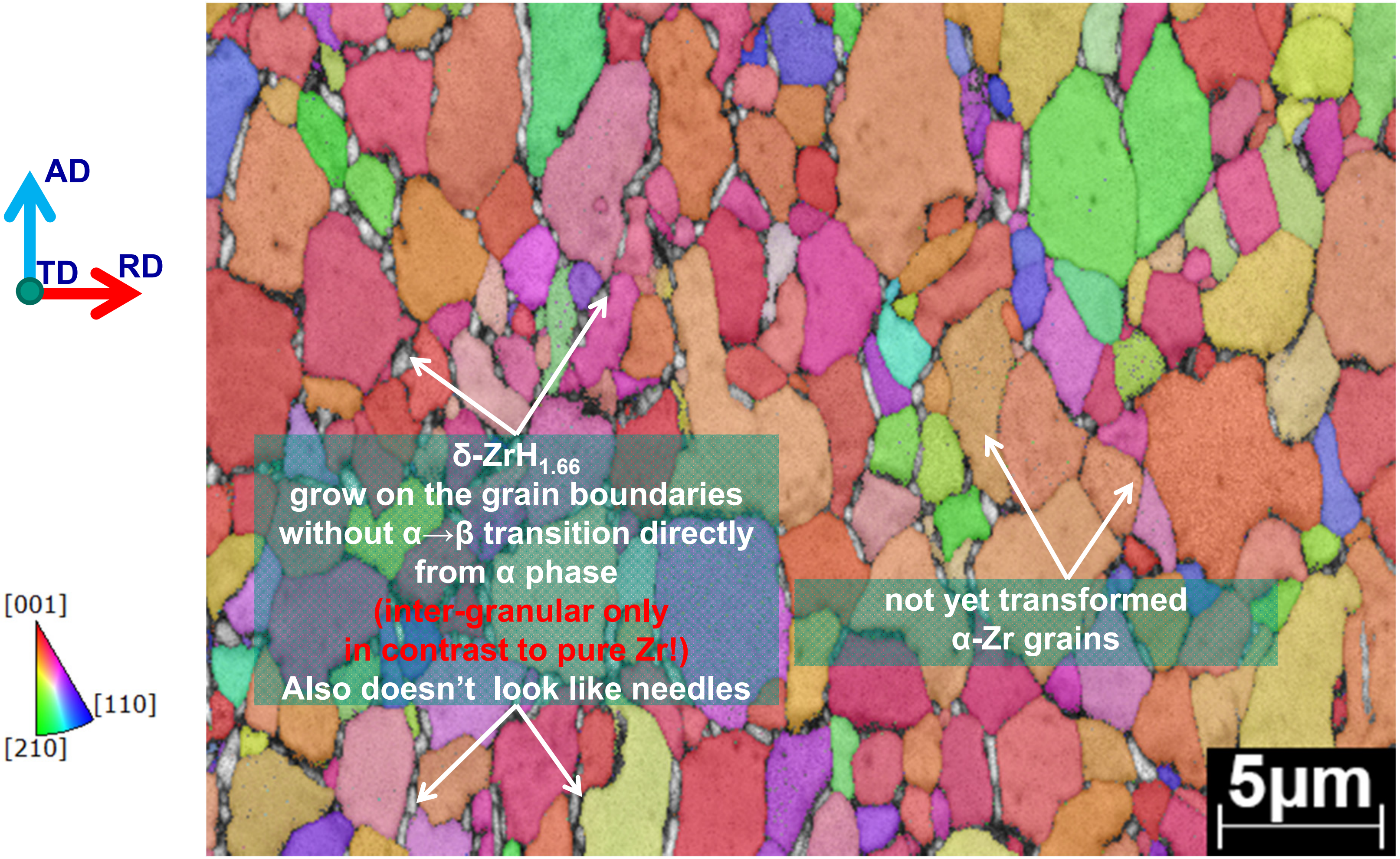
Microtexture $\{001\}_{\alpha Zr}$ (basal plane)**

*More on texture analysis can be found for example in ***E. Tenckhoff, Journal of ASTM International*****, April 2005, Vol. 2, No. 4**

**Please keep in mind that for Zr lattice planes also three indices will be used.

Zircaloy-4 hydrogenated at 600 °C 2650 wppm H

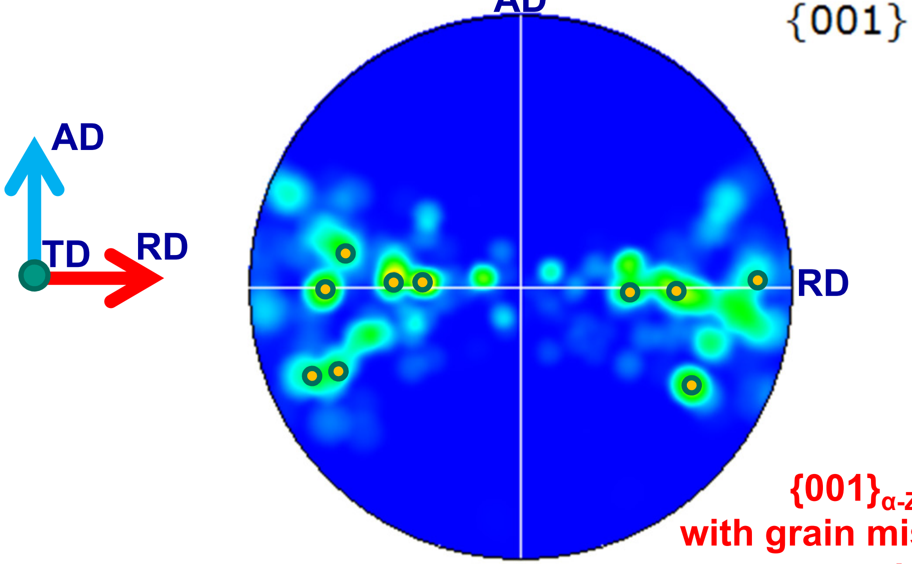
EBSD pattern quality map **Grain orientation distribution in RD**



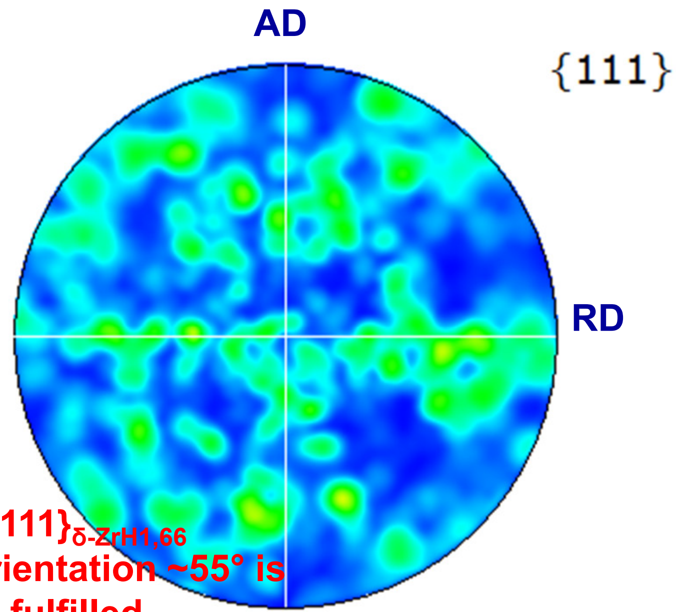
94.8% Zr, 5.2% δ-$ZrH_{1.66}$, γ-ZrH – not detected (on the basis of image analysis)

