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

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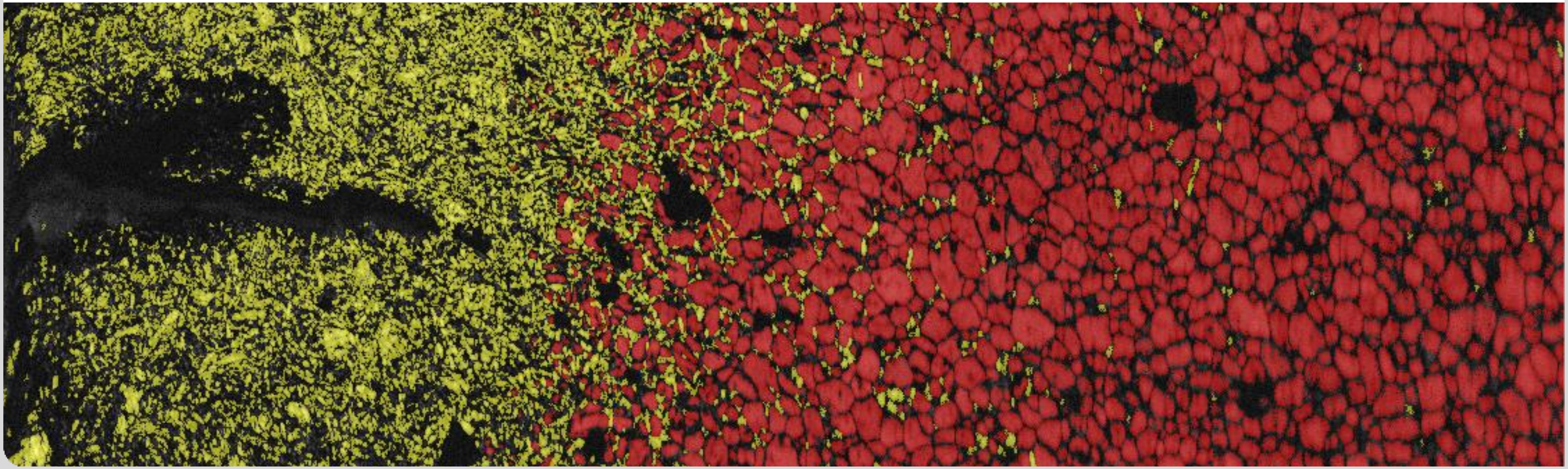


# Orientation relationships

## Already-known relationships

| No. | Author | Relationship |
|---|---|---|
| 1 | Kearns 1966, Arunachalam et al. 1967, Bradbrook 1972, Carpenter 1973, Chung 2000, Puls 2012, Une 2004, Kiran Kumar 2011, Wang 2013, Qin 2014… | $\{001\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$ |
| 2 | Westlake 1968, Ells 1968, Roy 1969, Chung 2000, Une 2004, Puls 2012, Qin 2014 | $\{107\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$ |
| 3 | Langeron 1956, Bailey 1963, Westlake 1965, Ells 1968 | $\{100\}_{\alpha\text{-Zr}}$ or reported direction <110> |
| 4 | Babyak 1967 | Pyramidal planes angled 5-25° to the basal plane |
| 5 | Bradbrook 1972, Kiran Kumar 2011 | $\{001\}_{\alpha\text{-Zr}} \parallel \{100\}_{\delta}$ |
| 6 | Arunachalam et al. 1967 | $\{101\}_{\alpha\text{-Zr}}$, $\{103\}_{\alpha\text{-Zr}}$, $\{10m\}_{\alpha\text{-Zr}}$ |
| 7 | Qin 2014 | $\{101\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$, $\{103\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$, $\{100\}_{\alpha\text{-Zr}} \parallel \{111\}_{\delta}$ |

# Objectives

- Hydrogenation of tube samples of Zr and Zircaloy-4
- Electron backscatter diffraction (EBSD) analysis of hydrogenated specimens
- Grain- and phase boundary spectra analysis
- Zr – δ-Zr hydride orientation relationships refinement

# Materials and methods of investigation

**Materials:** **1) Zircaloy-4 cladding tube 75 mm length.**

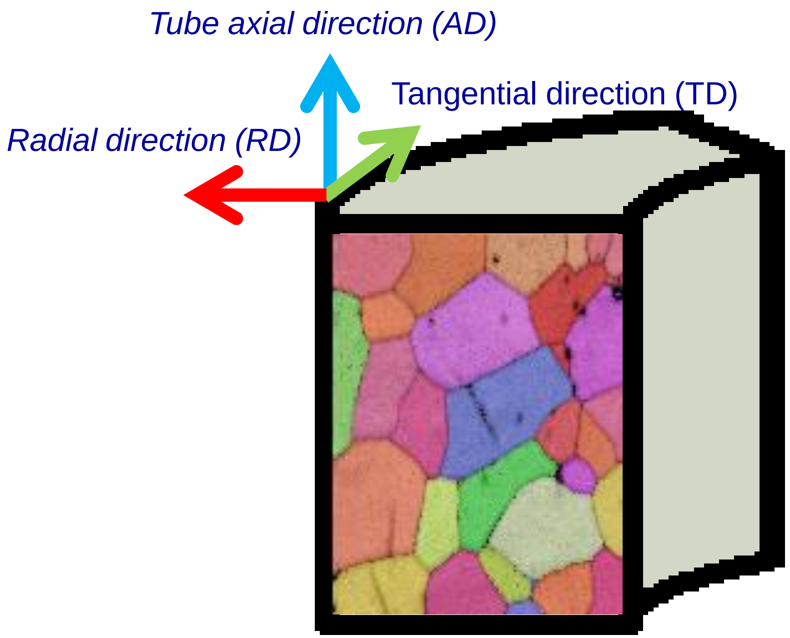
**2) pure Zr 99.5%, Hf < 0.3%, (Fe+Cr+O+N+H) < 0.2%. Tube length 50 mm;**

**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 the high temperature LORA-furnace**
- **Conventional X-Ray Diffraction analysis**
- **EBSD measurements of the cladding tube axial section in Zeiss EVO MA 10 microscope**
- **Phase detection by means of QUANTAX microanalysis system combined with Esprit software (Bruker Nano GmbH, Germany)**

