Orientation relationships of δ-hydrides in zirconium and Zircaloy-4

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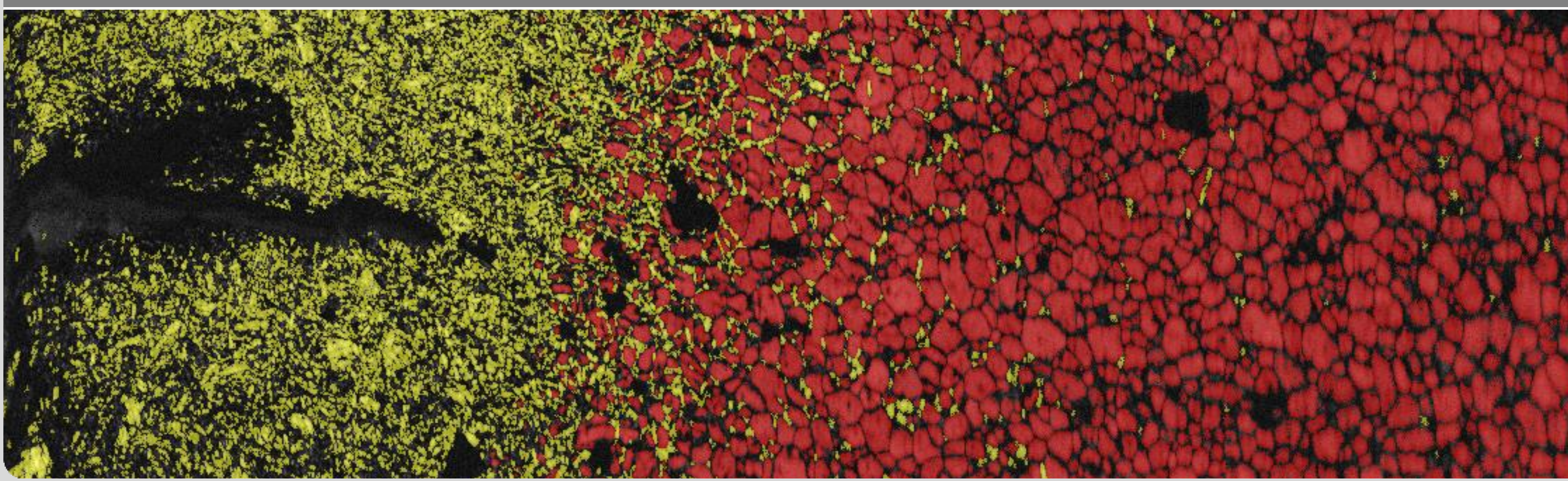
Institute for Applied Materials (IAM), Program NUSAFE



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A. Pshenichnikov, J. Stuckert, M. Walter

Abstract

In the framework of the QUENCH-LOCA program at Karlsruhe Institute of Technology single rod hydrogenation tests were performed to investigate changes in microstructure and mechanical properties of hydrogenated Zircaloy-4 claddings. The cladding tube segments with length of 70 mm as well similar tubes made of pure Zr were hydrogenated to hydrogen contents between 400 and 9500 wppm under temperatures 600 - 900 °C (typical for the LOCA transient) in Ar and H_2 gas mixture. The hydrogenation regime was chosen concerning the phase diagram of Zr-H system. Microstructure was investigated after cooling from temperatures, corresponding to all of the main regions of an equilibrium phase diagram, to room temperature. The traces of intermediate stages of $\alpha \rightarrow \beta \rightarrow \alpha$ transition induced by hydrogen were observed. Hydrides of δ- and γ- type were detected after all hydrogenation tests as it was established by X-Ray Diffraction (XRD) analysis. But their location inside the microstructure was unknown until the Electron Back Scattered Diffraction (EBSD) analysis was implemented.

The EBSD analysis has proved to be the best tool to detect hydride phase distribution map and analyze grain orientation and microtexture. More than 120 measurements gave good statistical information on hydride nucleation and development. On the basis of the EBSDanalysis the difference in the hydride formation and growth between pure Zr and Zircaloy-4 has been shown.

Grain boundary distribution spectra showed the seven peaks, which represent seven possible orientation relationships. The art of the orientation was established by means of microtexture analysis for Zr and Zircaloy-4.

The comparison of literature data with the obtained orientation relationships showed a very good agreement, though some of relationships were not confirmed. The most often detected orientation relationship $\{001\}_{\alpha\text{-Zr}}||\{111\}_{\delta}$ is in full accordance with literature. The question of primary and secondary habit plane as stated by some authors is of less importance as we observed mostly the whole spectrum of possible orientations in each sample. Only low hydrogenated specimens have demonstrated one or two the most dominant kinds of relationship.

For pure Zr the orientation relationships $\{001\}_{\alpha\text{-Zr}}||\{111\}_{\delta}$ and $\{106\}_{\alpha\text{-Zr}}||\{111\}_{\delta}$ and for Zircaloy-4 $\{001\}_{\alpha\text{-Zr}}||\{111\}_{\delta}$ and $\{11,30\}_{\alpha\text{-Zr}}||\{100\}_{\delta}$ were established as the most dominant among the others summarized in a crystallographic relationships table.

The performed experiments show the applicability of this method for explanation of increased embrittlement of some claddings after QUENCH-LOCA experiments. It can be related to the δ-hydrides formed in cladding during secondary hydrogenation through the inner cladding surface near to the burst opening. The thorough analysis of claddings after QUENCH-LOCA experiment is going on.

Objectives

- **Electron back scattered diffraction (EBSD) analysis of hydrogenated specimens**
- **Grain boundary spectra analysis**
- **Metal-hydride orientation relationships refinement**

Materials and methods of investigation

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

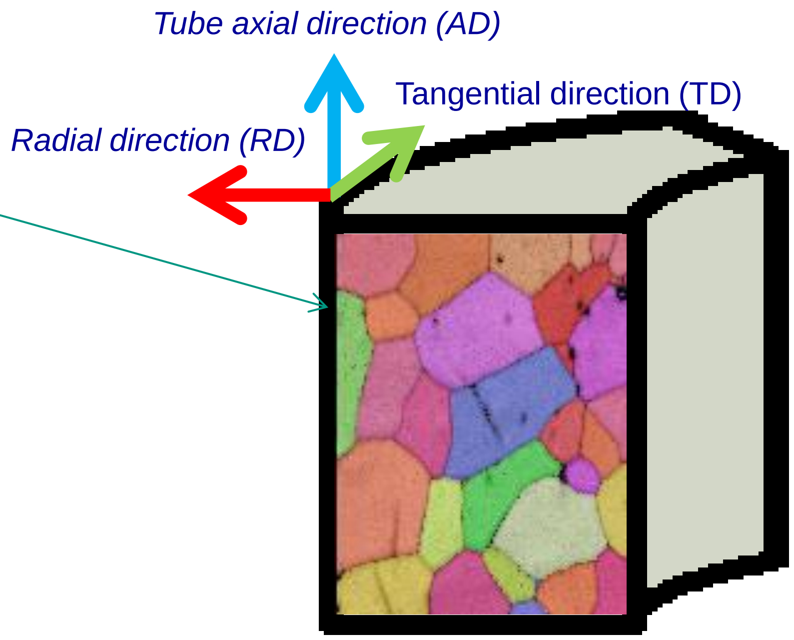
2) Conventional Zircaloy-4 cladding tube