Zircaloy-4 hydrogenated at 600 °C 2650 wppm H

Microtexture analysis

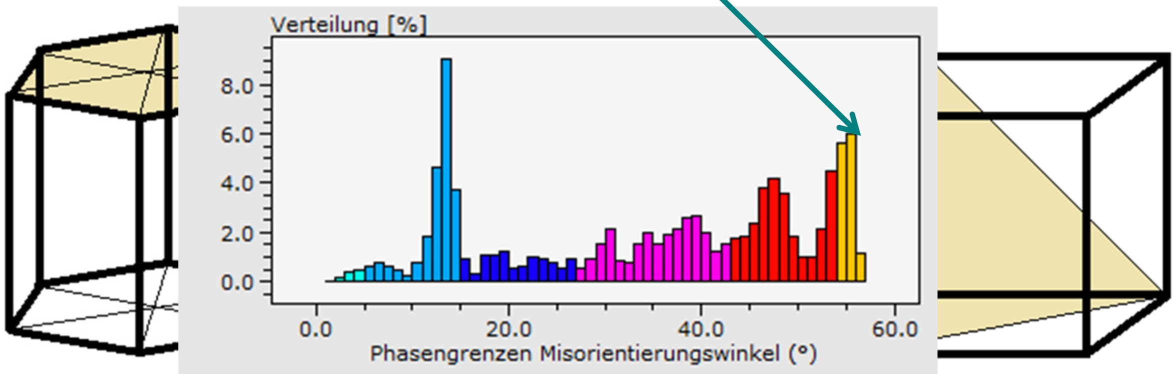


basal plane normal of α-Zr lattice



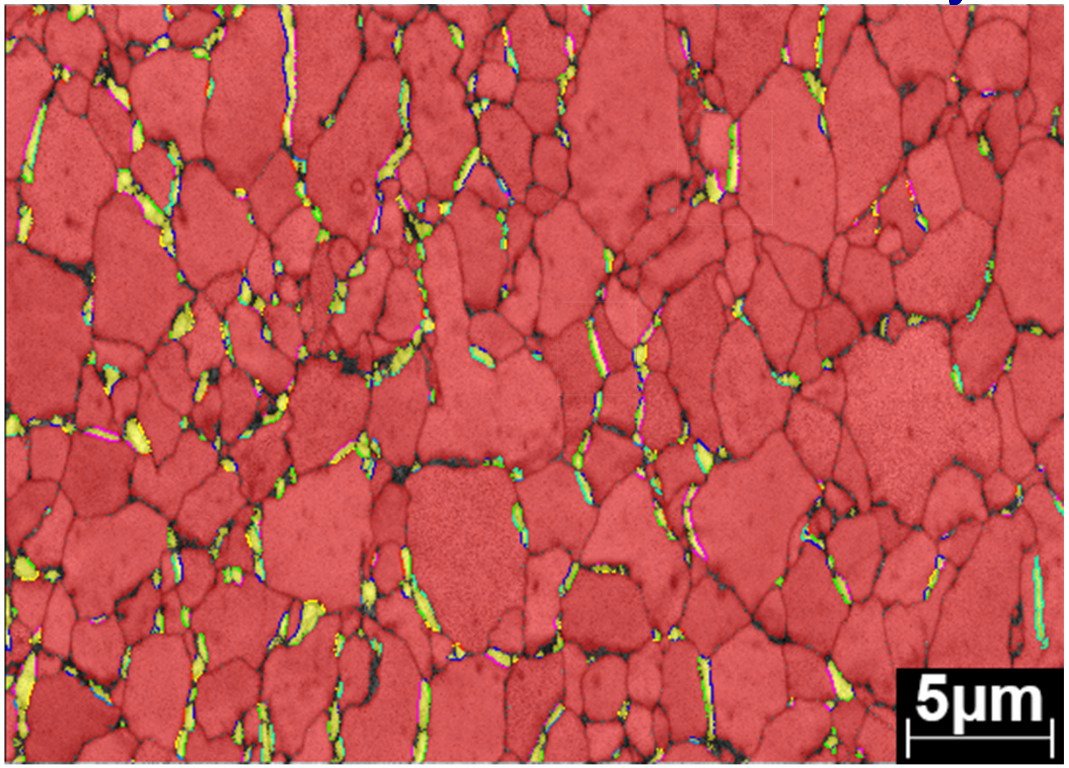
normal to cube diagonal of δ-$ZrH_{1.66}$ lattice

$\{001\}_{\alpha\text{-}Zr} \| \{111\}_{\delta\text{-}ZrH1,66}$ with grain misorientation ~55° is partially fulfilled



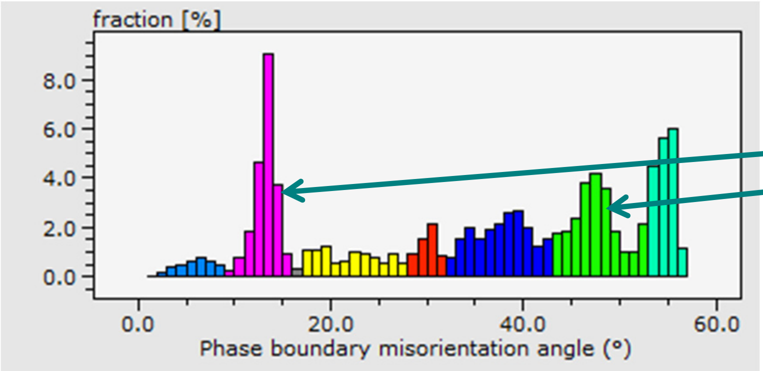
Zircaloy-4 hydrogenated at 600 °C 2650 wppm H

