

Microstructure and Mechanical Properties of Zircaloy-4 Cladding Hydrogenated at Temperatures Typical for Loss-of-Coolant Accident (LOCA) Conditions

A. Pshenichnikov, J. Stuckert, M. Walter

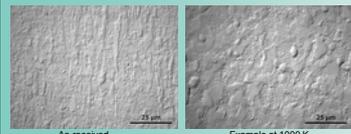
anton.pshenichnikov@kit.edu, juri.stuckert@kit.edu, mario.walter@kit.edu

Introduction

It is known that relatively small amounts of hydrogen as a solid solution can lead to hydrides precipitation, which in turn leads to sufficient degradation of mechanical properties. It is much worse when a fuel cladding undergoes LOCA conditions when after ballooning and burst the inner cladding surface absorbs the hydrogen released due to oxidation (so called secondary hydrogenation). Though a lot of investigations on the hydrogen embrittlement were performed, there were no attempts to describe the influence of hydrogenation at temperatures typical for LOCA. The problem is sophisticated since typical LOCA temperatures are close to phase transformation point and hydrogen itself decreases $\alpha \rightarrow \beta$ transition boundary. With aim to investigate the Zircaloy-4 behaviour under these conditions the series of single rod hydrogenation tests was performed at KIT in framework of the new QUENCH-LOCA programme.

Metallography investigations

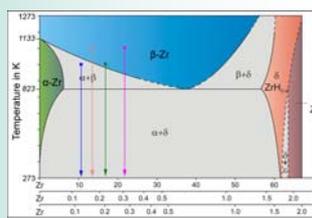
Microstructure of Zircaloy-4 cladding after annealing in Ar and fast cooling in air (5 K/s) results in recrystallization of as-received textured structure



Annealing above the Zircaloy-4 phase transformation point (1083 K) results in Widmanstätten-type of structure with precipitates redistributed towards boundaries of structure elements.



Equilibrium phase diagram of Zr-H system*

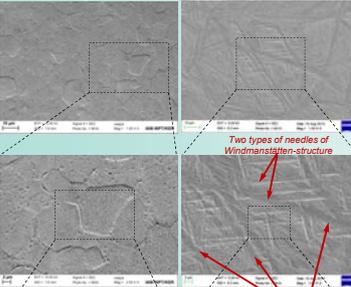


* According to E. Zuzek et al., Bull. Alloy Phase Diagr. (1990), 385

Scanning Electron Microscopy

Grinded and polished specimen

Annealing in Ar at 1100 K during 240 s



Hydrogenation in Ar+H₂ gas mixture at 1100 K during 360 s to 8620 wppm H

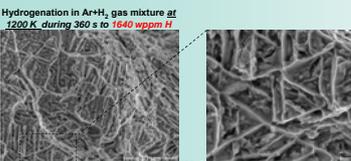
Two types of needles of Widmanstätten-structure

according to α -Zr β -Zr γ -Zr hydrides are inside of β -Zr hydrides

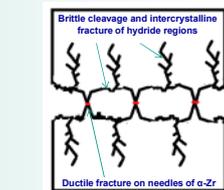
The as-received sample was highly textured. During the heat treatment in absence of hydrogen the usual process of recrystallization and then phase transformation take place. The grain size increases (5 to 10 μ m) and after phase transition relative large regions (30-50 μ m) of same oriented sub-grains are forming.

Hydrogen changes the appearance of microstructural pattern cardinaly. Instead typical grain structure a quite complicate mixture of acicular hydrides and α -Zr clusters will be developed. During the cooling phase of hydrogenated specimens a new acicular prior β (or α' -phase) of martensite-type was developed. The fracture was in all cases brittle even at the lowest obtained hydrogenation degree of 720 wppm H. But there is a fact that at 900 and 1000 K the fracture surfaces look very brittle while at 1100 and 1200 K at the similar hydrogenation degree there are a lot of big needles with plasticity indications inside. The specimens have shown a better plasticity (5%) in comparison to 900 and 1000 K ($<1\%$). The phenomenon of such type of plasticity can be explained as follows (see the scheme below).

A scheme of plasticity after hydrogenation above 1100 K



Though fracture surfaces at 1100 and 1200 K were brittle a signs of ductility still can be observed. The white stripe in the middle of every needle shows that the needles deformed plastically in comparison to flake-like regions between them. This results are in accordance with tension tests (see on the right-hand side of this poster). It was not clear why at the same hydrogenation degree the specimens hydrogenated at 1100 and 1200 K still had 5% of plastic strain while specimens hydrogenated at lower temperatures had $<1\%$. The SEM investigations allow to suggest this kind of ductility as the main reason of this behavior. As soon as after cooling from 1200 K the needle structure is dominant it can be suggested that at equal degree of hydrogenation the specimens with developed acicular structure will be more ductile at room temperature than the specimens hydrogenated at lower temperatures. At 900 and 1000 K they will be fully brittle. This is confirmed by our series of SEM investigations of fractured surfaces.