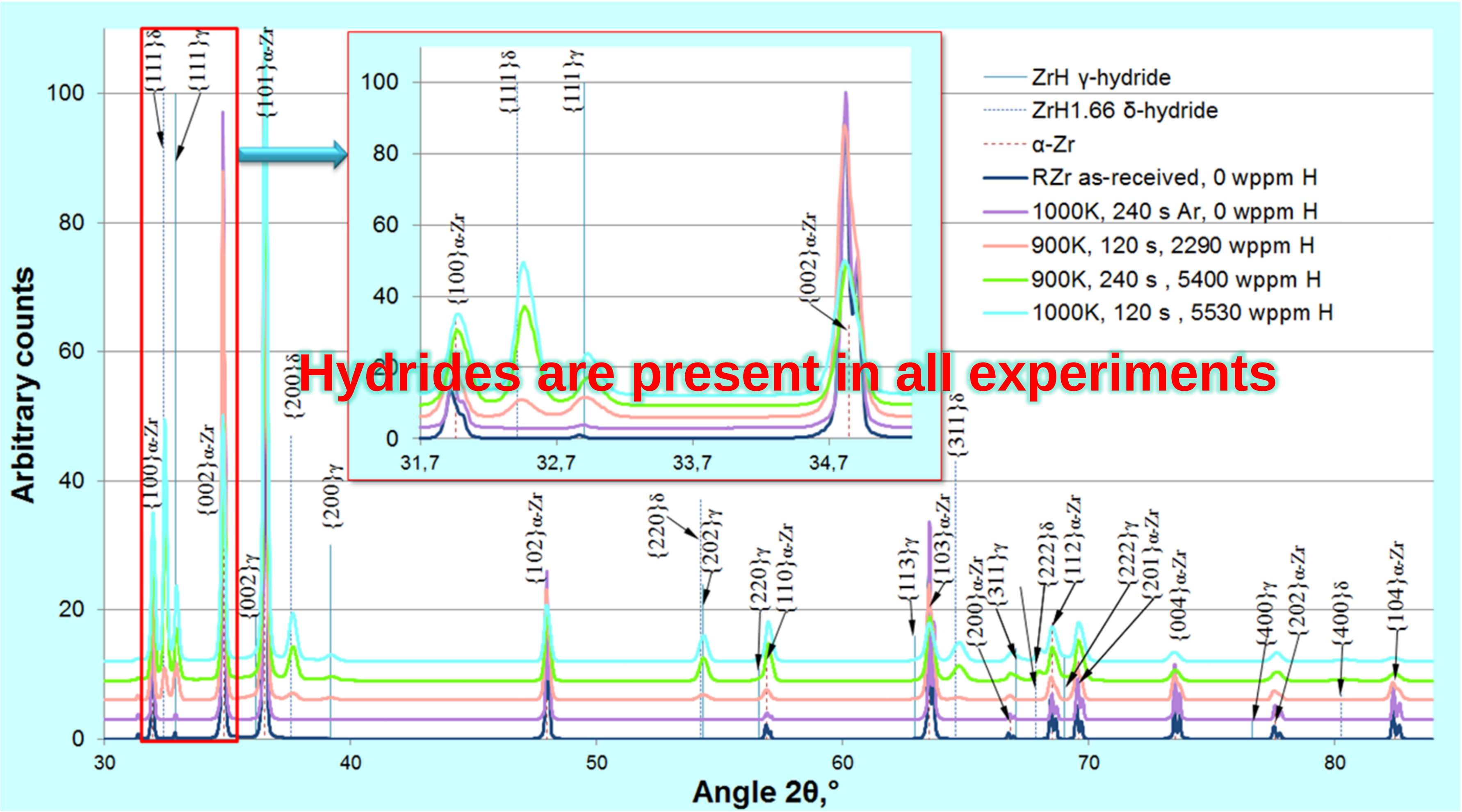



Cladding section:
scheme of EBSD measurements
of a cladding tube wall

# Results

# Phases detected in pure Zr

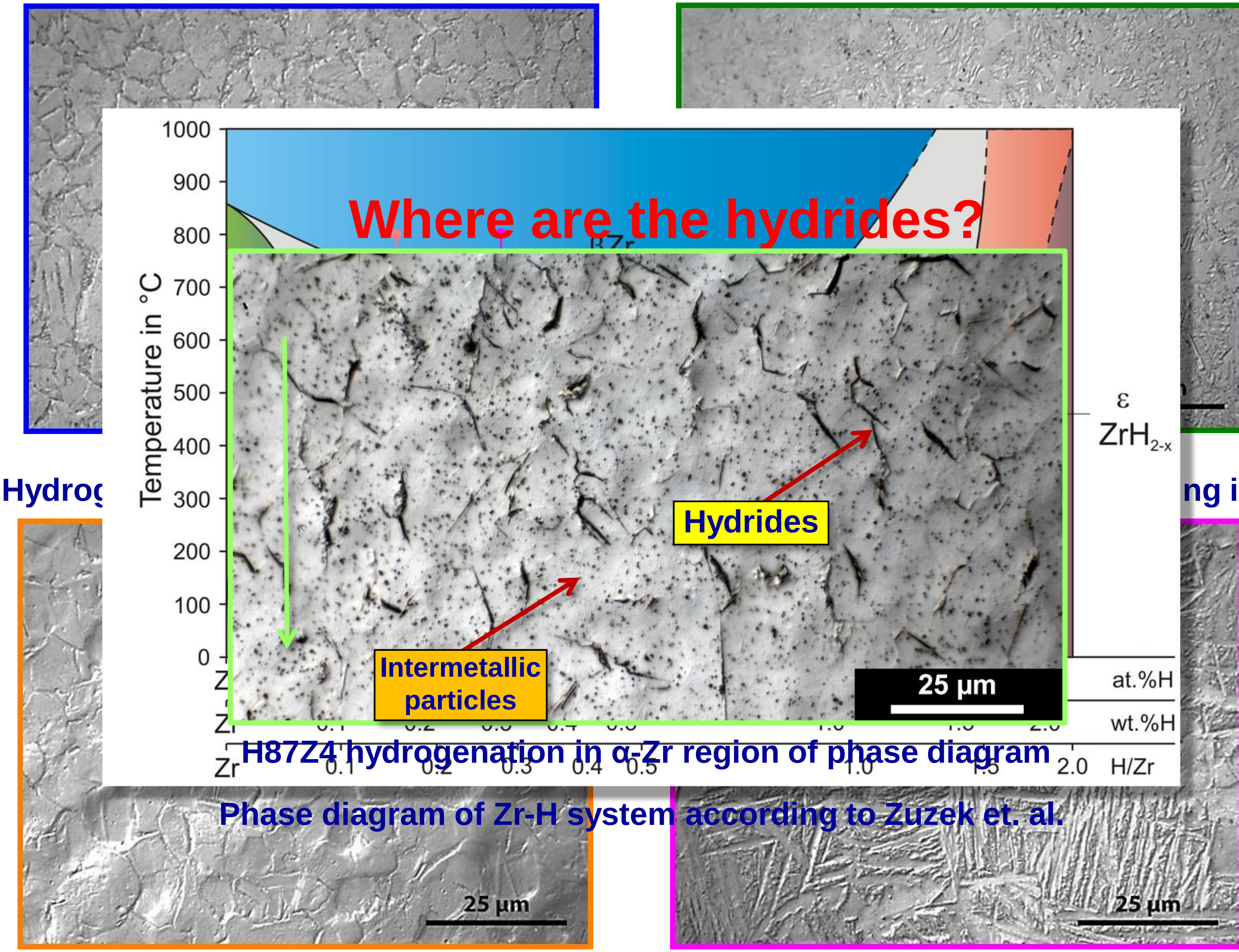
**Only γ-, and δ-hydrides in α-Zr were detected after hydrogenation**