Grain boundary analysis



High angle Low angle

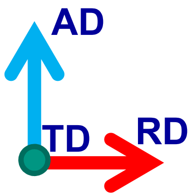
High angle Low angle

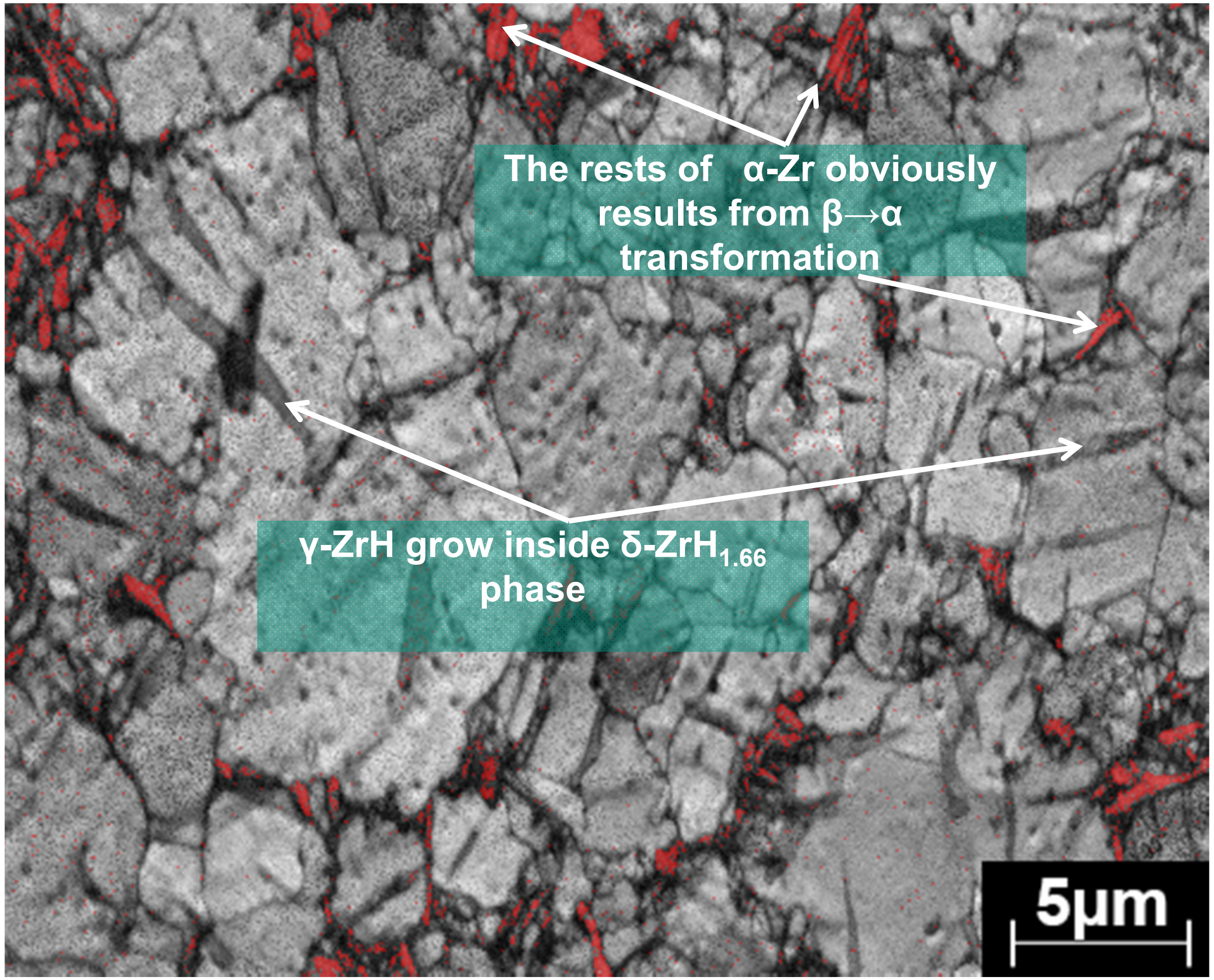


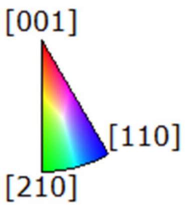
There is also another accommodation mechanism on the grain boundaries of Zircaloy-4 – low angle from one side and high angle boundary on the other side of hydride together give ~60° which is a characteristic direction for hexagonal lattice

Zircaloy-4 hydrogenated at 600 °C 12550 wppm H

EBSD pattern quality map **Grain orientation distribution in RD**



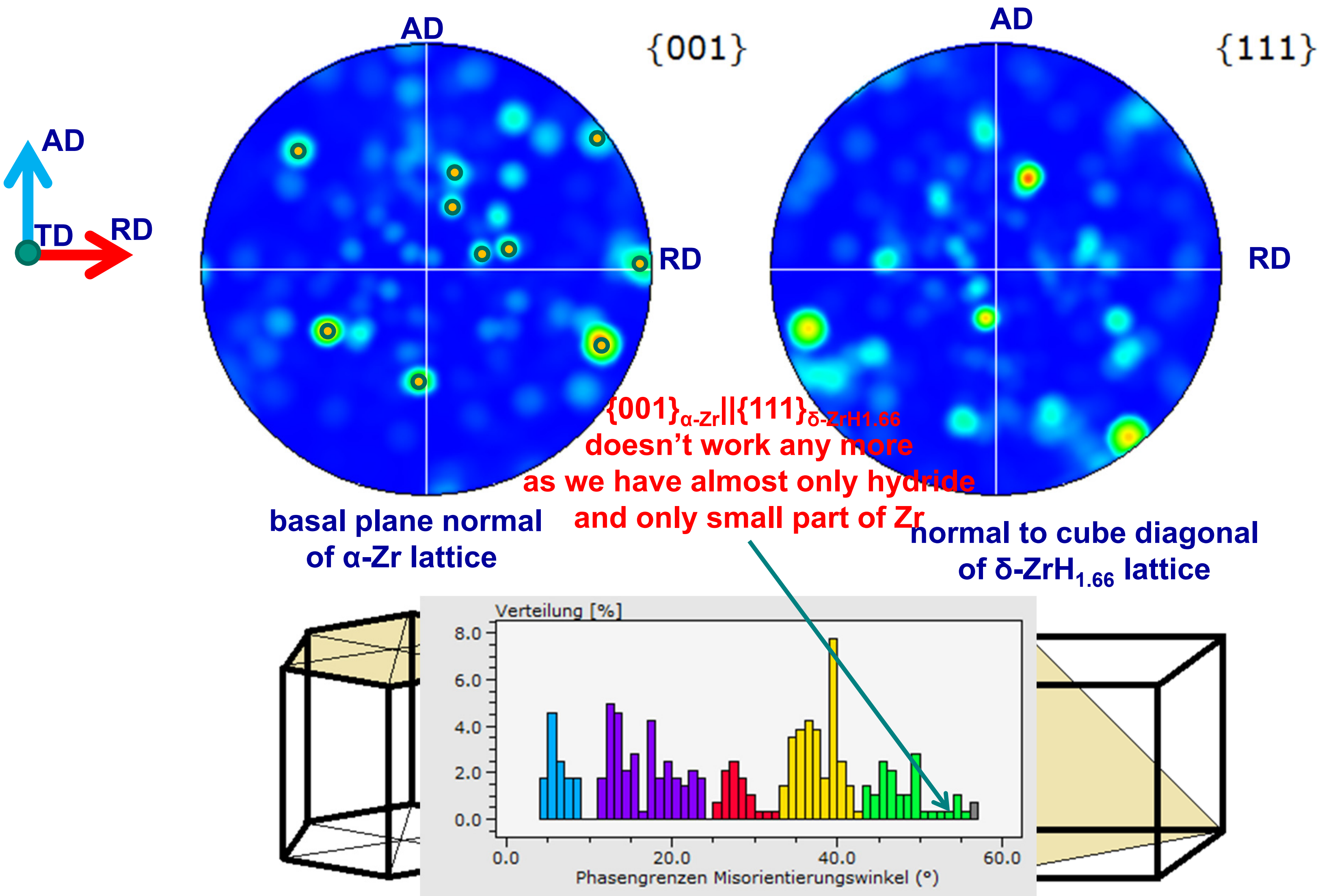




3.9% Zr, 92% δ-$ZrH_{1.66}$, 4.1% γ-ZrH (on the basis of image analysis)

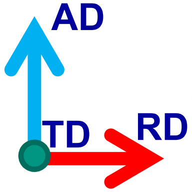
Zircaloy-4 hydrogenated at 600 °C 12550 wppm H

