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

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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*

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

Region of interest is LOCA conditions

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

400 wppm H 12550 wppm H

selected examples of our tests
**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+H₂ 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
Experimental procedure

Hydrogenation facility
LORA furnace

Hydrogen gas partial
pressure 0.1 bar

Specimen before
hydrogenation

H₂ 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

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

Hydrides must be compressed which is indicated by 0.5% of local strain.

Hydrides are present in all experiments.
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)

Parameter "a"

- a (Dicvol06)
- a Riley-Nelson

Linear (a (Dicvol06))
Linear (a Riley-Nelson)

\[ y = 1E-07x + 3.2305 \]
Level of \( \alpha \)-Zr

Parameter "c"

\[ y = -3E-10x^2 + 4E-06x + 5.1463 \]

- c (Dicvol06)
- c Riley-Nelson
- Poly. (c (Dicvol06))
- Poly. (c Riley-Nelson)

Level of \( \alpha \)-Zr

\( \text{a – didn’t change noticeably} \)
\( \text{c – significantly increased after hydrogenation} \)
Optical metallography of hydrogenated Zircaloy-4

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

Where are the hydrides?

1330 wppm H
2250 wppm H

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

How do they look like?

1790 wppm H
3060 wppm H
New results on EBSD-analysis
Zr as-received

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

Grain orientation distribution in RD

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

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

pure Zr tube has usual fiber texture

EDS-pattern quality map
Zr hydrogenated at 600 °C 400 wppm H

EBSD pattern quality map
Grain orientation distribution in AD

Two halves of the same color in three orthogonal directions is the evidence that it is one grain.

δ-ZrH_{1.66} look like needles, which are growing from grain boundaries into the grain.

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

basal plane normal of α-Zr lattice

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

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

repeated reflections are removed

Perfect coincidence

the grain boundaries with ~55° are dominant
Zr hydrogenated at 600 °C 2290 wppm H

α-Zr needles (acicular structure) after martensitic type of transformation \( \beta \rightarrow \alpha + \delta \)

not yet transformed (intact) α-Zr grains

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

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

obviously there are also other mechanisms of hydride growth
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

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

This relation is only valid when the hydride is inside of Zr grain. But we have only hydride grains that is why this relation is not valid any more.
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

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

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

Grain orientation distribution in RD

EBSD pattern quality map

94.8% Zr, 5.2% δ-ZrH₁.₆₆, γ-ZrH – not detected (on the basis of image analysis)

δ-ZrH₁.₆₆ grow on the grain boundaries without α→β transition directly from α phase
(inter-granular only in contrast to pure Zr!)
Also doesn’t look like needles

not yet transformed α-Zr grains
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}_{α-Zr} || {111}_{δ-ZrH_{1.66}} with grain misorientation ~55° is partially fulfilled
Zircaloy-4 hydrogenated at 600 °C 2650 wppm H

Grain boundary analysis

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

The rests of $\alpha$-Zr obviously results from $\beta \rightarrow \alpha$ transformation

$\gamma$-ZrH grow inside $\delta$-ZrH$_{1.66}$ phase

3.9% Zr, 92% $\delta$-ZrH$_{1.66}$, 4.1% $\gamma$-ZrH (on the basis of image analysis)
Zircaloy-4 hydrogenated at 600 °C 12550 wppm H

Microtexture analysis

basal plane normal of α-Zr lattice

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

{001}_{α-Zr}\parallel{111}_{δ-ZrH_{1.66}} doesn’t work any more as we have almost only hydride and only small part of Zr
Zr hydrogenated at 700 °C 5880 wppm H

EBSD pattern quality map

Grain orientation distribution in AD

Zr needles

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

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

Typical Widmanstätten type of structure

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

basal plane normal of α-Zr lattice

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

only small part of grain fulfill this relation

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

<table>
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<th>Verteilung [%]</th>
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Phasengrenzen Misorientierungswinkel (°)

20.05.2015  A. Pshenichnikov , J. Stuckert, M. Walter, D. Litvinov
23rd International Conference on Nuclear Engineering
The analysis is on the way but it is clear that we have a mechanism of hydride accommodation 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

Brittle fracture zone on hydrides

1640 wppm H

Ductile fracture on needles of α-Zr
Fracture schemes for Zr and Zircaloy-4

Ductile fracture on needles of α-Zr

Brittle fracture zones on hydrides

Needles cross-section

Above phase transition point

Below phase transition point
Understanding the mechanism
Change of lattice parameters after hydrogenation of Zircaloy-4 samples

Parameter "a"
- didn’t change noticeably

Parameter "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

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*

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 qualitatively 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.

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

- The XRD-analysis showed the presence of $\gamma$, $\delta$-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.
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