**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.**

# Optical metallography of hydrogenated Zircaloy-4

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




**H87Z4 hydrogenation in α-Zr region of phase diagram**

**Phase diagram of Zr-H system according to Zuzek et. al.**

**Hydrog… ng in air**

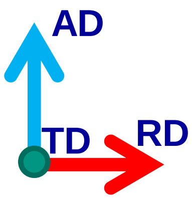
**1790 wppm H**

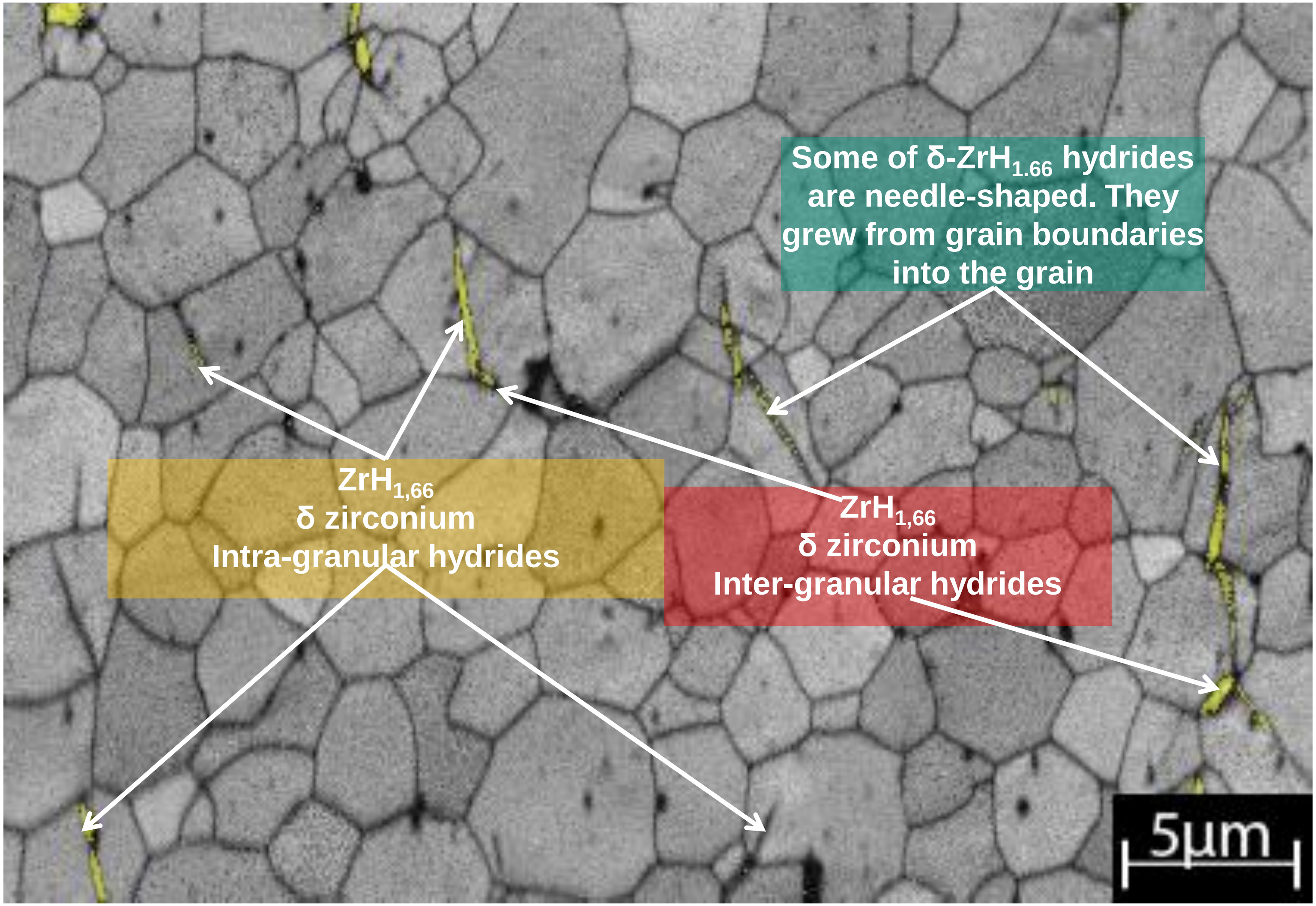
**3060 wppm H**

# EBSD analysis

# Zr hydrogenated at 600 °C 400 wppm H

**Example of δ in α after cooling from α-Zr region (no β transformation occurred)**

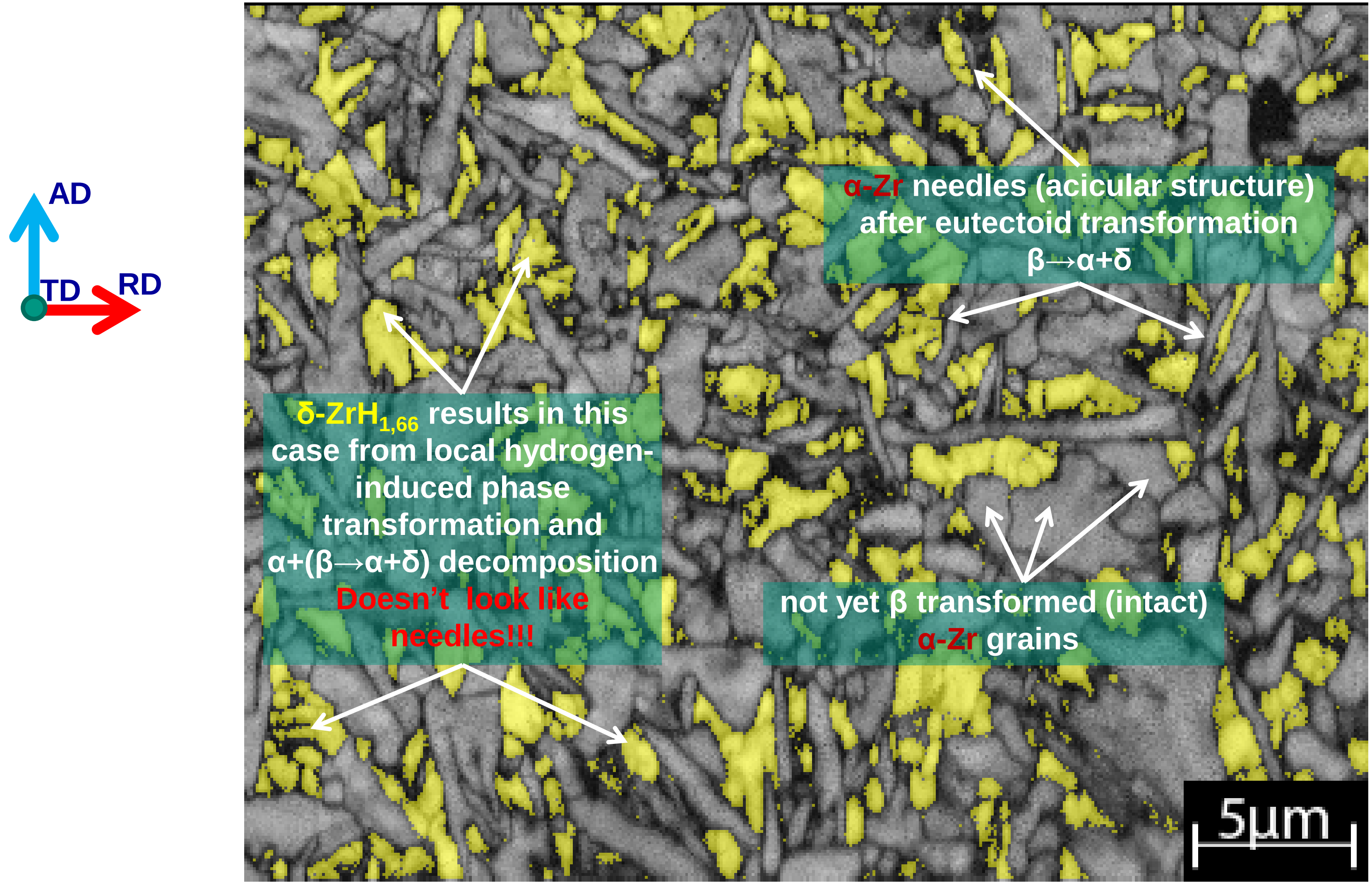



**99.3% Zr, 0.7% δ-$ZrH_{1.66}$, γ-ZrH – not detected (on the basis of image analysis)**

# Zr hydrogenated at 600 °C 2290 wppm H

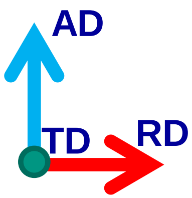
**Example of δ in α after α (intact) +(β→α+δ) decomposition**