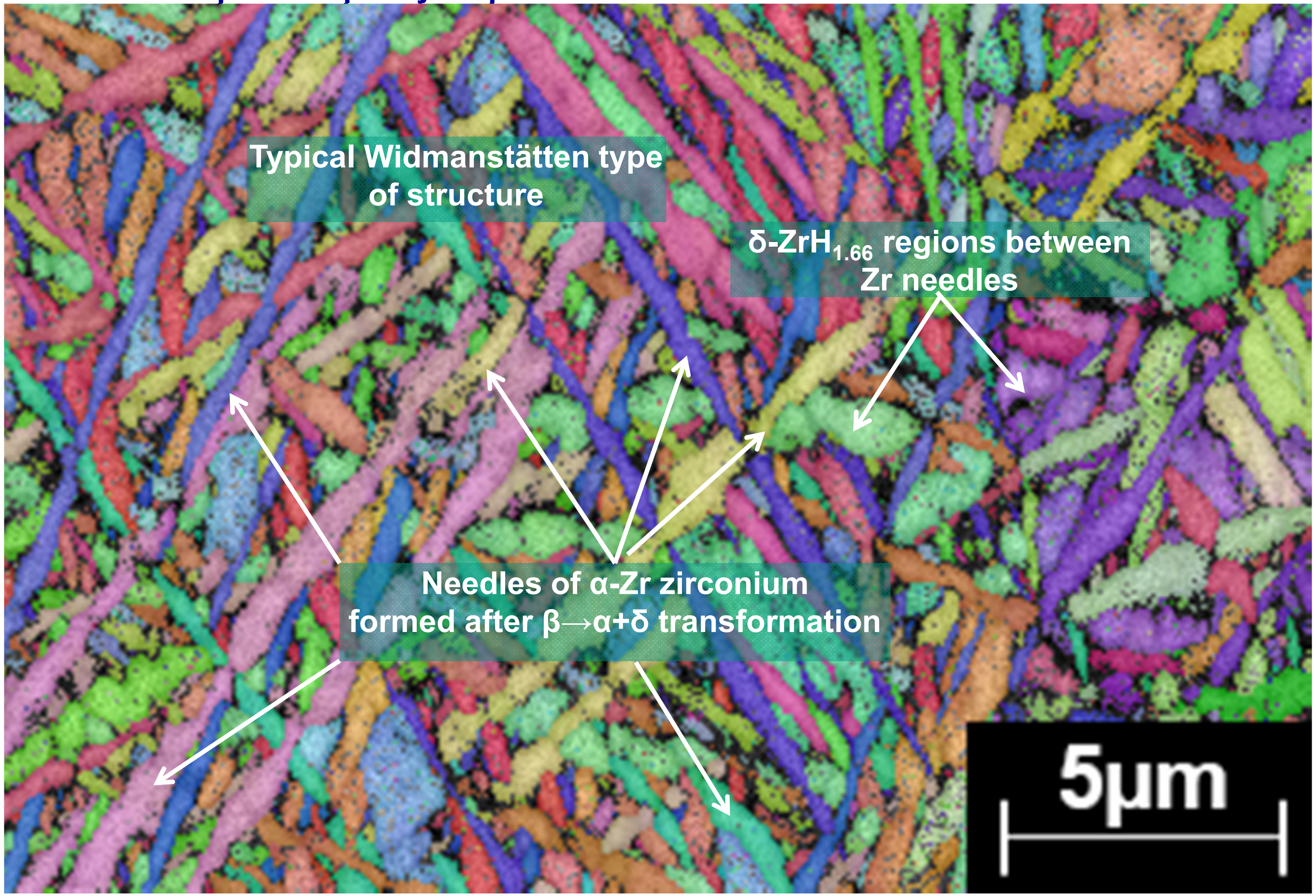
Microtexture analysis

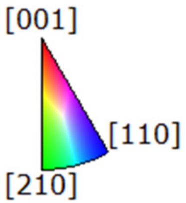


Zr hydrogenated at 700 °C 5880 wppm H

EBSD pattern quality map **Grain orientation distribution in RD**



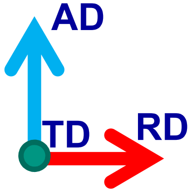


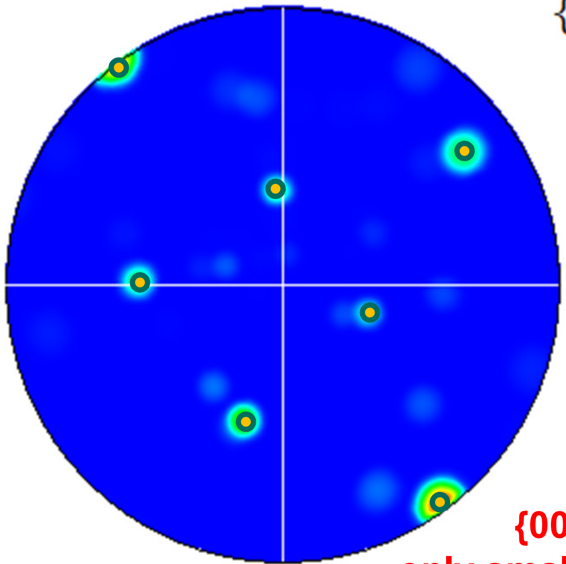


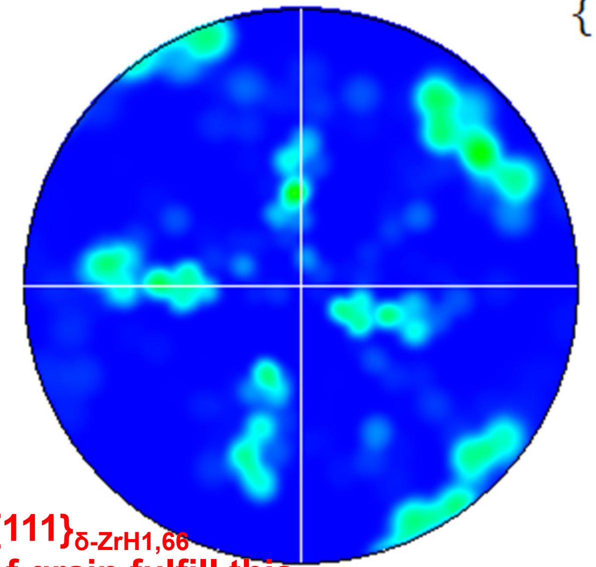
60% Zr, 39% δ-$ZrH_{1.66}$, 1% γ-ZrH (on the basis of image analysis)

