Orientation relationships of $\delta$-hydrides in zirconium and Zircaloy-4

Anton Pshenichnikov, Juri Stuckert

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## Orientation relationships

### Already-known relationships

<table>
<thead>
<tr>
<th>No.</th>
<th>Author</th>
<th>Relationship</th>
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<tbody>
<tr>
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<td>Langeron 1956, Bailey 1963, Westlake 1965, Ells 1968</td>
<td>${100}_{\alpha-Zr}$ or reported direction $&lt;110&gt;$</td>
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<td>${101}<em>{\alpha-Zr}$, ${103}</em>{\alpha-Zr}$, ${10m}_{\alpha-Zr}$</td>
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<tr>
<td>7</td>
<td>Qin 2014</td>
<td>${101}<em>{\alpha-Zr} \parallel {111}</em>\delta$, ${103}<em>{\alpha-Zr} \parallel {111}</em>\delta$, ${100}<em>{\alpha-Zr} \parallel {111}</em>\delta$</td>
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</table>
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+H₂ 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 $\gamma$-, and $\delta$-hydrides in $\alpha$-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

Where are the hydrides?

H87Z4 hydrogenation in α-Zr region of phase diagram

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

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)

Some of δ-ZrH$_{1.66}$ hydrides are needle-shaped. They grew from grain boundaries into the grain.

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

δ-ZrH<sub>1.66</sub> results in this case from local hydrogen-induced phase transformation and α + (β → α + δ) decomposition

Doesn’t look like needles!!!

α-Zr needles (acicular structure)

after eutectoid transformation

β → α + δ

not yet β transformed (intact)

α-Zr grains

72.6% Zr, 26.5% δ-ZrH<sub>1.66</sub>, 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

γ-ZrH looks like needles growing within the hydride grains from the grain boundaries into the δ-ZrH$_{1.66}$ grain

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

<table>
<thead>
<tr>
<th>AD</th>
<th>TD</th>
<th>RD</th>
</tr>
</thead>
</table>

Grain orientation distribution in RD

Danger due to intergranular cracking along the hydride/grain interfaces!!!

δ-ZrH$_{1.66}$ (inter-granular only in contrast to pure Zr!)

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

Typical Widmanstätten type of structure

δ-ZrH$_{1.66}$ regions between Zr needles

Needles of α-Zr zirconium formed after β→α+δ transformation

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

{001} Perfect coincidence
One peak = one relationship!

{111} Repeated reflections were removed

Pole figure shows basal plane normal of α-Zr lattice

{001}_{α-Zr} || {111}_{δ-ZrH_{1.66}}

Pole figure shows normal to cube diagonal of δ-ZrH_{1.66} lattice

fraction [%]

Phase boundary misorientation angle (°)

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Zircaloy-4 hydrogenated at 600 °C 5880 wppm H

Microtexture analysis

basal plane normal of α-Zr lattice

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

{001}$_{\alpha}$-Zr||{111}$_{\delta}$-ZrH$_{1.66}$

only small part of grains fulfil this relationship

4 peaks more $=$ 4 relationships more!

Verteilung [%]

0.0  5.0  10.0  15.0

Phasengrenzen Misorientierungswinkel (°)
Grain boundary spectra

Zr – δ-ZrH$_{1.6}$ grain boundary misorientation spectra
The number of peaks = the amount of relationships

In Pure Zr

- 510 wppm H
- 1080 wppm H
- 2300 wppm H
- 5400 wppm H

In Zircaloy-4

- 2650 wppm H
- 5100 wppm H
- 2650 wppm H
- 9800 wppm H

In most common case 7 peaks = 7 relationships
## Orientation relationships

### Already-known relationships

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### Main result

Orientation relationships between $\delta$-hydride ($\text{ZrH}_{1.66}$) and $\alpha$-Zr obtained by means of microtexture analysis. Pole figures were obtained by the electron backscatter diffraction measurement.

<table>
<thead>
<tr>
<th>No.</th>
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<th>Visual Appearance</th>
<th>Probability</th>
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<tbody>
<tr>
<td>1</td>
<td>1 - 9</td>
<td>Close to ${11,30}_{\alpha-Zr}</td>
<td></td>
<td>{100}_\delta$</td>
</tr>
<tr>
<td>2</td>
<td>9 - 16</td>
<td>${11,30}_{\alpha-Zr}</td>
<td></td>
<td>{100}_\delta$</td>
</tr>
<tr>
<td>3</td>
<td>16 - 27</td>
<td>${106}_{\alpha-Zr}</td>
<td></td>
<td>{100}_\delta$</td>
</tr>
<tr>
<td>4</td>
<td>27 - 35</td>
<td>${110}_{\alpha-Zr}</td>
<td></td>
<td>{100}_\delta$</td>
</tr>
<tr>
<td>5</td>
<td>35 - 43</td>
<td>${106}_{\alpha-Zr}</td>
<td></td>
<td>{111}_\delta$</td>
</tr>
<tr>
<td>6</td>
<td>43 - 50</td>
<td>${11,15}_{\alpha-Zr}</td>
<td></td>
<td>{111}_\delta$</td>
</tr>
<tr>
<td>7</td>
<td>50 - 57</td>
<td>${001}_{\alpha-Zr}</td>
<td></td>
<td>{111}_\delta$</td>
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The XRD-analysis showed the presence of $\gamma$-, $\delta$-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 $\gamma$-needles inside of big $\delta$-hydrides and the variety of $\delta$-hydrides + $\alpha$-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 $\delta$-hydride phase in Zr grain.

The relationship $\{001\}_{\alpha-Zr}\{111\}_\delta$ obtained by the new EBSD method is in accord with many previous investigators.

We were not able to confirm the prismatic habit plane $\{100\}_{\alpha-Zr}$ for $\delta$-hydrides.

The new EBSD method allowed us to refine $\{106\}_{\alpha-Zr}\{111\}_\delta$ relationship and to establish some new pyramidal habit planes $\{11,15\}_{\alpha-Zr}\{111\}_\delta$, $\{11,30\}_{\alpha-Zr}\{100\}_\delta$ and to state that prismatic habit plane $\{110\}_{\alpha-Zr}\{100\}_\delta$ 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 $\{001\}_{\alpha-Zr}\{111\}_\delta$ and $\{106\}_{\alpha-Zr}\{111\}_\delta$ and for Zircaloy-4 $\{001\}_{\alpha-Zr}\{111\}_\delta$ and $\{11,30\}_{\alpha-Zr}\{100\}_\delta$ 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


- **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


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Thank you for your attention!

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