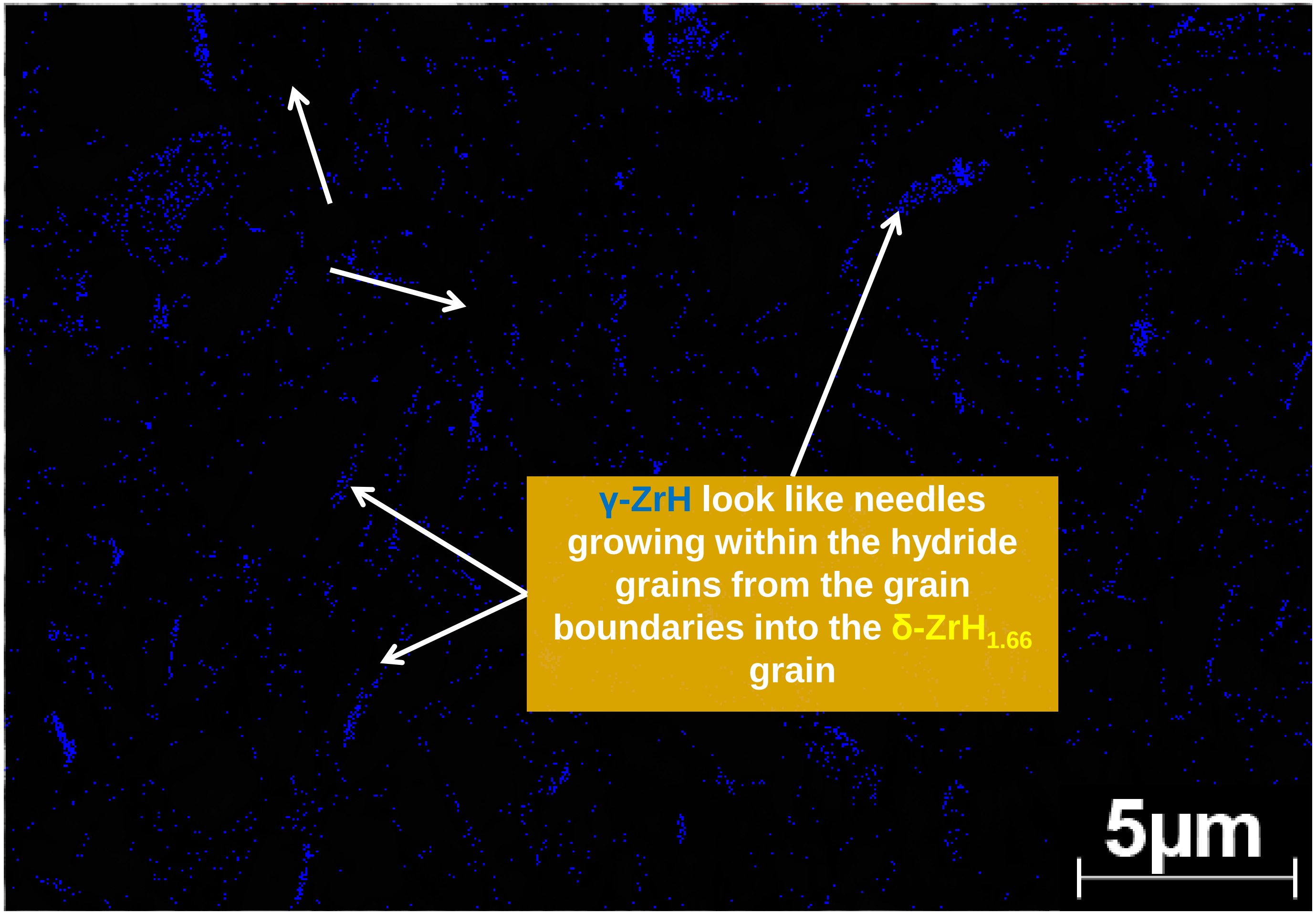



**72.6% Zr, 26.5% δ-$ZrH_{1.66}$, 0.8% γ-ZrH (on the basis of image analysis)**

# Zr hydrogenated at 600 °C 5400 wppm H

**Example of α + (γ in δ) structure after high hydrogenation degree cooled from fully β transformed region with α fraction and γ needles in δ**