Zircaloy-4 hydrogenated at 600 °C 5880 wppm H

Microtexture analysis





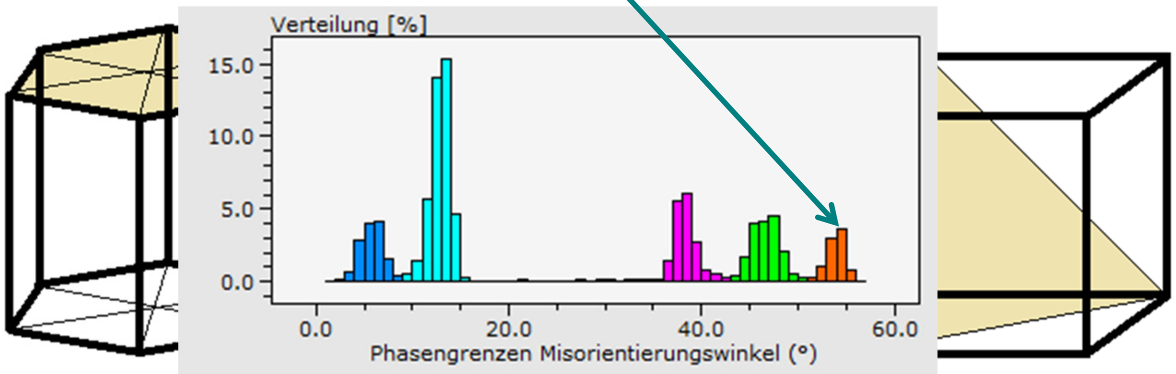


$\{001\}_{\alpha\text{-Zr}} || \{111\}_{\delta\text{-ZrH}1,66}$

only small part of grain fulfill this relation

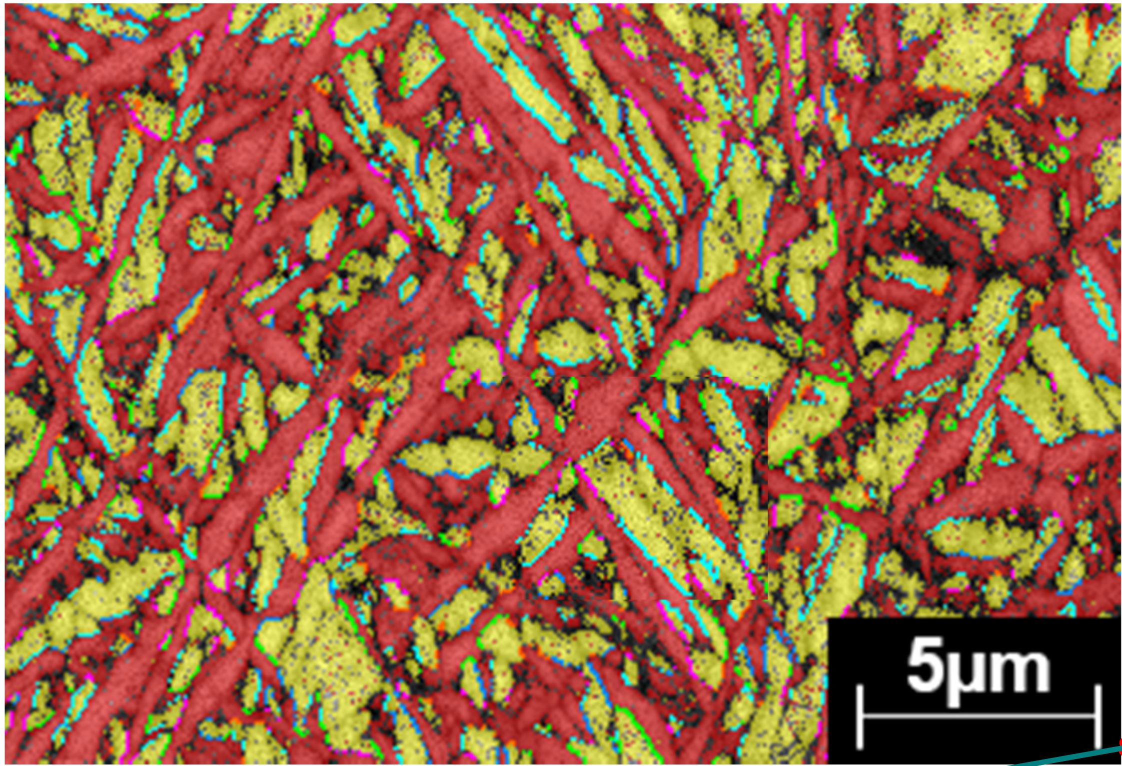
basal plane normal of α-Zr lattice

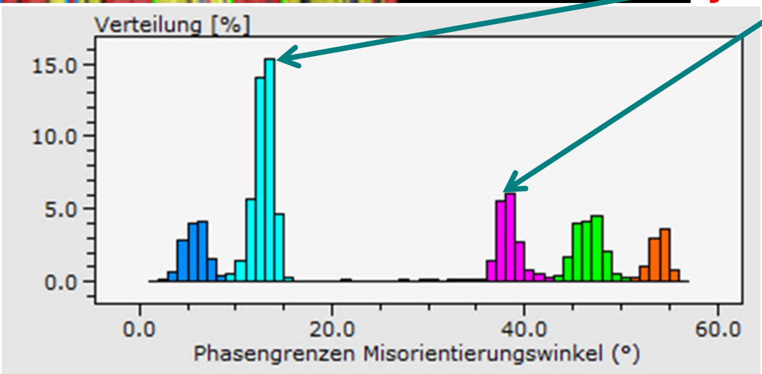
normal to cube diagonal of $\delta\text{-ZrH}_{1,66}$ lattice



Zircaloy-4 hydrogenated at 600 °C 5880 wppm H

Microtexture analysis





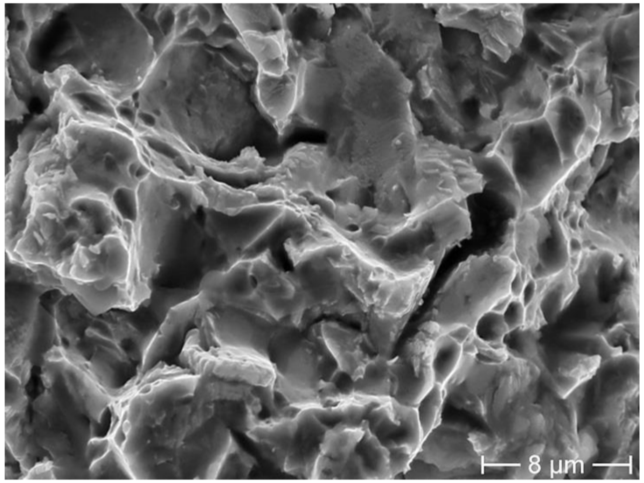
The analysis is on the way but it is clear that we have a mechanism of hydride accomodation which lead to such kind of orientation that results in ~ 60° rotation of hydride+grain system to minimise the whole energy of this system

There is obviously a possibility to generalise and classify the data of different authors, which has not been done until now

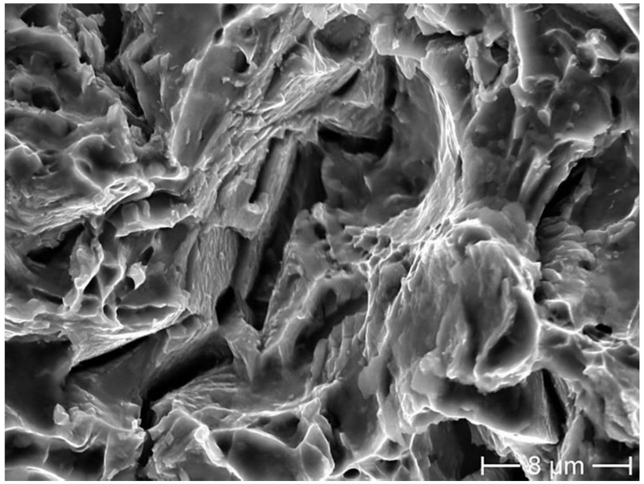
Scanning electron microscopy of fracture surfaces