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

<u>Methods of investigation:</u>

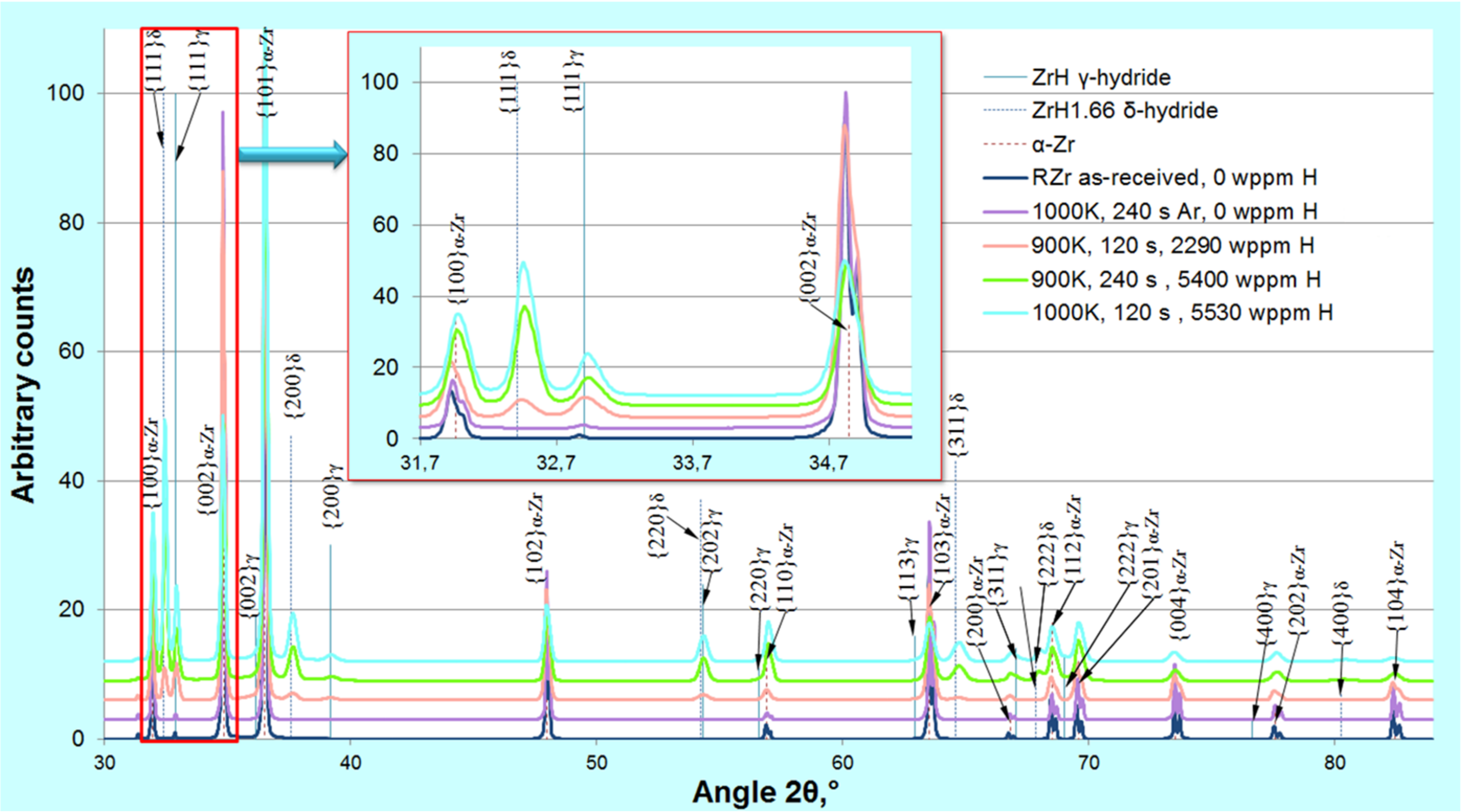
- Hydrogenation in Ar+H_2 gas mixture in LORA-furnace
- EBSD measurements of the cladding tube axial section
- Phase detection by means of QUANTAX microanalysis system combined with Esprit software (Bruker Nano GmbH, Germany)



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

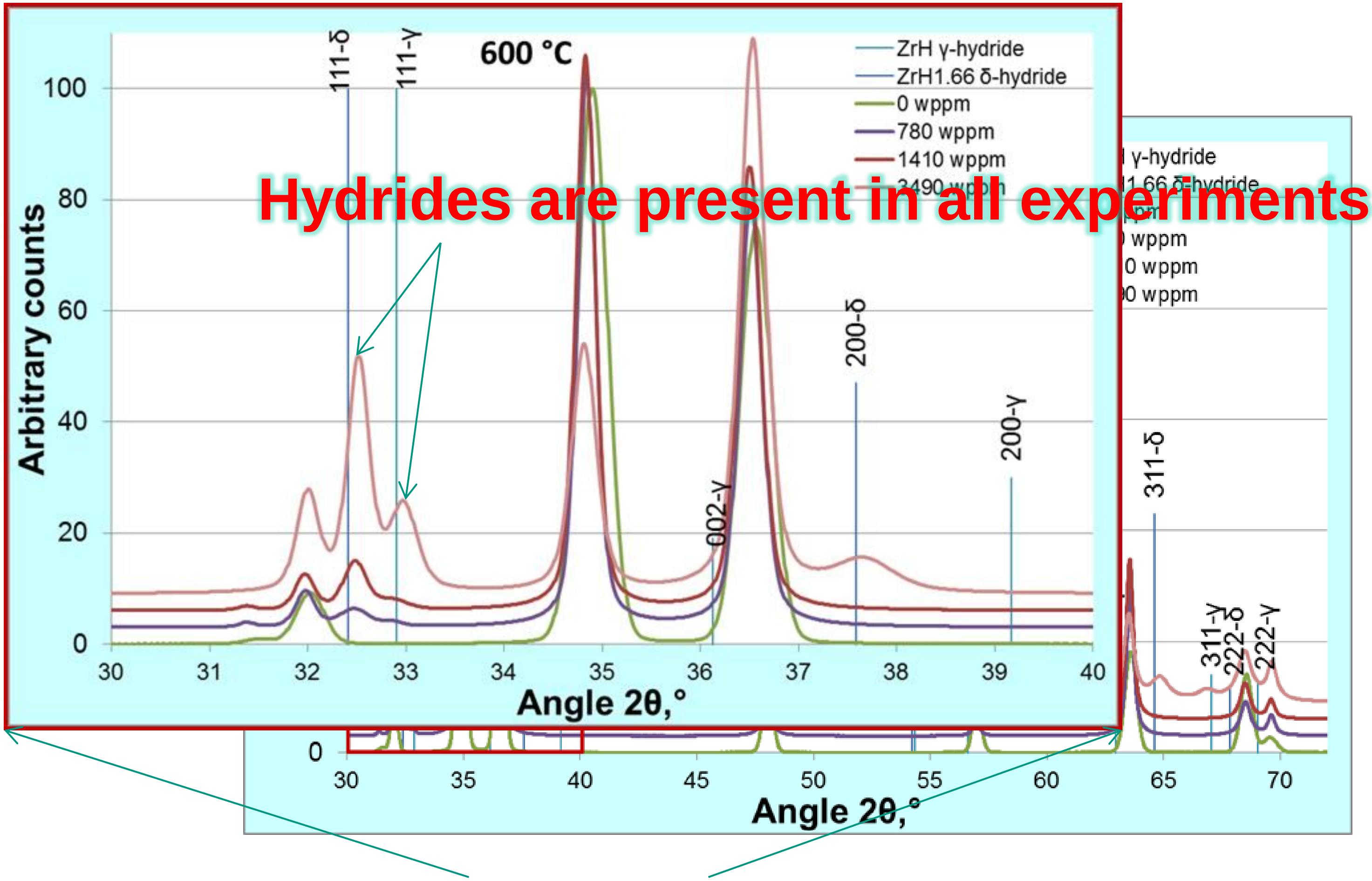
Present phases in pure Zr

Only γ-, and δ-hydrides in α-Zr were detected after hydrogenation



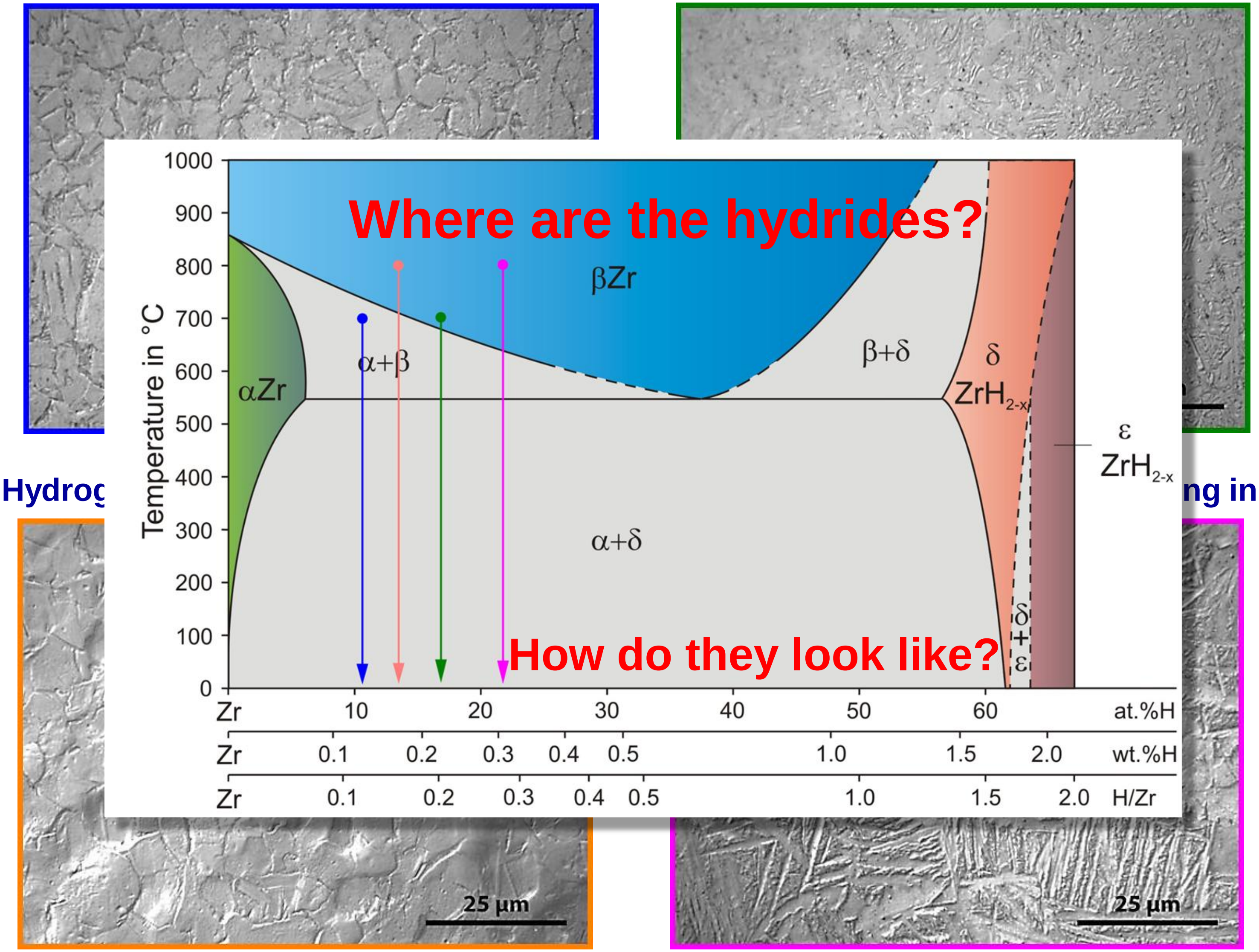
As soon as EBSD result is a lattice type and its orientation, there can be some phase detection problems. Preliminary XRD-analysis is necessary for exclusion of the errors during the phase detection by means of EBSD.