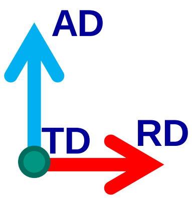



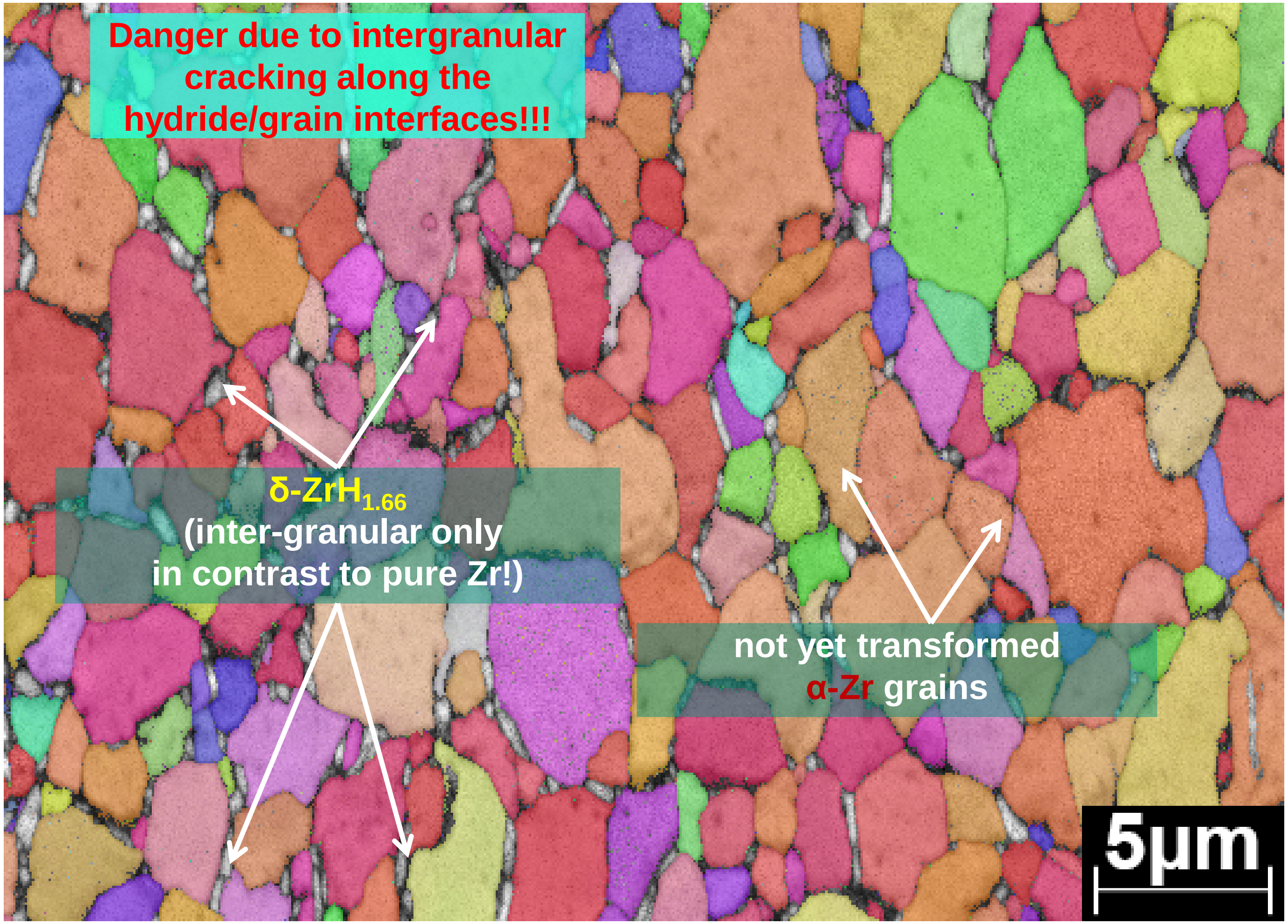

**27.1% Zr, 70.6% δ-$ZrH_{1.66}$, 2.35% γ-ZrH (on the basis of image analysis)**

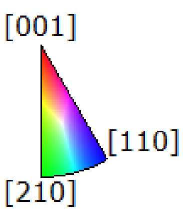
# Zircaloy-4 hydrogenated at 600 °C 2650 wppm H