Scanning electron microscopy of fracture surfaces of hydrogenated Zircaloy-4

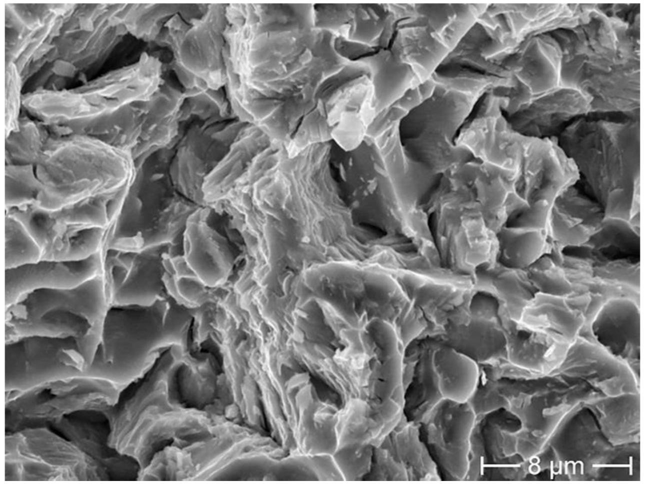
700 °C



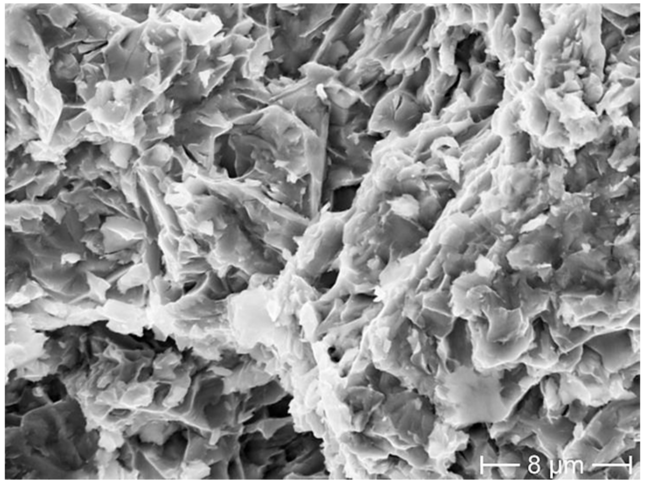
720 wppm H



1860 wppm H



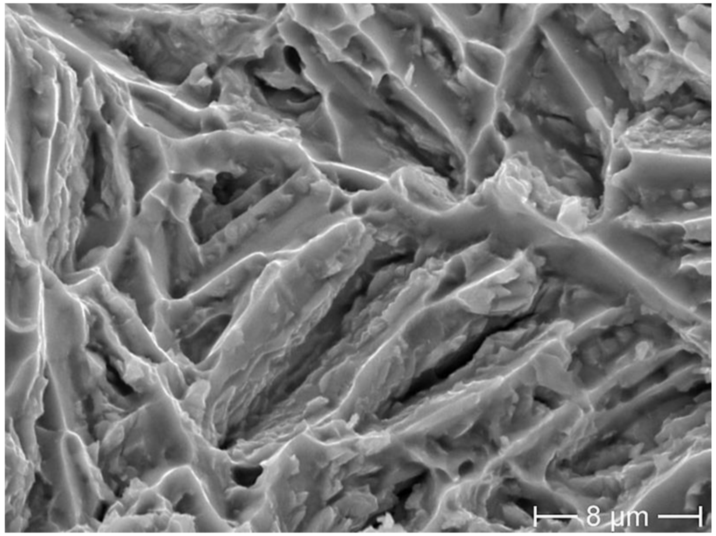
2790 wppm H

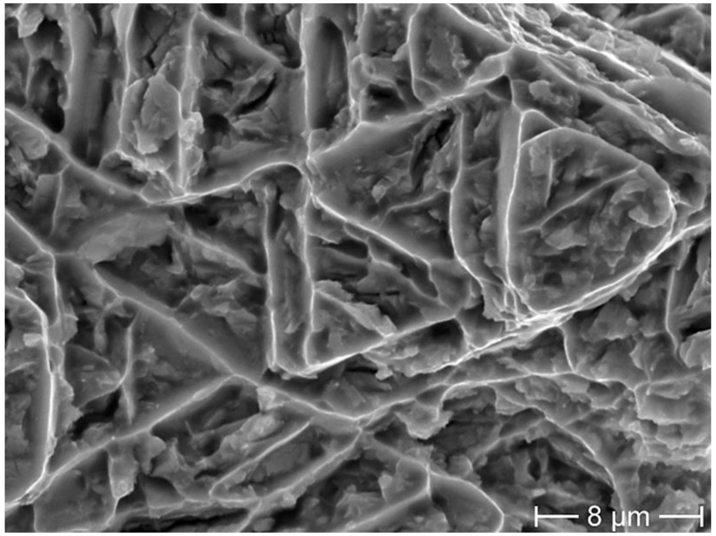


4850 wppm H

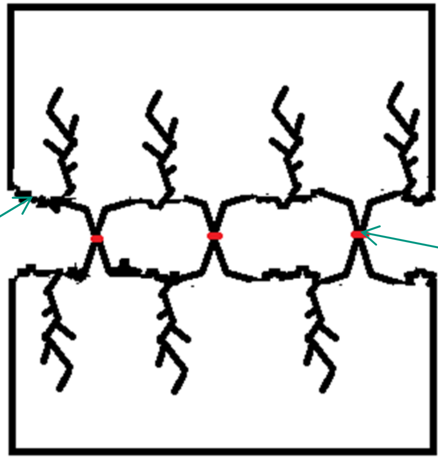
Scanning electron microscopy of fracture surfaces of hydrogenated Zircaloy-4