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



Optical metallography of hydrogenated Zircaloy-4

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



Hydrog … ng in air

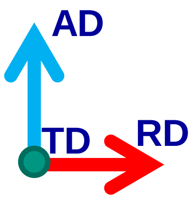
1790 wppm H

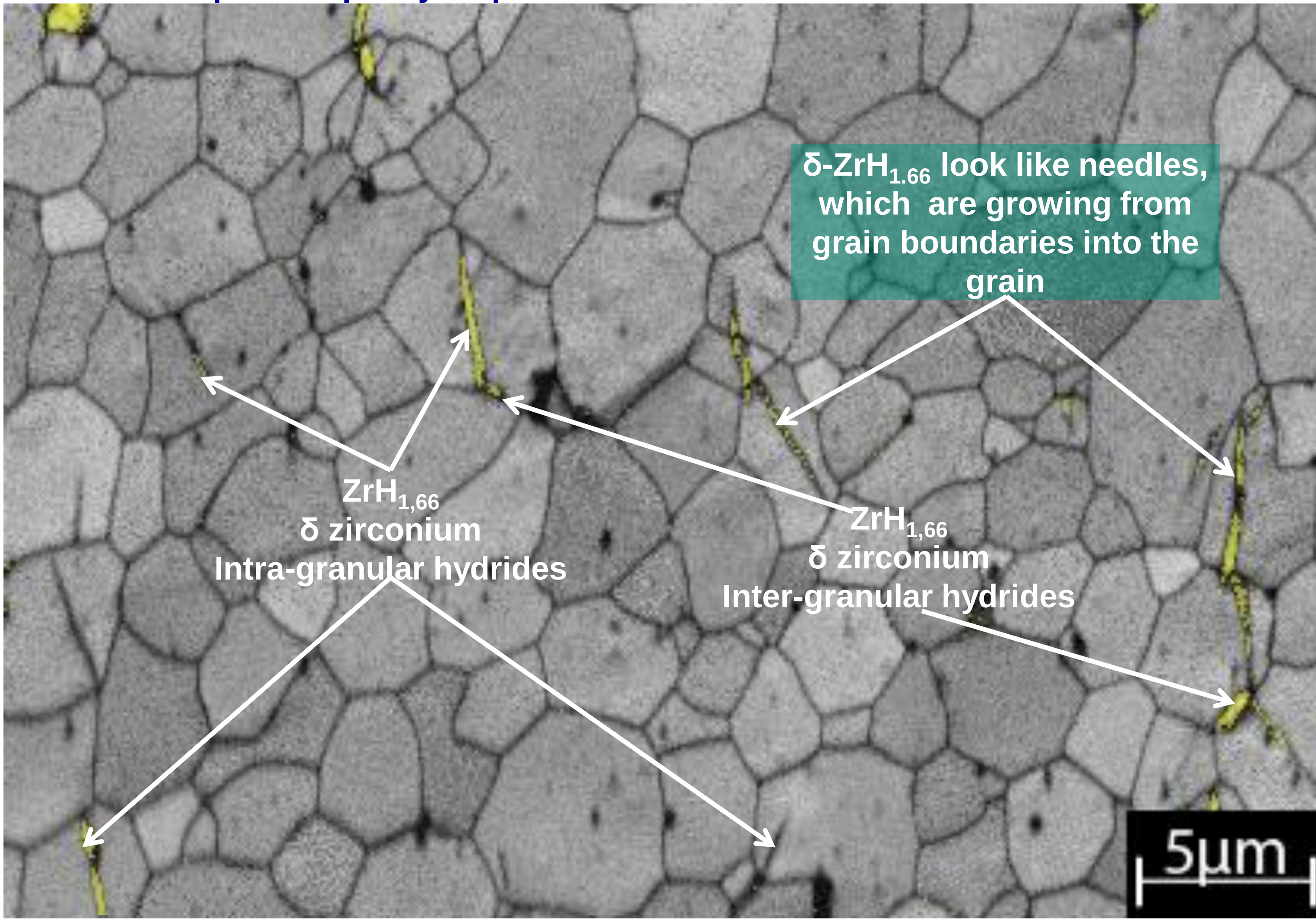
3060 wppm H

EBSD-analysis

Zr hydrogenated at 600 °C 400 wppm H

EBSD pattern quality map

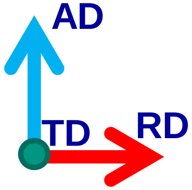


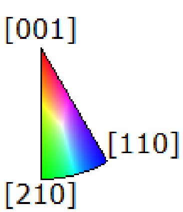


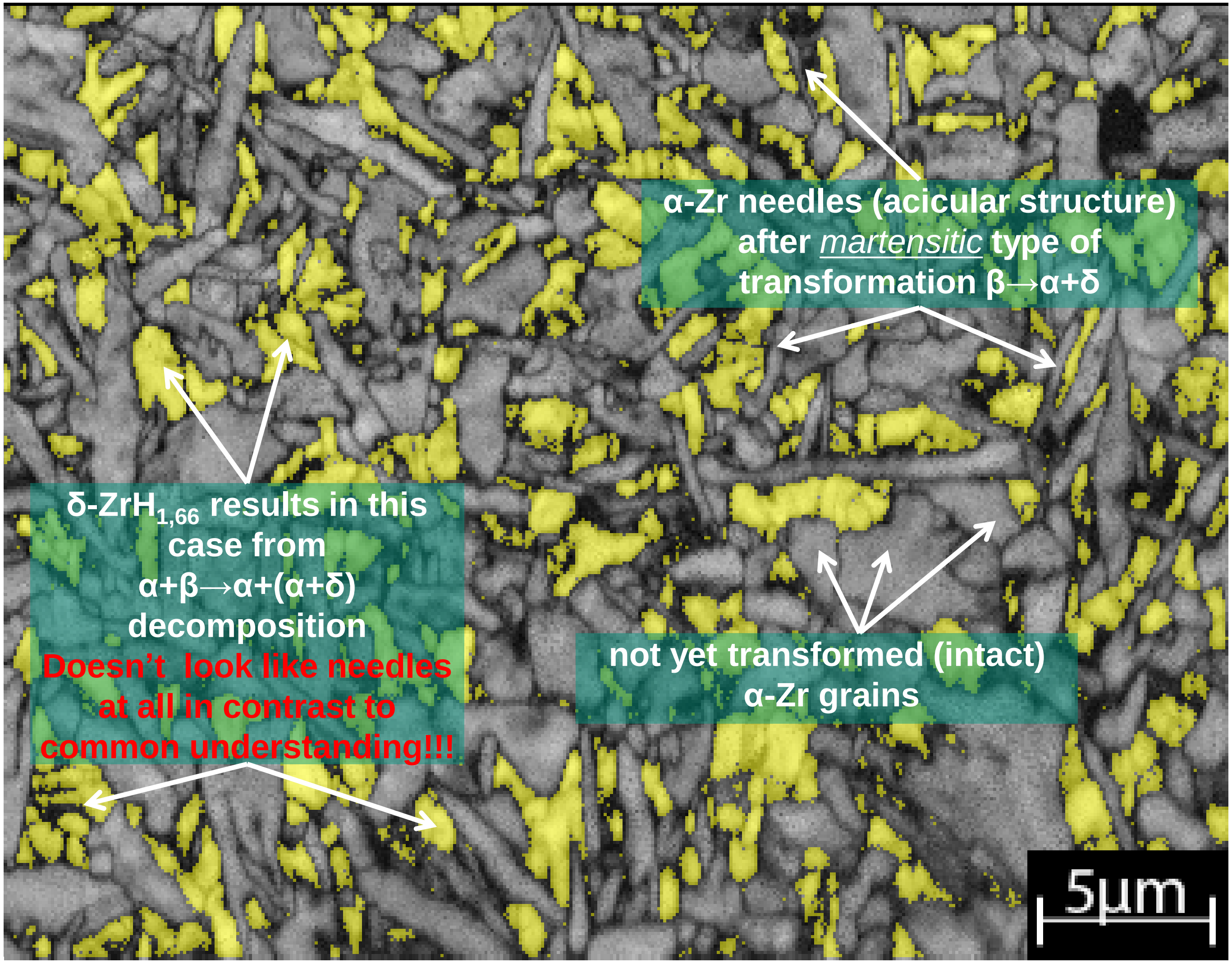
99.3% Zr, 0.7% $ZrH_{1.66}$, γ-ZrH – not detected (on the basis of image analysis)