Example of δ in α

**Grain orientation distribution in RD**



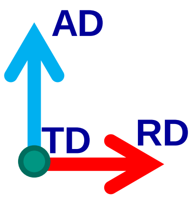



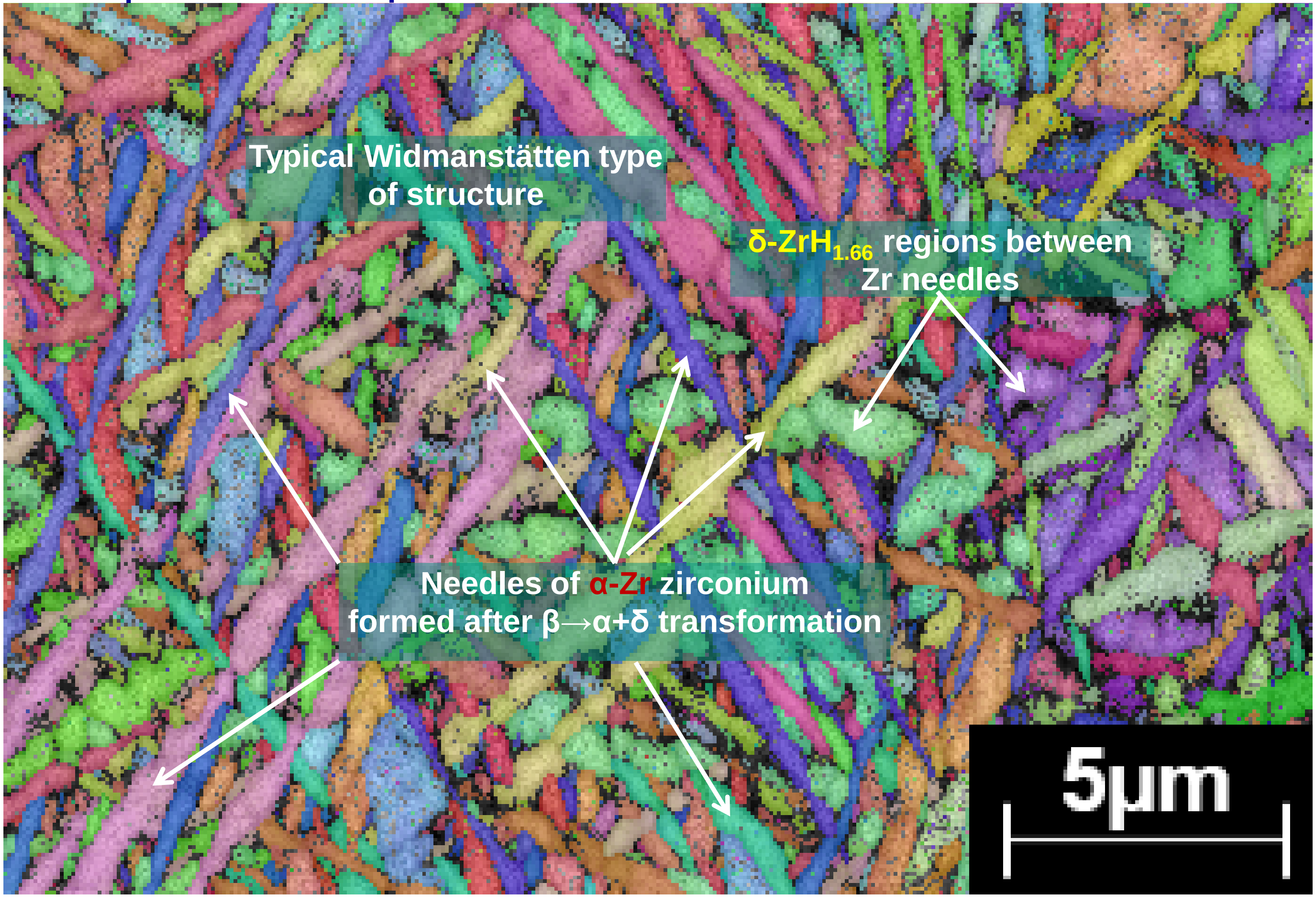



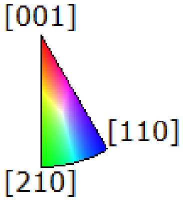

**94.8% Zr, 5.2% δ-$ZrH_{1.66}$, γ-ZrH – not detected (on the basis of image analysis)**

# Zr hydrogenated at 700 °C 5880 wppm H

**Example of δ in α after β→α+δ** **Grain orientation distribution in RD**



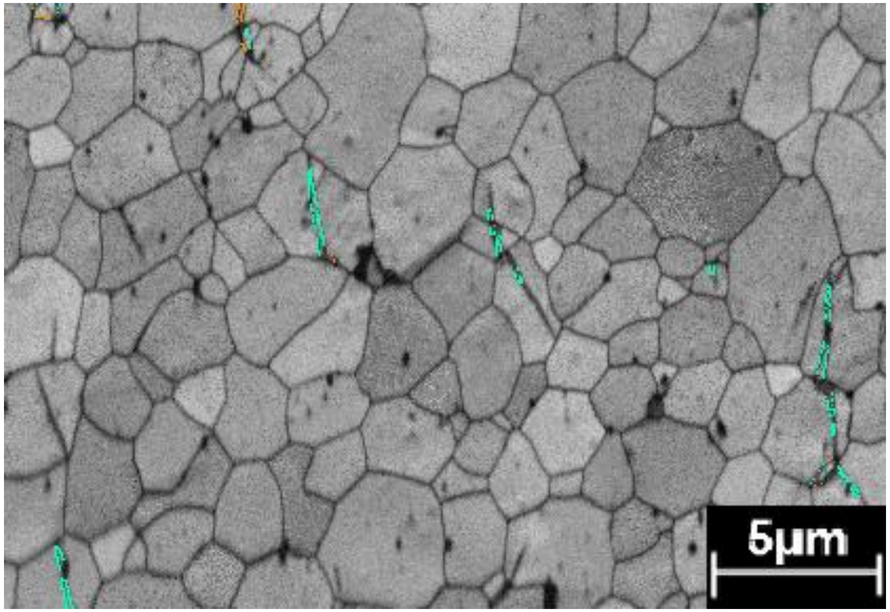



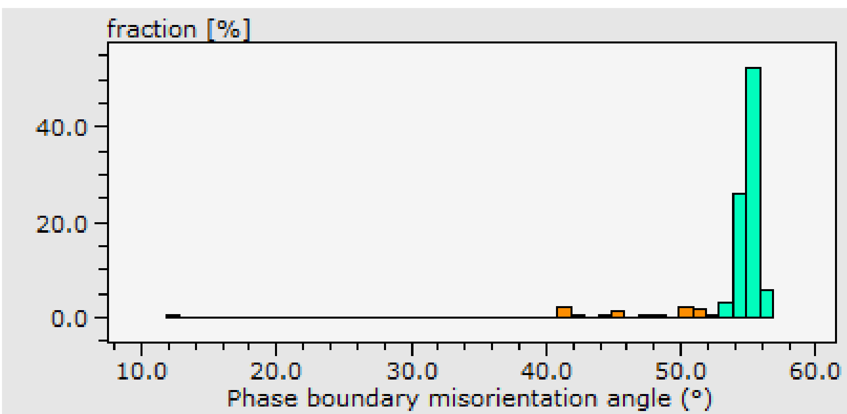

**60% Zr, 39% δ-$ZrH_{1.66}$, 1% γ-ZrH (on the basis of image analysis)**

# New results on grain boundary spectra and microtexture analysis

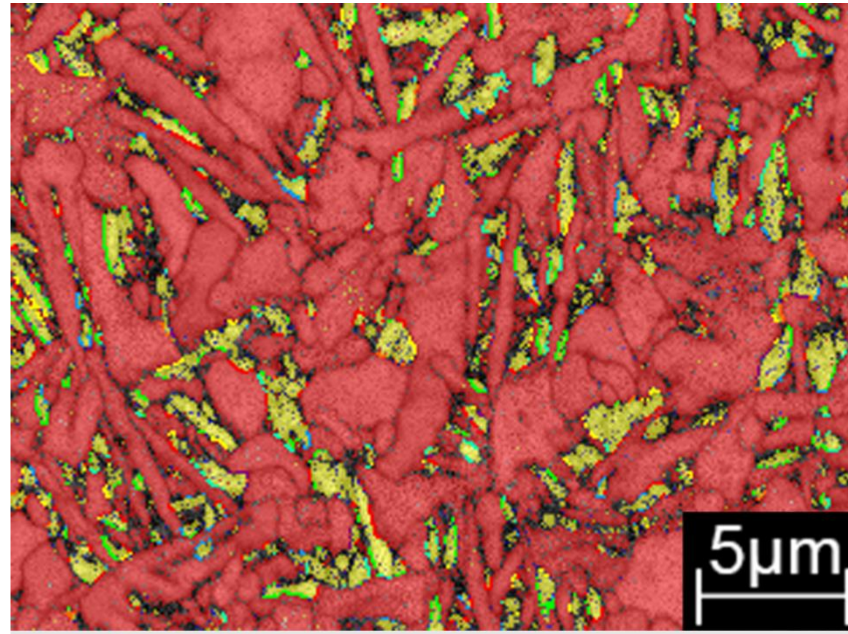
# Examples of grain boundary spectra

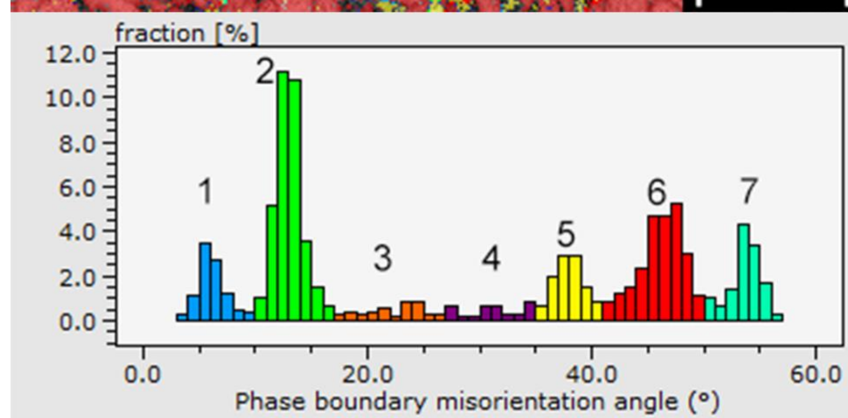
**Pure Zr 400 wppm H**



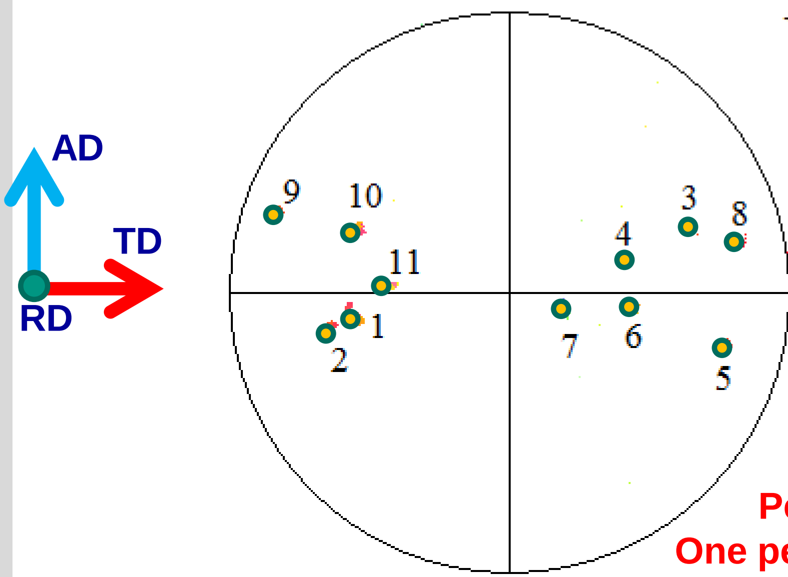

**Zircaloy-4 4820 wppm H**

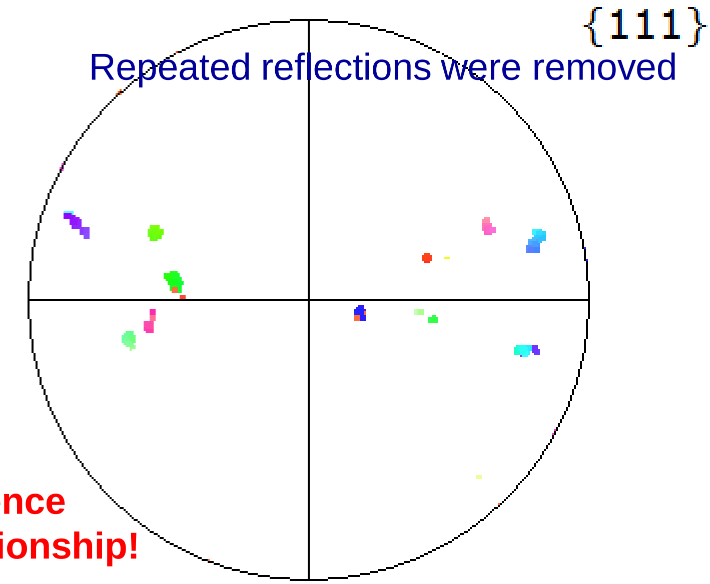


# Zr hydrogenated at 600 °C 400 wppm H

## Microtexture analysis



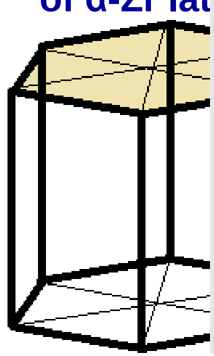

Repeated reflections were removed

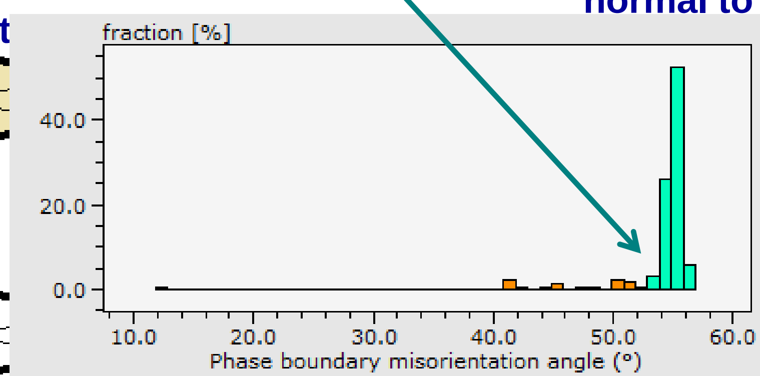
**Perfect coincidence**
**One peak = one relationship!**