900 °C





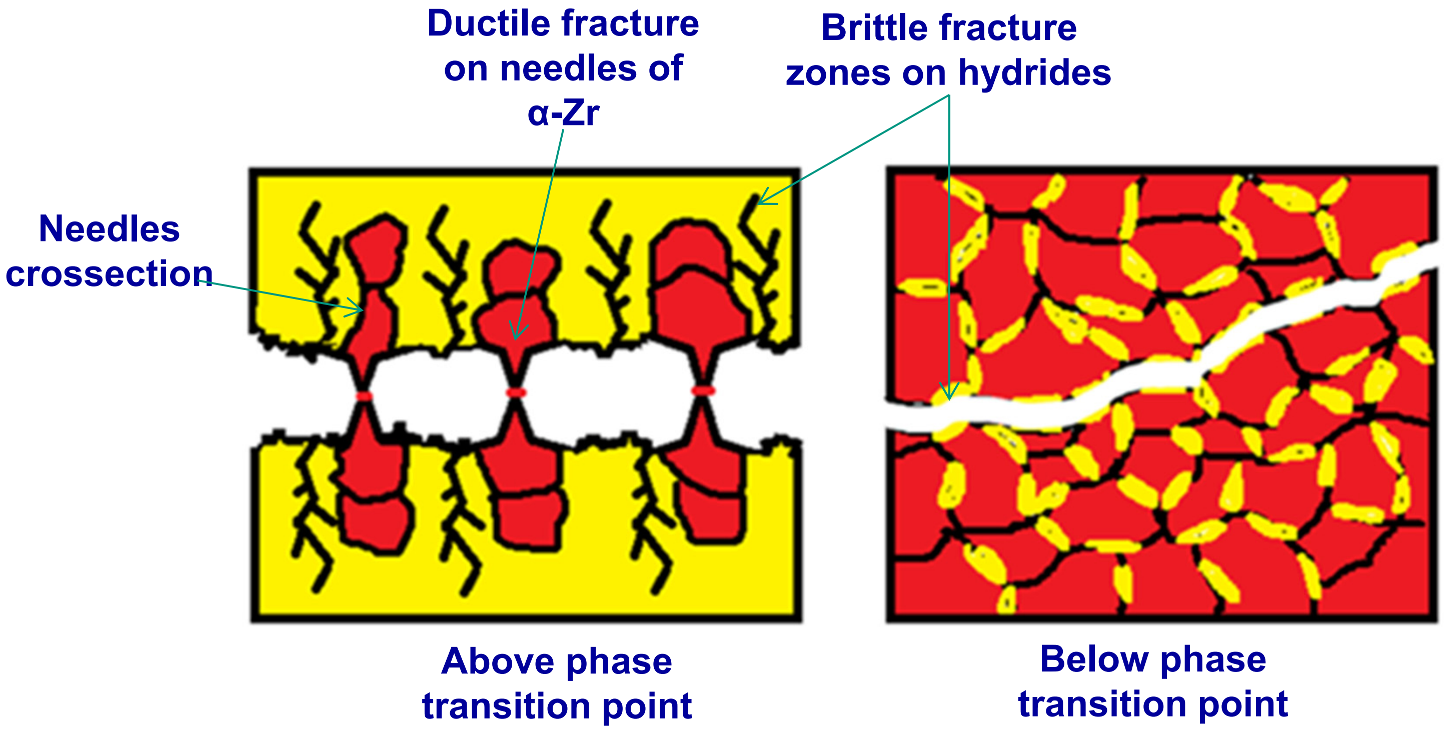
1170 wppm H | **1640 wppm H**



Brittle fracture zone on hydrides

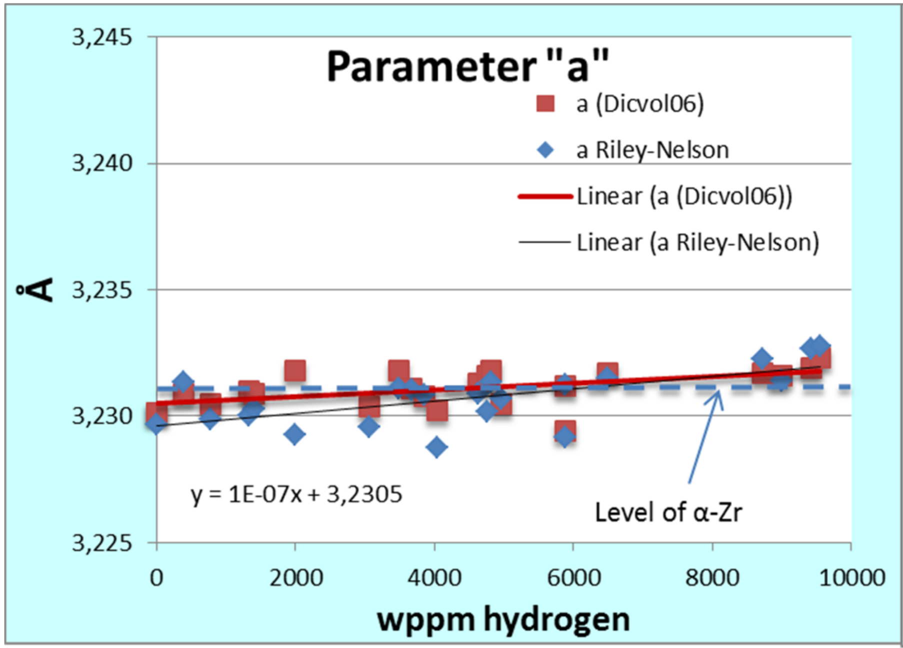
Ductile fracture on needles of α-Zr

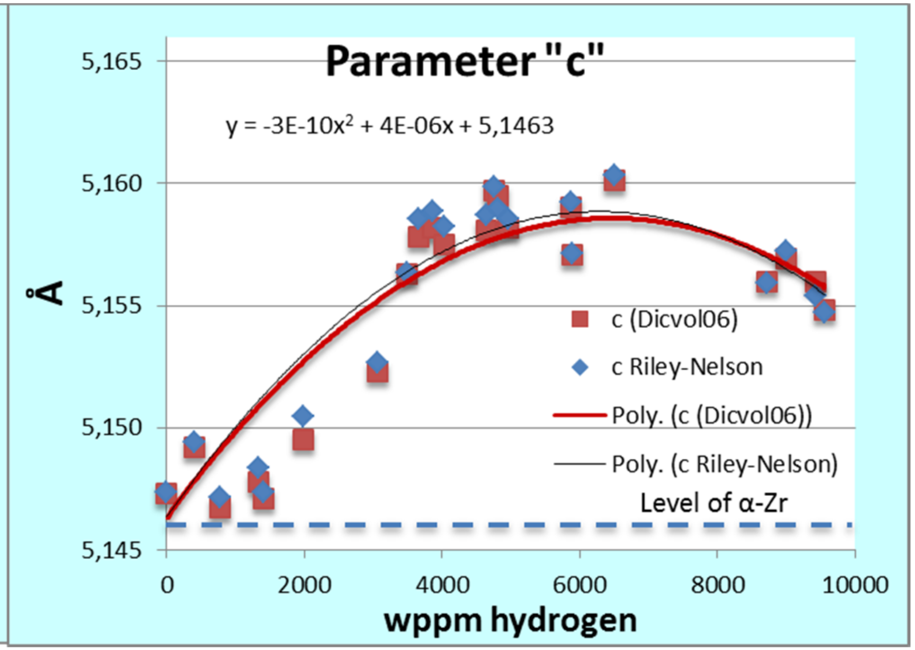
Fracture schemes for Zr and Zircaloy-4



Understanding the mechanism

Change of lattice parameters after hydrogenation of Zircaloy-4 samples





a – didn't change noticeably

c – significantly increased after hydrogenation

Keeping in mind this dependencies of lattice parameters we suggest that the following mechanism of embrittlement can be the cause of premature fracture in Zircaloy-4