Zr hydrogenated at 600 °C 2290 wppm H

EBSD pattern quality map



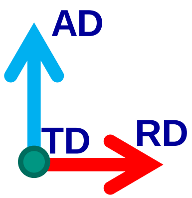


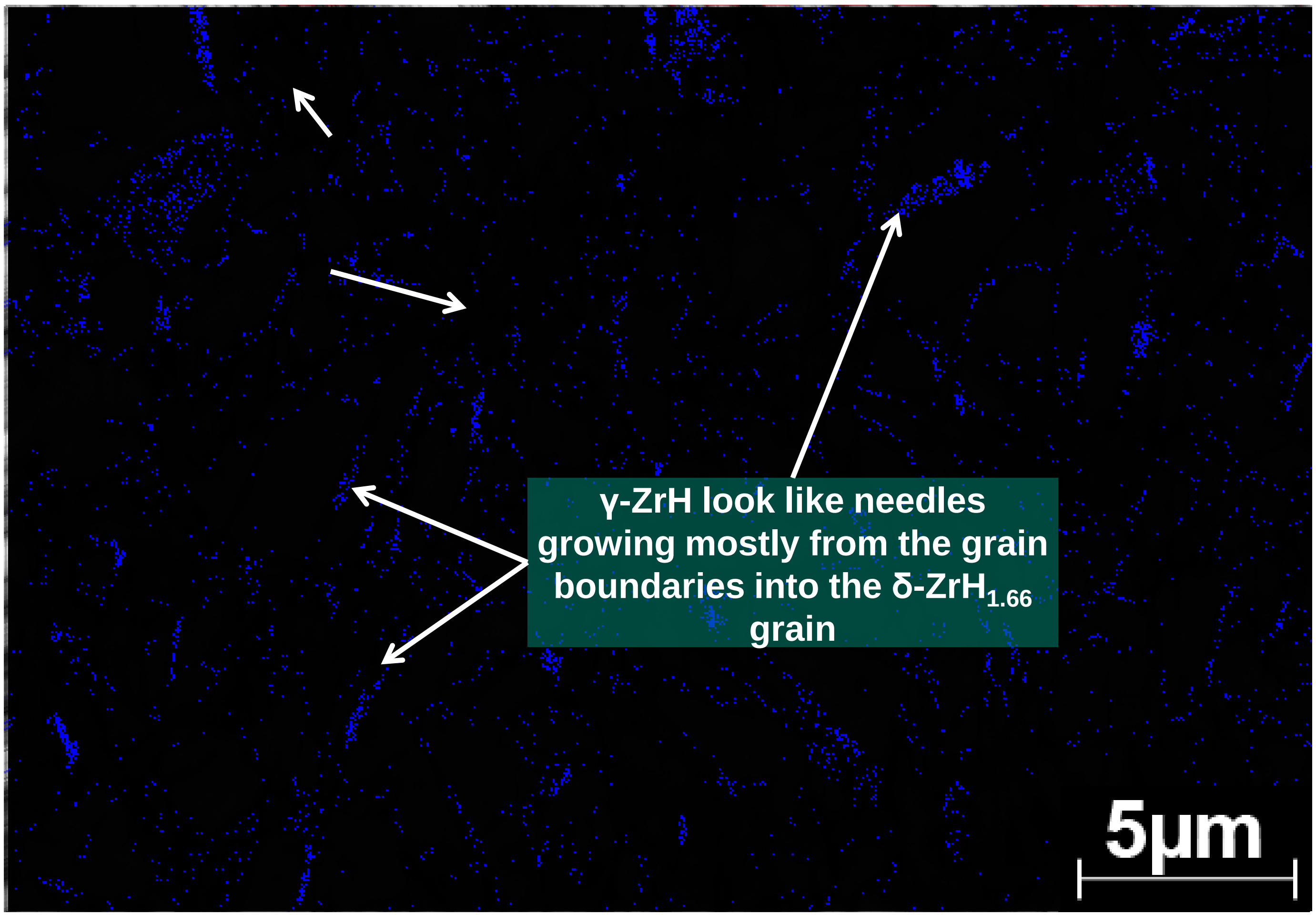


72.6% Zr, 26.5% δ-$ZrH_{1.66}$, 0.8% γ-ZrH (on the basis of image analysis)

Zr hydrogenated at 600 °C 5400 wppm H

EBSD pattern quality map + Phase map

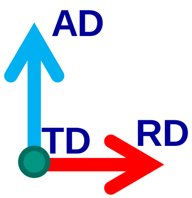


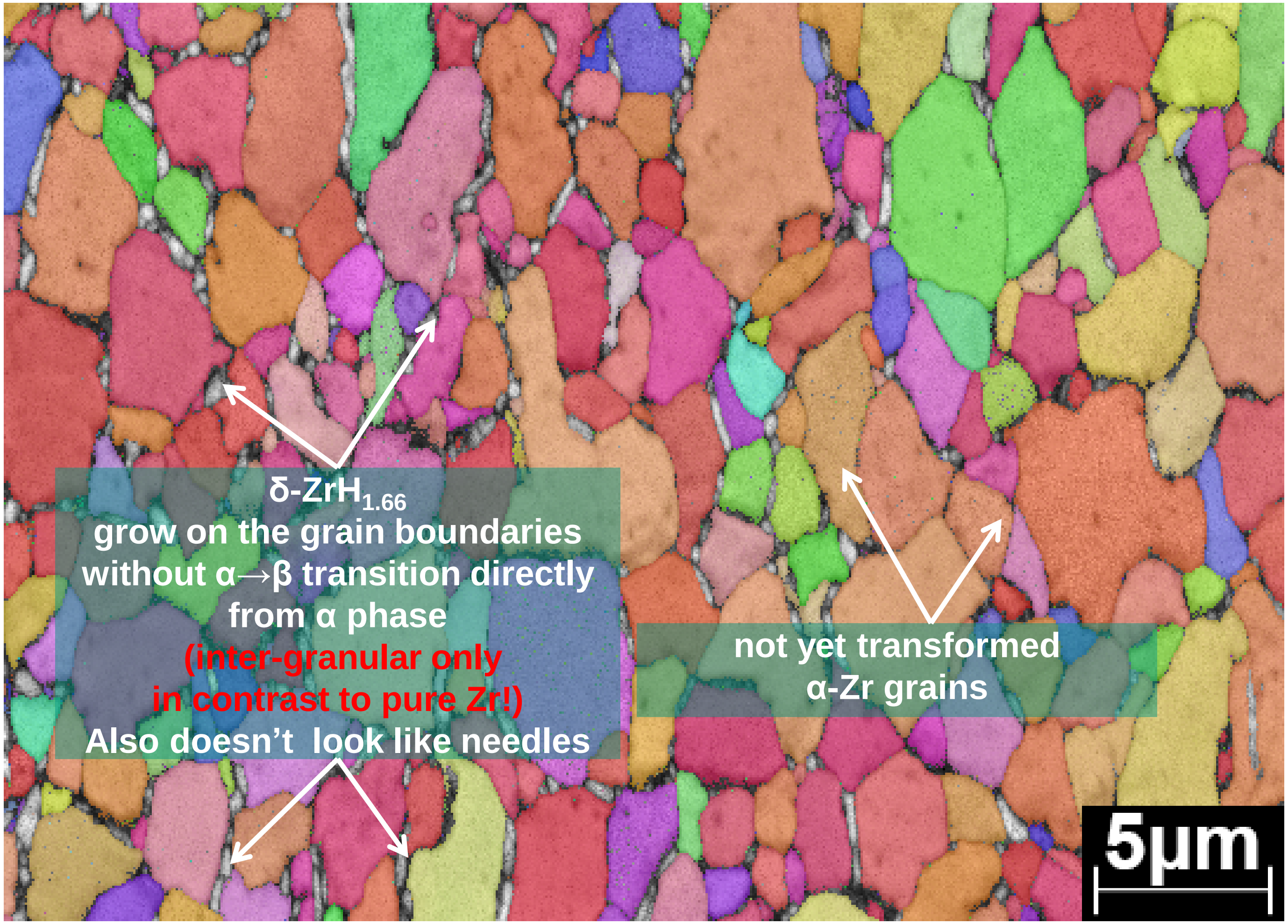


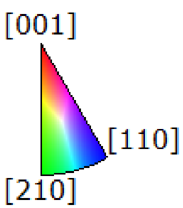
27.1% Zr, 70.6% δ-$ZrH_{1.66}$, 2.35% γ-ZrH (on the basis of image analysis)