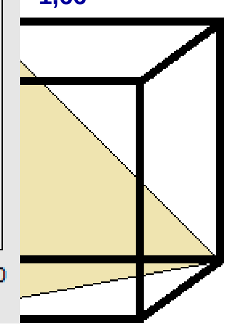
**Pole figure shows basal plane normal of α-Zr lat**

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

**Pole figure shows normal to cube diagonal**
**$H_{1,66}$ lattice**

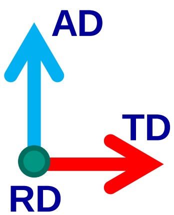


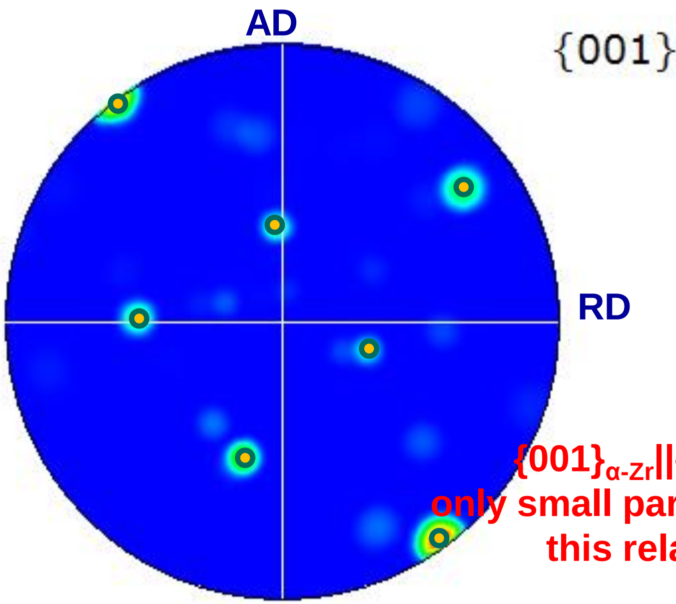


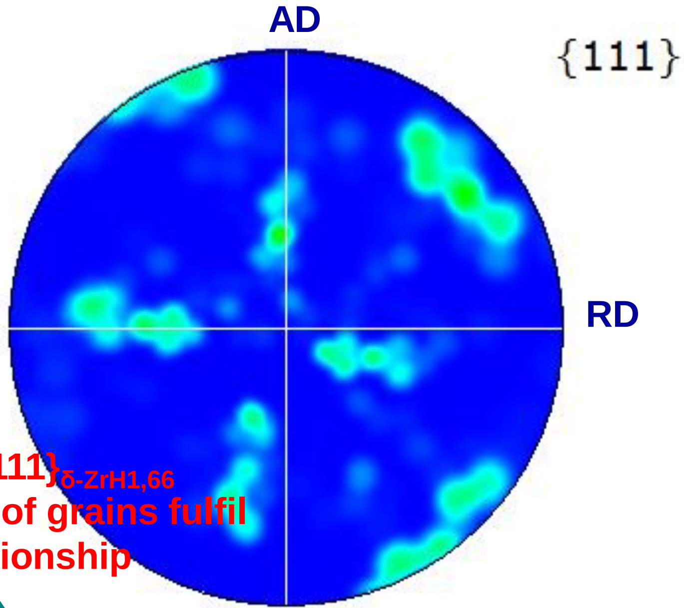



# Zircaloy-4 hydrogenated at 600 °C 5880 wppm H

## Microtexture analysis



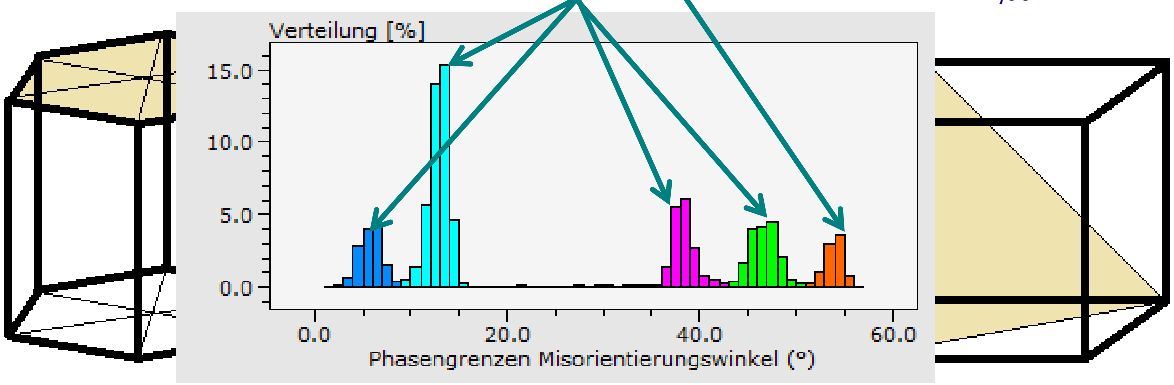

$\{001\}_{\alpha\text{-Zr}} || \{111\}_{\delta\text{-ZrH1,66}}$

only small part of grains fulfil this relationship

basal plane normal of α-Zr lattice

4 peaks more = 4 relationships more!