Change of lattice parameters after hydrogenation of Zircaloy-4 samples

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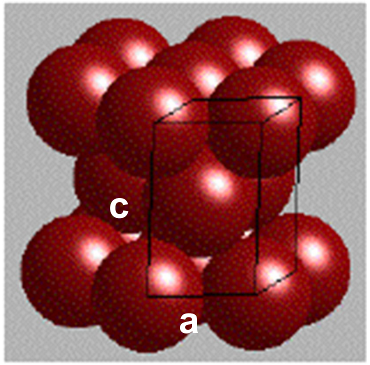
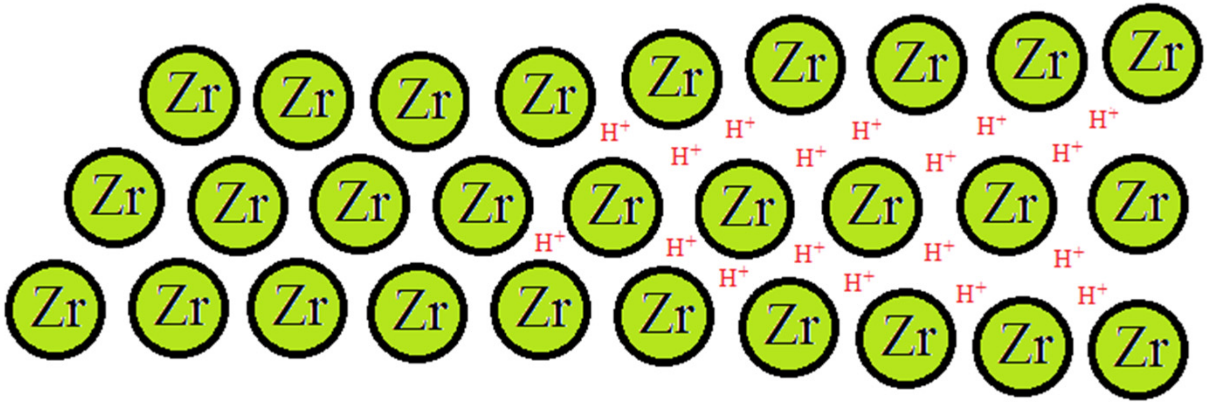
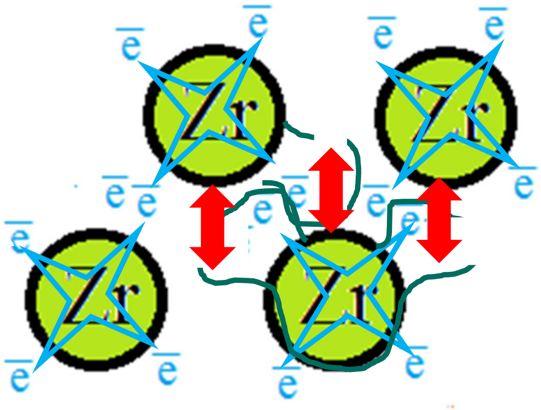


3D model of HCP-lattice



2D scheme of HCP-lattice

2D scheme of HCP-lattice with hydrogen presented as proton



Every Zr atom has 4 free electrons to maintain lattice integrity

In the presence of hydrogen only 2 electrons are left unbounded in hydride and they must be regrouped between atoms to compensate the repulsion force

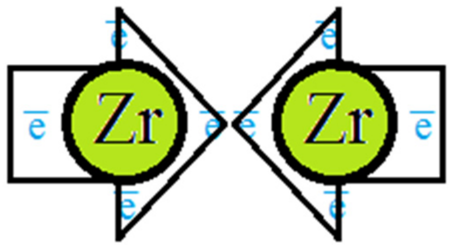
As a result:

a) **Loss of plasticity because of lack of free electrons**

b) **Decrease the strength of atomic bonds (decohesion) between Zr atomic layers → lower energy to form a new surface**

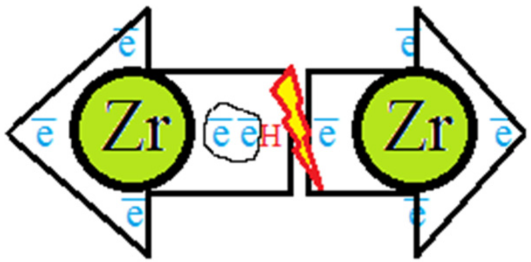
c) **Increased internal stresses because of charge redistribution** (hydrogen starts acting as a proton after giving his electron to Zr and repulses another layer being in connection with his Zr atom in current layer)

Decohesion mechanism*

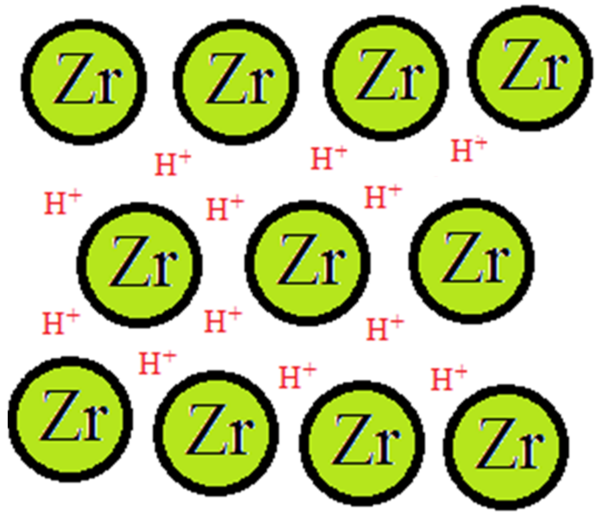


Cohesion

2D simplified understanding of atomic layers



Decohesion



***an overview on hydrogen embrittlement mechanisms can be found in *Stan Lynch* Hydrogen-embrittlement phenomena and mechanisms. Corros Rev 30 (2012): 105–123**

"A decohesion theory was first proposed (on iron) in 1926 by L.B. Pfeil and subsequently developed by A.R. Troiano. The decohesion hypothesis – involving charge transfer and weakening of interatomic bonds so that tensile separation of atoms (decohesion) occurred in preference to slip – was later quantitatively developed by R. Oriani."

Taking into account the work of S. Yamanaka et al. Analysis of the electronic structure of zirconium hydride, Journal of Alloys and Compounds 330–332 (2002) 313–317, and results on EBSD, SEM and XRD obtained during our investigation we understand that decohesion is exactly the case in Zr and its alloys and this is the main mechanism of destruction of medium- and high hydrogenated specimens. The mechanism of preliminary destruction of low hydrogenated Zr is not sufficiently investigated. The work is going on.

Conclusion

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- The XRD-analysis showed the presence of γ-, δ-phases of zirconium hydrides in all of performed experiments on Zry hydriding at temperatures from 600 °C to 900 °C. 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".
- The electron back scattered diffraction is up to date the best tool to detect hydrides and to build the phase distribution map and analyze grain orientation and microtexture. On the basis of the EBSD-analysis the difference in the hydride formation and growth between pure Zr and Zircaloy-4 is shown.
- Fracture surface analysis helps to understand the mechanisms of fracture of a brittle material after hydrogenation and hydride formation. There are the "islands" of retained plasticity detected. The scheme of such kind of plasticity and fracture was determined.
- The decohesion mechanism helps to understand the embrittlement of zirconium and Zircaloy-4 and other hydride forming alloys with hexagonal close-packed crystal lattice. The fact of the increase of the lattice parameter "c" allows to suggest that the decohesion mechanism accompanied by increscent internal stress due to hydrogen atoms inside the lattice could be responsible for cladding material destruction.
- The increased brittleness of some zirconium claddings after QUENCH-LOCA tests could be caused by hydrides which are distributed in the bulk of material. The thorough analysis of claddings after QUENCH-LOCA experiment is planned.

Aknowledgements

The authors would like to thank the following KIT colleagues:

- Mrs. Ursula Peters for her technical assistance with the hydrogenation tests
- Ms. Julia Lorenz for the help during preparation of the specimens for metallographic observations
- Dr. Harald Leiste for carrying out of X-Ray diffraction measurements

Thank you for your attention!

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http://www.iam.kit.edu/wpt/471.php