Zircaloy-4 hydrogenated at 600 °C 2650 wppm H

EBSD pattern quality map   Grain orientation distribution in RD



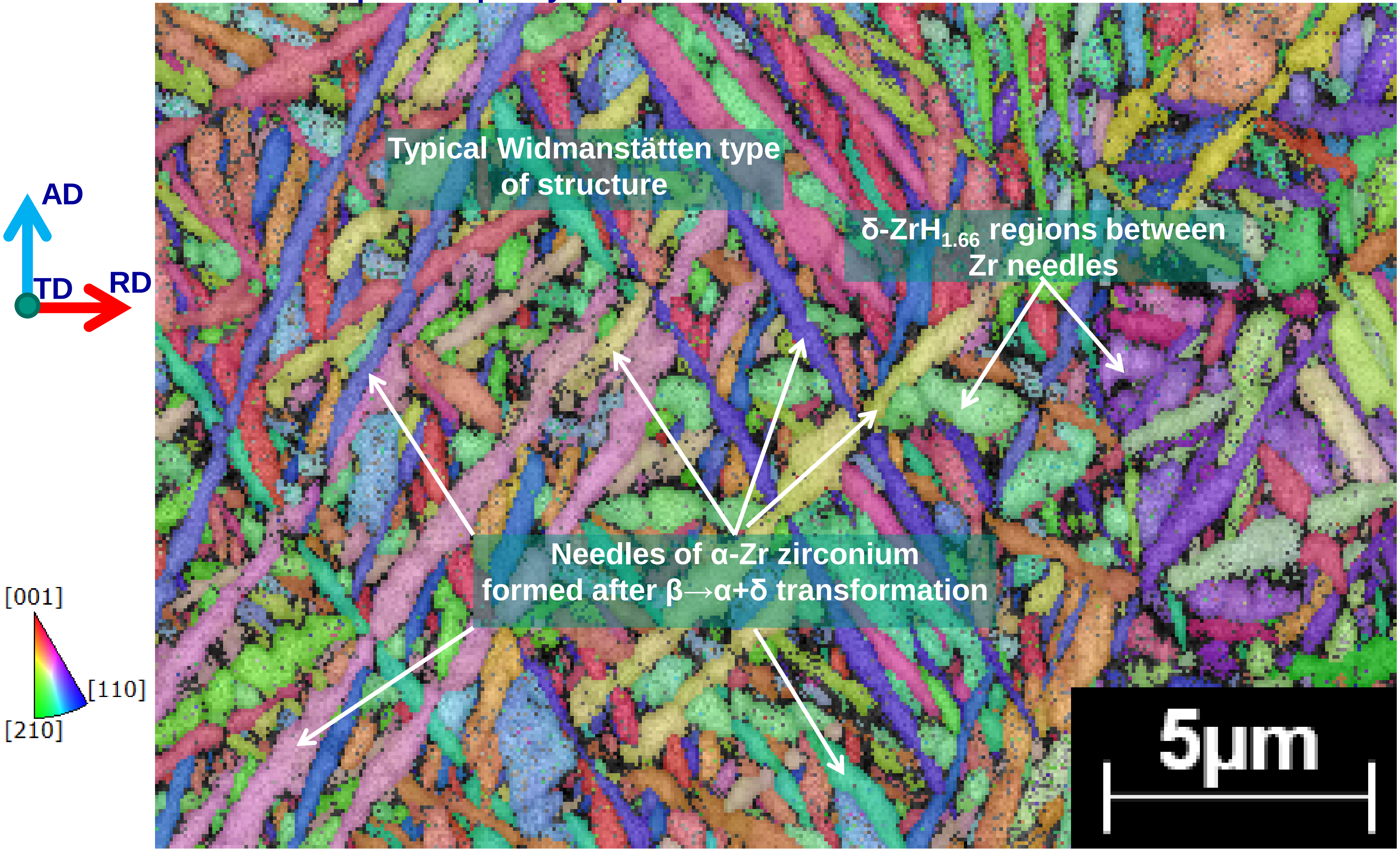




94.8% Zr, 5.2% δ-$ZrH_{1.66}$, γ-ZrH – not detected (on the basis of the image analysis)

Zircaloy-4 hydrogenated at 700 °C 5880 wppm H

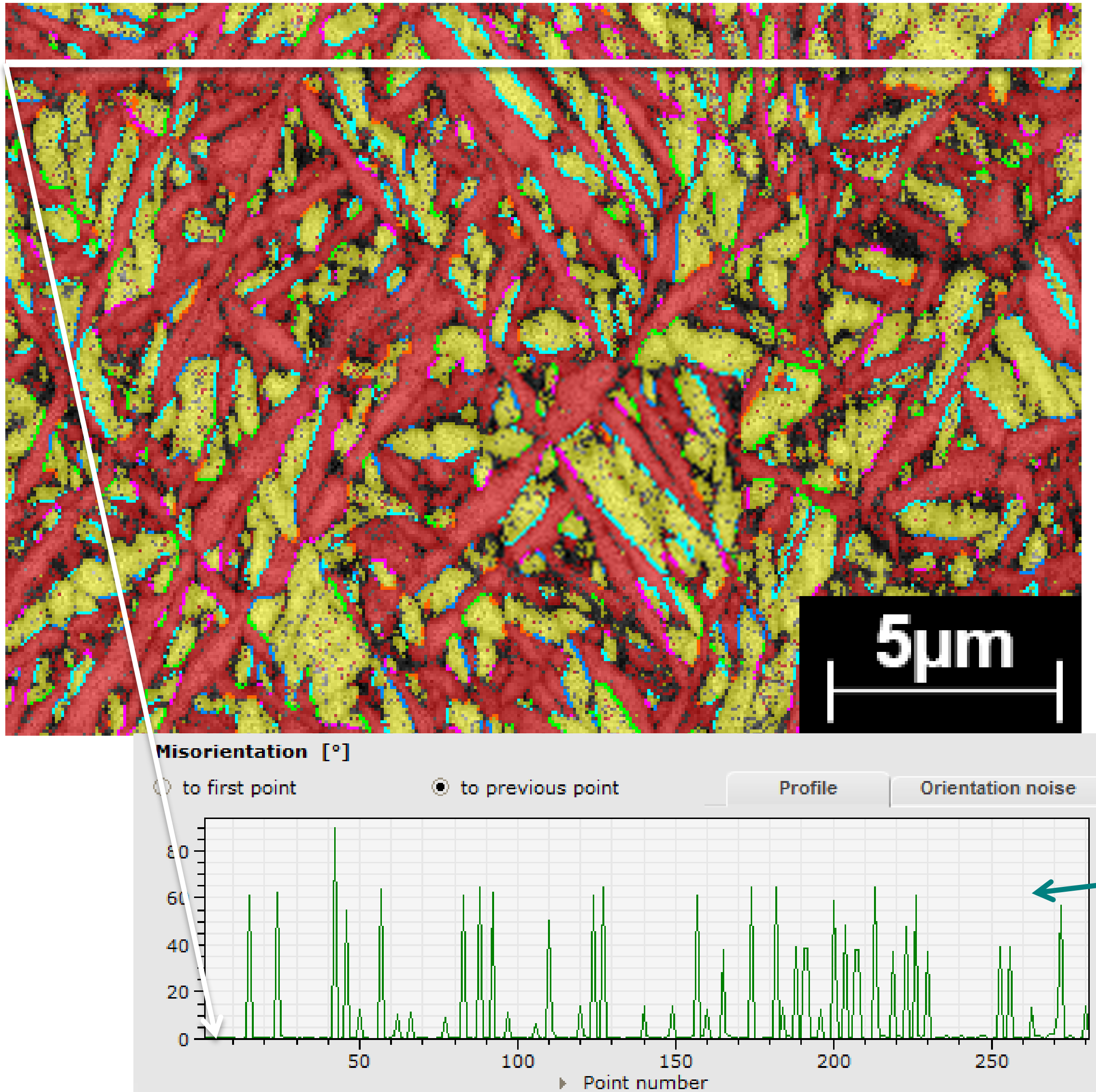
EBSD pattern quality map **Grain orientation distribution in RD**



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

Microstructure analysis



The analysis showed that after the eutectoid type of transformation we have a mechanism of hydride accommodation which lead to an accommodation of hydrides in ~ 60° or 90° of summary misorientation angle of the "hydride + Zr grain" system.

All rotations are compensated, so there are no stresses.