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



# Grain boundary spectra

**Zr – δ-$ZrH_{1.6}$ grain boundary misorientation spectra**

**The number of peaks = the amount of relationships**

**In Pure Zr** | **In Zircaloy-4**

**510 wppm H**

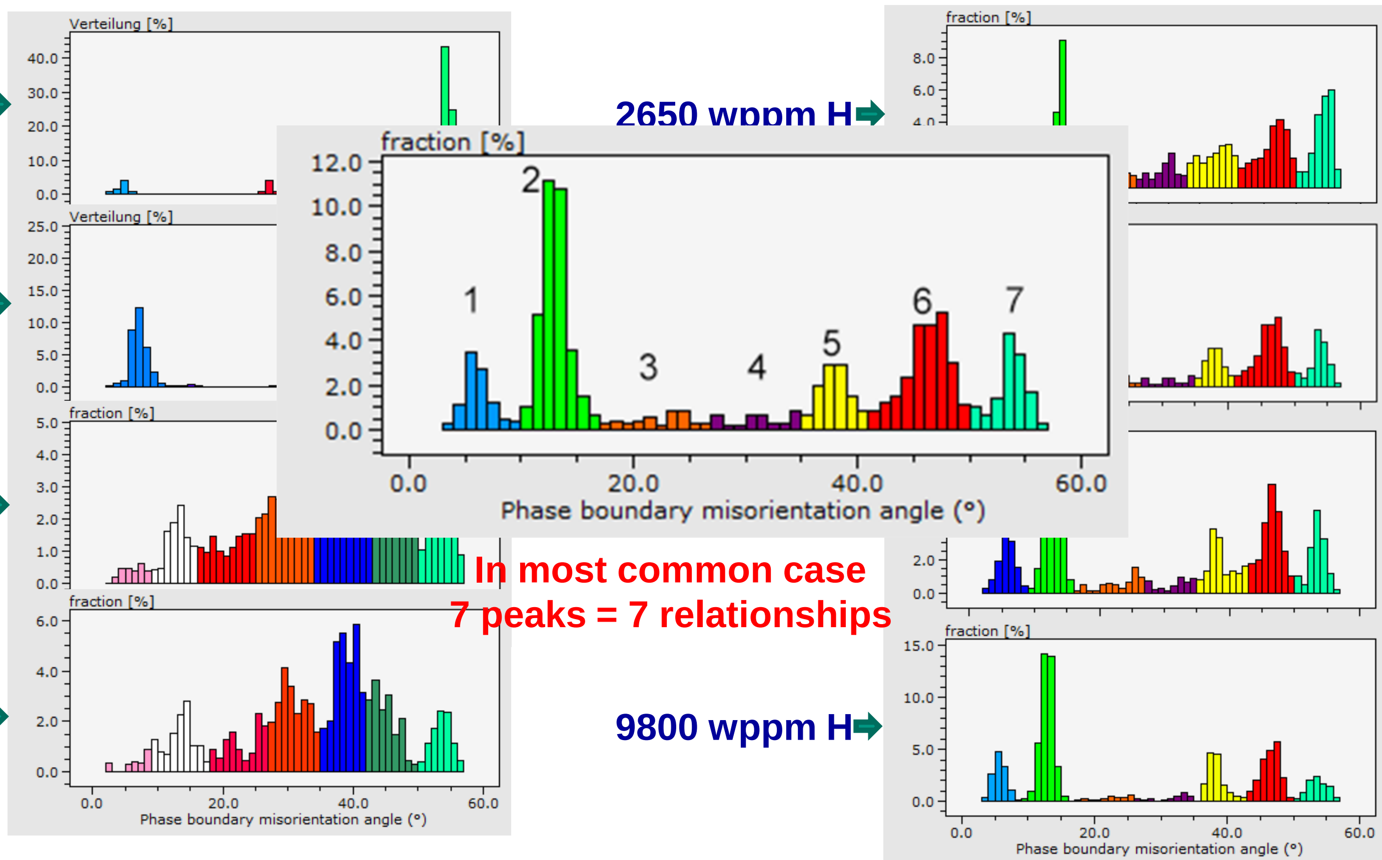
**1080 wppm H**

**2300 wppm H**

**5400 wppm H**

**2650 wppm H**

**9800 wppm H**




**In most common case**
**7 peaks = 7 relationships**

# Orientation relationships

## Already-known relationships

| No. | Author | Relationship | Observed in our investigation |
|---|---|---|---|
| 1 | Kearns 1966, Arunachalam et al. 1967, Bradbrook 1972, Carpenter 1973, Chung 2000, Puls 2012, Une 2004, Kiran Kumar 2011, Wang 2013, Qin 2014… | $\{001\}_{\alpha\text{-Zr}} \| \{111\}_{\delta}$ | + |
| 2 | Westlake 1968, Ells 1968, Roy 1969, Chung 2000, Une 2004, Puls 2012, Qin 2014 | $\{107\}_{\alpha\text{-Zr}} \| \{111\}_{\delta}$ | + |
| 3 | Langeron 1956, Bailey 1963, Westlake 1965, Arunachalam et al. 1967, Ells 1968 | $\{100\}_{\alpha\text{-Zr}}$ or reported direction <110> | - |
| 4 | Langeron 1956, Babyak 1967 | Pyramidal planes angled 5-25° to the basal plane or $\{11m\}_{\alpha\text{-Zr}}$ | + |
| 5 | Bradbrook 1972, Kiran Kumar 2011 | $\{001\}_{\alpha\text{-Zr}} \| \{100\}_{\delta}$ | - |
| 6 | Arunachalam et al. 1967 | $\{103\}_{\alpha\text{-Zr}}$, $\{105\}_{\alpha\text{-Zr}}$, $\{10m\}_{\alpha\text{-Zr}}$ | - |
| 7 | Qin 2014 | $\{101\}_{\alpha\text{-Zr}} \| \{111\}_{\delta}$, $\{103\}_{\alpha\text{-Zr}} \| \{111\}_{\delta}$, $\{100\}_{\alpha\text{-Zr}} \| \{111\}_{\delta}$ | - |

# Main result

**Orientation relationships between δ-hydride ($ZrH_{1,66}$) and α-Zr obtained by means of microtexture analysis. Pole figures were obtained by the electron backscatter diffraction measurement.**

| No. | Angle, ° | Relationship | Visual 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 | 16 - 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 after all of performed experiments at temperatures from 600 °C to 900 °C.
- Hydride phase distribution, phase boundary spectra and microtexture were analyzed with the good statistics and data reproducibility by the electron backscatter diffraction (EBSD).
- On the basis of the EBSD observations the similarities and differences in the hydride formation and growth between pure Zr and Zircaloy-4 has been shown.
- The γ-needles inside of big δ-hydrides and the variety of δ-hydrides + α-Zr structures showed by EBSD.
- Phase boundary distribution spectra showed similar behaviour by emerging of the seven peaks on the phase misorientation angle diagram, which were put in compliance with seven possible orientation relationships of δ-hydride phase in Zr grain.
- The relationship $\{001\}_{\alpha\text{-Zr}} || \{111\}_{\delta}$ obtained by the new EBSD method is in accord with many previous investigators.
- We were not able to confirm the prismatic habit plane $\{100\}_{\alpha\text{-Zr}}$ for δ-hydrides.
- The new EBSD method allowed us to refine $\{106\}_{\alpha\text{-Zr}} || \{111\}_{\delta}$ relationship and to establish some new pyramidal habit planes $\{11,15\}_{\alpha\text{-Zr}} || \{111\}_{\delta}$, $\{11,30\}_{\alpha\text{-Zr}} || \{100\}_{\delta}$ and to state that prismatic habit plane $\{110\}_{\alpha\text{-Zr}} || \{100\}_{\delta}$ is the less common but possible case.
- Low hydrogenated specimens have demonstrated one or two the most dominant kinds of relationships. For medium and high hydrogenation we observed always the whole spectrum of possible orientation relationships, which refutes the assumption of experimental conditions impact on it.
- 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.

# Recent publications

- ***A. Pshenichnikov, J. Stuckert, M. Walter*** Hydride precipitation, fracture and plasticity mechanisms in pure zirconium and Zircaloy-4 at temperatures typical for the postulated loss-of-coolant accident // Nuclear Engineering and Design (2016), P. 366-377. http://dx.doi.org/10.1016/j.nucengdes.2016.03.024
- ***Anton Pshenichnikov, Juri Stuckert, Mario Walter*** Orientation relationships of δ-hydrides in zirconium and Zircaloy-4 // Proceedings of the 21th QUENCH Workshop, 27-29 October 2015, Karlsruhe, Germany
- ***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. http://dx.doi.org/10.1016/j.nucengdes.2014.06.022
- ***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.
- ***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.

# Acknowledgements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- Ms. 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. Mario Walter and Dr. Dimitri Litvinov for the help during EBSD measurements

# Thank you for your attention!

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