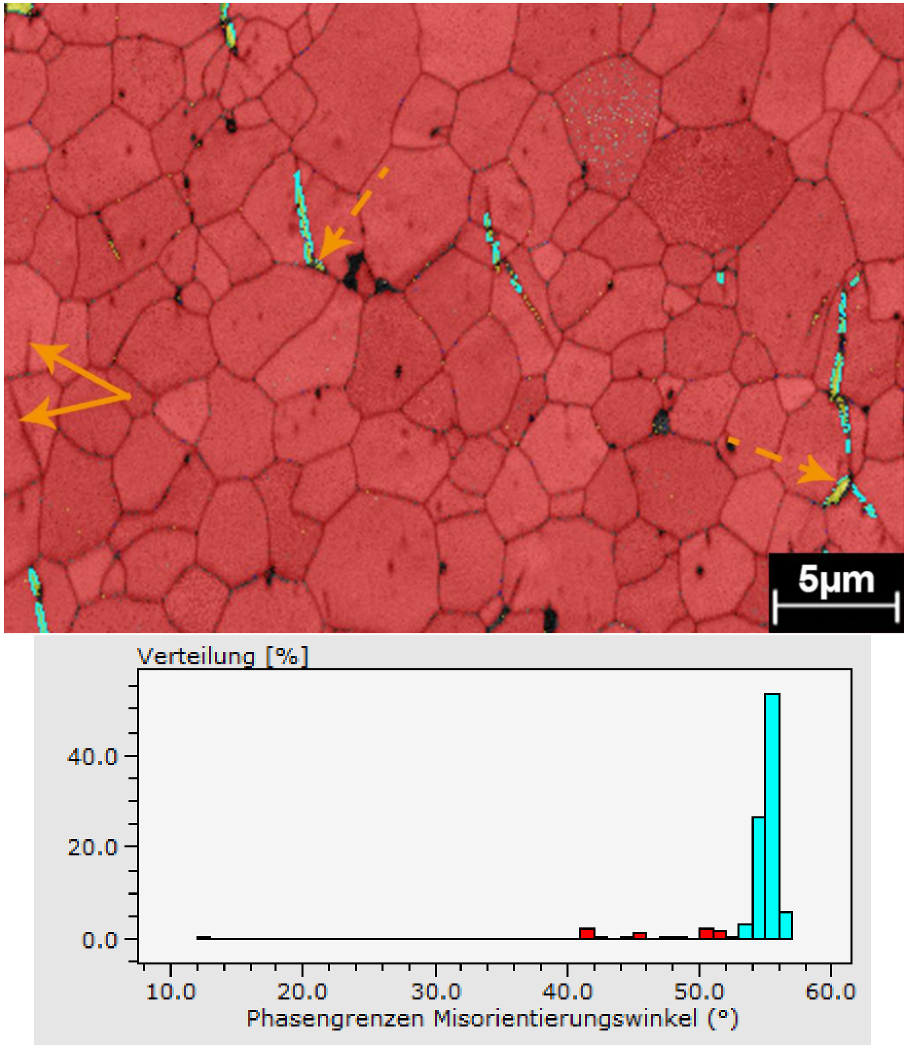
All these previous results were published in

1. ***A. P. Pshenichnikov*, J. Stuckert, M. Walter*** Hydrides and fracture of pure zirconium and Zircaloy-4 at temperatures typical for loss-of-coolant accident conditions ***//*** **Proceedings of the 20th QUENCH Workshop, 11 - 13 November 2014, Karlsruhe, Germany.**
2. ***Anton Pshenichnikov, Juri Stuckert, Mario Walter*** Microstructure and Mechanical Properties of Zircaloy-4 Cladding Hydrogenated at Temperatures Typical for LOCA Conditions ***//*** **Nuclear Engineering and Design, 2015, Vol. 283, P. 33 – 39.**
3. ***A. P. Pshenichnikov*, J. Stuckert, M. Walter, D. Litvinov*** Hydrides and fracture of pure zirconium and Zircaloy-4 hydrogenated at temperatures typical for loss-of-coolant accident conditions ***//*** **Proceedings of the 23rd International Conference on Nuclear Engineering (ICONE23), 17 - 21 May 2015, Makuhari, Chiba, Japan.**

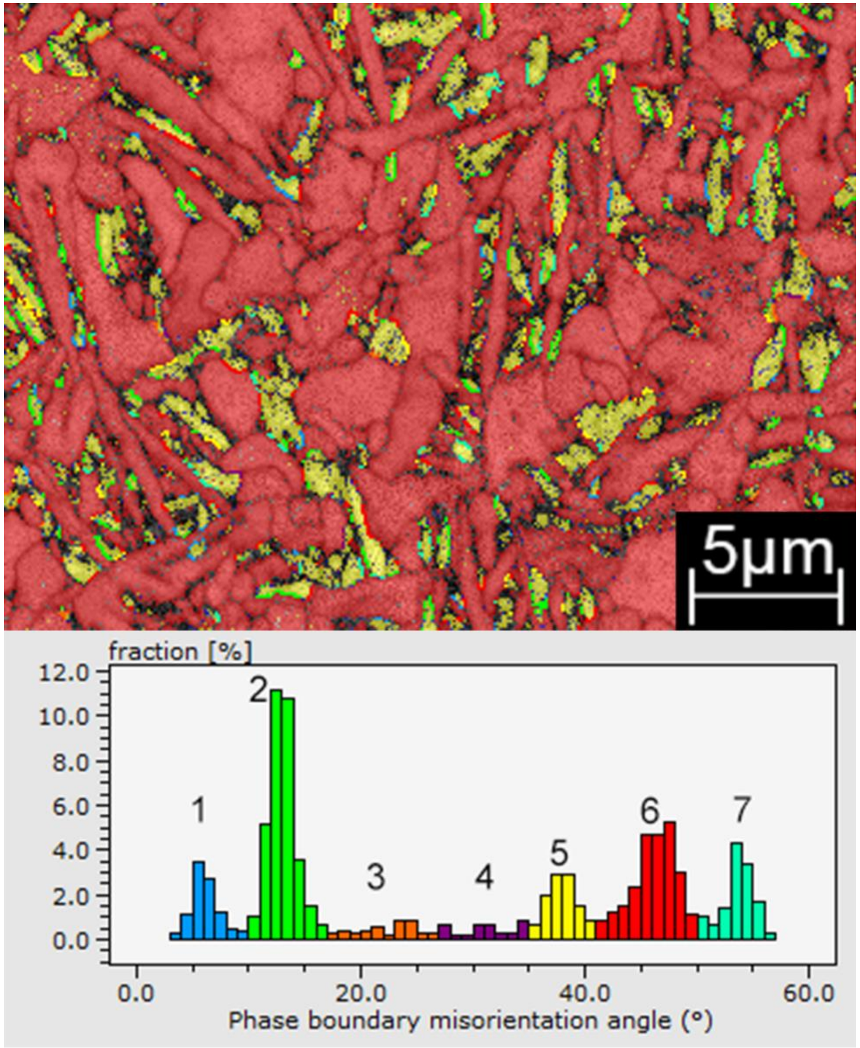
New results on EBSD-analysis

Examples of grain boundary spectra

Pure Zr 400 wppm H

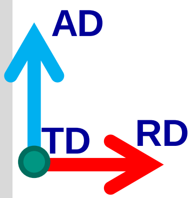


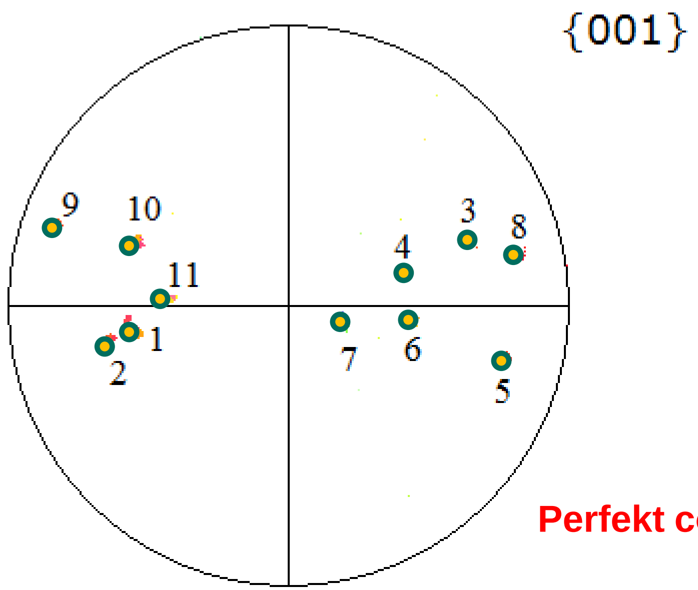
Zircaloy-4 4820 wppm H

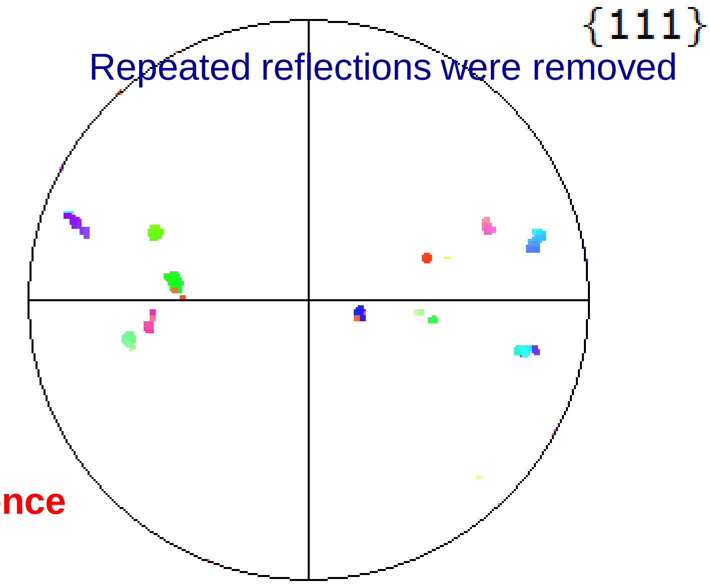


Zr hydrogenated at 600 °C 400 wppm H

Microtexturanalysis

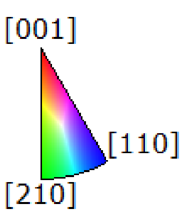






Repeated reflections were removed

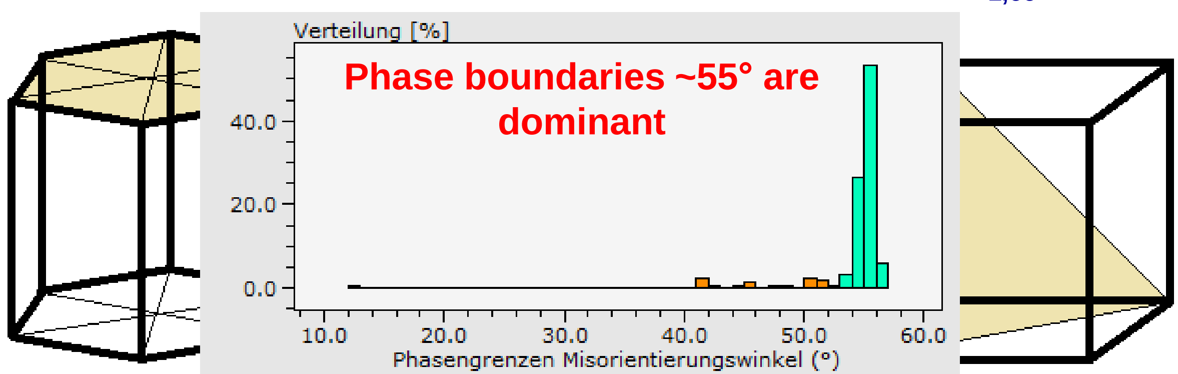
Perfekt coincidence



basal plane normal of α-Zr lattice

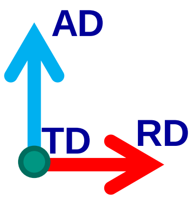
$\{001\}_{\alpha\text{-}Zr} \| \{111\}_{\delta\text{-}ZrH1.66}$

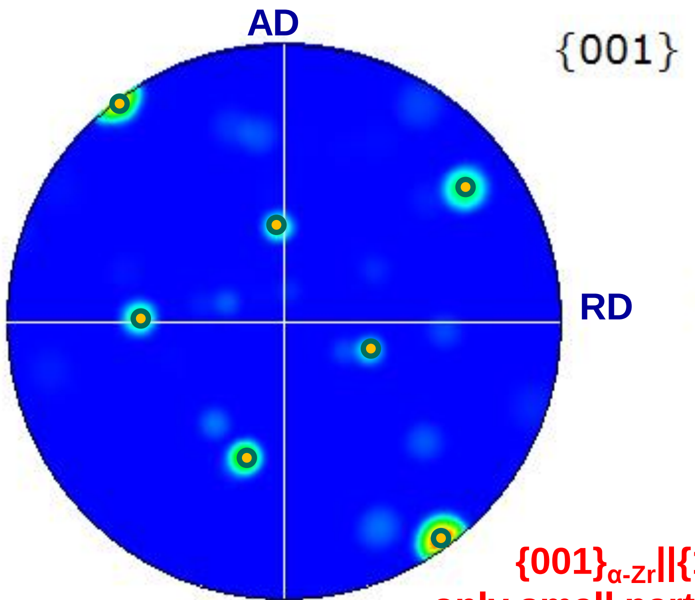
normal to cube diagonal of δ-$ZrH_{1,66}$ lattice



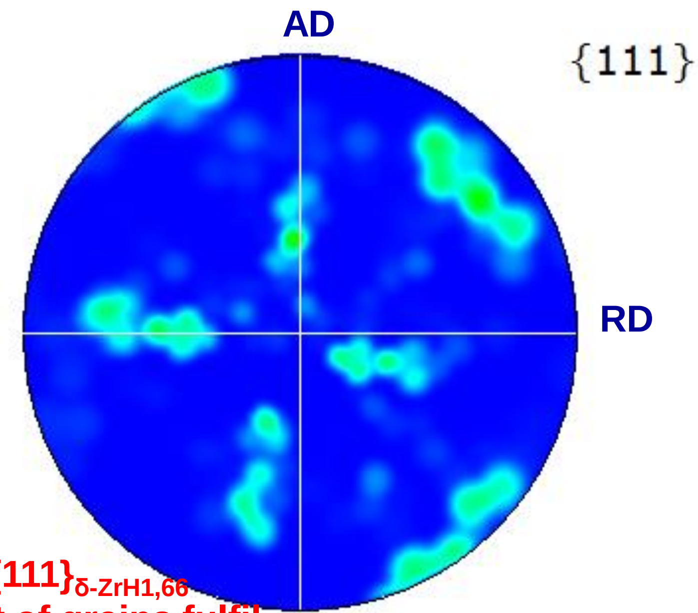
Zircaloy-4 hydrogenated at 600 °C 5880 wppm H

Microtexture analysis





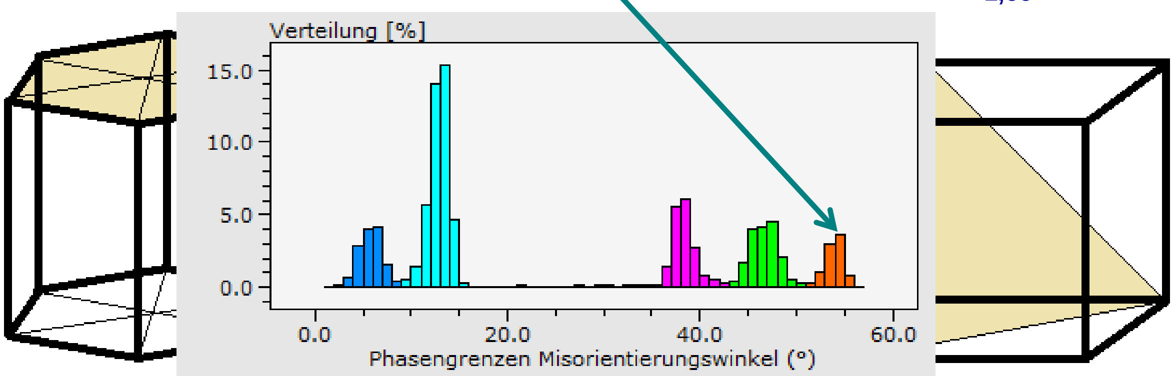
basal plane normal of α-Zr lattice



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

only small part of grains fulfil this relationship

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



Grain boundary spectra

Pure Zr

Zr-Zr grain boundary

Zr-δ-$ZrH_{1.6}$ grain boundary

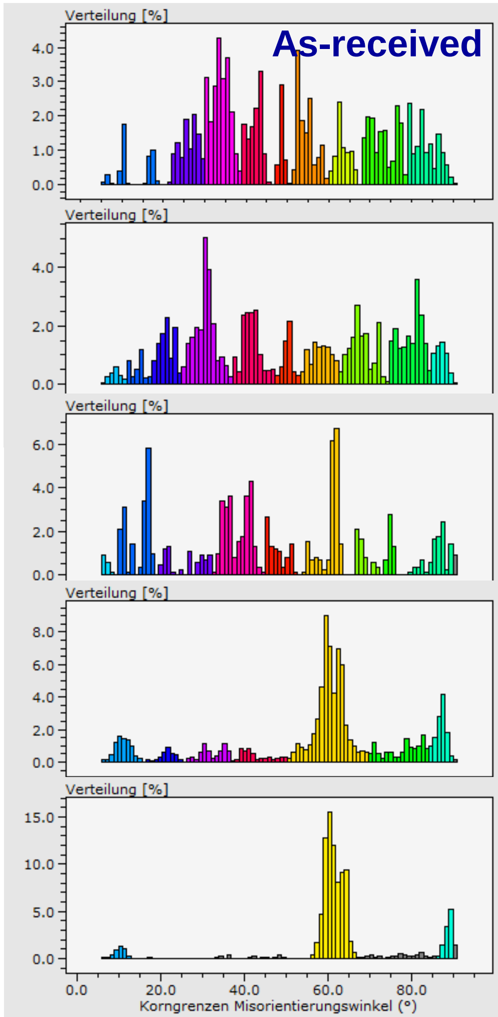
RZr — 0 wppm H

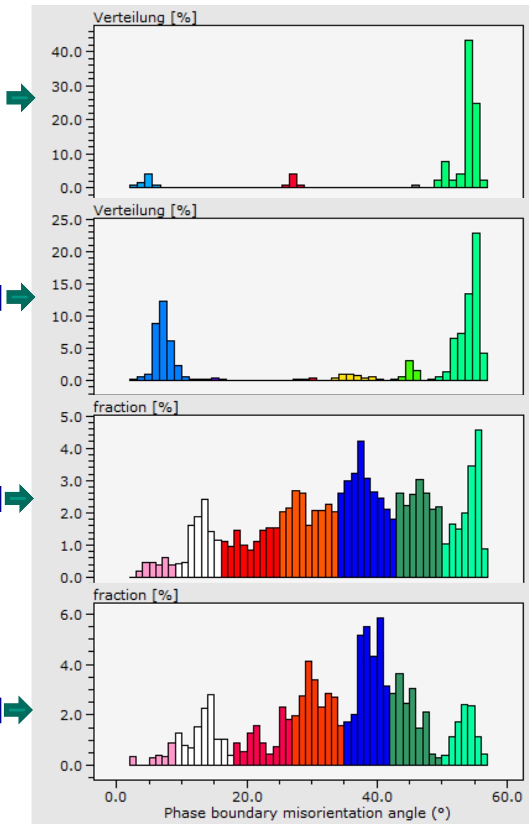
H16RZr — 510 wppm H

H17RZr — 1080 wppm H

H3RZr — 2300 wppm H

H4RZr — 5400 wppm H



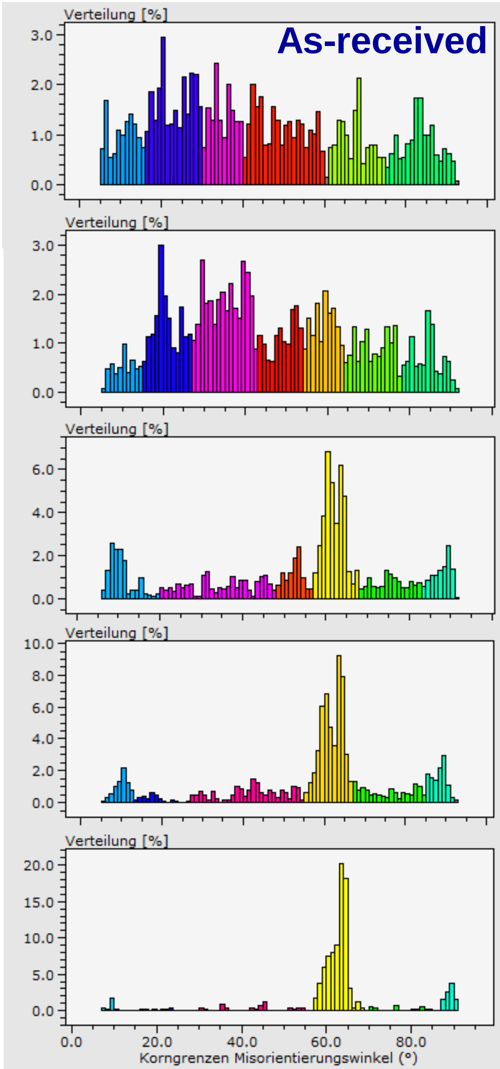


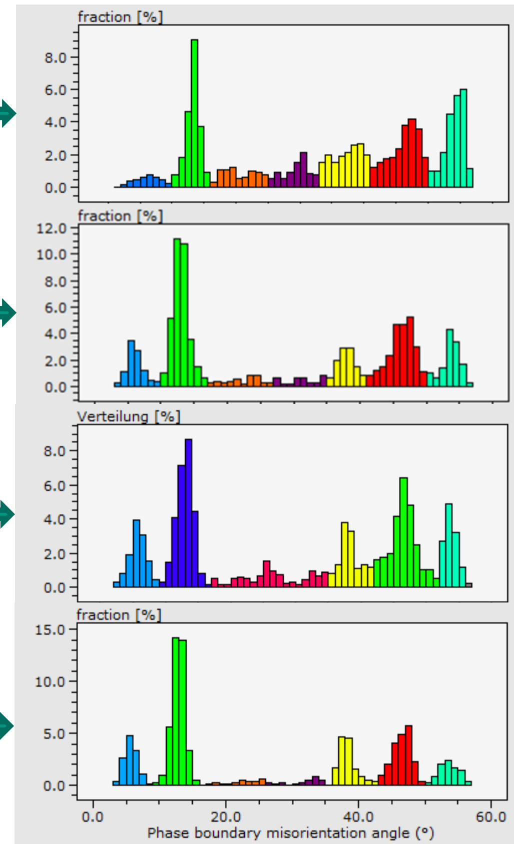
Grain boundary spectra

Zircaloy-4

Zr-Zr grain boundary

Zr-δ-$ZrH_{1.6}$ grain boundary





Z4	**0 wppm H**	
H59Z4	**2650 wppm H**	
H60Z4	**4820 wppm H**	
H61Z4	**6500 wppm H**	
H62Z4	**9800 wppm H**	

Orientation relationships

Already-known relationships

No.	Author	Relationship	Confirmed in our investigation
1	Une 2004, Kiran Kumar 2011, Wang 2013, Bradbrook 1972, Chung 2000, Puls 2012, Arunachalam et al. 1967, Qin 2014	$\{001\}_{\alpha\text{-}Zr} \parallel \{111\}_{\delta}$	+
2	Une 2004, Chung 2000, Puls 2012, Qin 2014	$\{107\}_{\alpha\text{-}Zr} \parallel \{111\}_{\delta}$	+
3	Bailey 1963, Ells 1968	$\{100\}_{\alpha\text{-}Zr}$ is a primary habit plane $\{107\}_{\alpha\text{-}Zr}$ is a secondary habit plane	+/-
4	Babyak 1967	Pyramidal planes angled 5-25° to the basal plane	+
5	Kiran Kumar 2011, Bradbrook 1972	$\{001\}_{\alpha\text{-}Zr} \parallel \{100\}_{\delta}$	-
6	Arunachalam et al. 1967	$\{101\}_{\alpha\text{-}Zr}$, $\{103\}_{\alpha\text{-}Zr}$, $\{105\}_{\alpha\text{-}Zr}$	-
7	Qin 2014	$\{101\}_{\alpha\text{-}Zr} \parallel \{111\}_{\delta}$, $\{103\}_{\alpha\text{-}Zr} \parallel \{111\}_{\delta}$, $\{100\}_{\alpha\text{-}Zr} \parallel \{111\}_{\delta}$	-

Main result

δ-hydride/α-Zr orientation relationships (habit planes)

No.	Angle, °	Relationship	Appearance	Probability
1	1 - 9	Close to $\{11,30\}_{\alpha\text{-Zr}} \parallel \{100\}_{\delta}$	ball	medium
2	9 - 16	$\{11,30\}_{\alpha\text{-Zr}} \parallel \{100\}_{\delta}$	ball	high
3	17 - 27	$\{106\}_{\alpha\text{-Zr}} \parallel \{100\}_{\delta}$	indefinite	low
4	27 - 35	$\{110\}_{\alpha\text{-Zr}} \parallel \{100\}_{\delta}$	indefinite	low
5	35 - 43	$\{106\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$	ball	medium
6	43 - 50	$\{11,15\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$	ball	medium
7	50 - 57	$\{001\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$	needle	high

Conclusion

- The XRD-analysis showed the presence of γ-, δ-phases of zirconium hydrides in all of performed experiments on Zr and Zircaloy-4 hydrogenated at temperatures from 600 °C to 900 °C.
- The electron back scattered diffraction is up to date the best tool to detect hydrides and to obtain the phase distribution map and analyze grain orientation and microtexture. More than 120 measurements gave a good statistical information on hydride nucleation and development. On the basis of the EBSD-analysis the difference in the hydride formation and growth between pure Zr and Zircaloy-4 has been shown.
- Grain boundary distribution spectra showed the seven peaks, which represent seven possible orientation relationships. The art of the orientation was established by means of microtexture analysis for Zr and Zircaloy-4.
- The comparison of literature data with the obtained orientation relationships showed a very good agreement, though some of relationship were not confirmed. The most often detected orientation relationship $\{001\}_{\alpha\text{-}Zr} \| \{111\}_{\delta}$ is in full accordance with literature. The question of primary and secondary habit plane as stated by some authors is of less importance as we observed mostly the whole spectrum of possible orientations in each sample. Only low hydrogenated specimens have demonstrated one or two the most dominant kinds of relationship.
- For pure Zr the orientation relationships $\{001\}_{\alpha\text{-}Zr} \| \{111\}_{\delta}$ and $\{106\}_{\alpha\text{-}Zr} \| \{111\}_{\delta}$ and for Zircaloy-4 $\{001\}_{\alpha\text{-}Zr} \| \{111\}_{\delta}$ and $\{11,30\}_{\alpha\text{-}Zr} \| \{100\}_{\delta}$ were established as the most dominant among the others, denoted in the table of orientation relationships.
- The thorough analysis of claddings after QUENCH-LOCA experiment is going on.

Acknowledgements

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
- Dr. Dimitri Litvinov for the help during EBSD measurements

Thank you for your attention!

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