Hydrogenation in Ar+H₂ gas mixture at 1000 K during 120 s to 720 wppm H

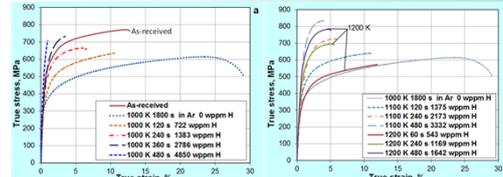
Hydrogenation in Ar+H₂ gas mixture at 1100 K during 240 s to 2100 wppm H

Hydrogenation in Ar+H₂ gas mixture at 1000 K during 480 s to 4850 wppm H

Hydrogenation in Ar+H₂ gas mixture at 1100 K during 480 s to 3332 wppm H

Labels: cleavage, intercrystalline fracture, dimples, no more dimples, Lots of microcracks, Intercrystalline fracture, Needle-like structure, Lots of microcracks, Rests of the acicular structure.

Tensile test at room temperature



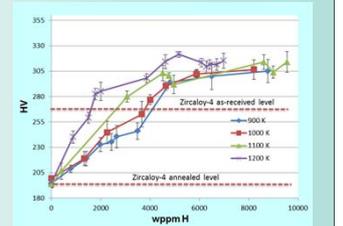
As-received Zircaloy-4 tube showed approximately 13% of true strain and 750 MPa of ultimate stress. Annealing during 1800 s in Ar atmosphere has led to the reduction of maximal true stress down to 600 MPa. True strain at rupture has risen up to almost 30%, which is usual for annealed Zircaloy-4.

As soon as hydrogen was absorbed, it has had an immediate impact on mechanical properties. Just 700 wppm absorbed at 1000 K reduces the plasticity drastically. The rupture was in all cases brittle. In extreme cases at the maximum detected level of picked-up hydrogen of 4850 wppm the maximal strain was only 1%. In the case of 1100 K and 1200 K the plasticity of alloy still remained not less than 4-5% due to lower hydrogen concentration (according to Sievert's law for Zr).

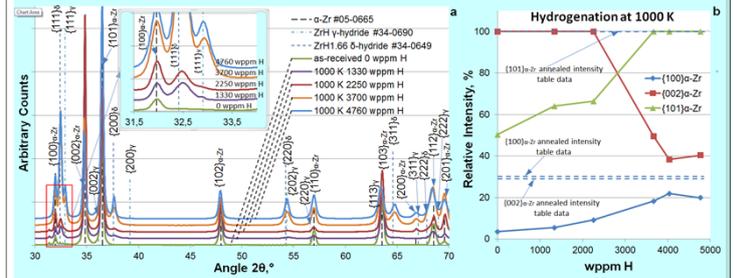
Microhardness test

Microhardness tests of annealed and hydrogenated samples were carried out. The heat treatment led to immediate decrease in microhardness in comparison to as-received state. It is usual phenomenon after recrystallization.

In the presence of hydrogen microhardness started to increase from the very beginning after hydrogenation at 900 K where beta transition was detected only in small local regions near to grain boundaries. The one of the first possible reasons for microhardness increase is β -quenching and martensitic transformation in presence of hydrogen which occur after cooling with 5 K/s. The temperature and hydrogen together will boost β formation process. So at 1100 and 1200 K more β -phase after short time period will be formed, and at a fast increase of microhardness already at low hydrogen level occur. But there is a saturation limit approximately at 320 HV as most of materials will be converted to δ -hydrides.



X-Ray diffraction analysis

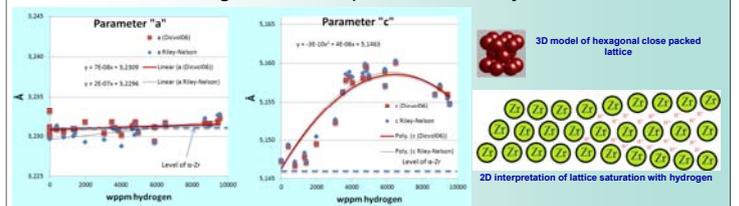


The method which distinctly shows the presence of hydrides is an X-ray diffraction analysis. Here is a green profile of an as-received material for convenience. Only peaks of alpha-Zr were present. The α - and γ -hydride peaks are present in all of our hydrogenated specimens. All hydride peaks were shifted to the right from their table values (up to $+0.1^\circ$), which is the sign that they must be hydrostatically compressed in Zr matrix. The question of stress-strain state of hydrides still remains opened in literature.

Increase of hydrogen content to 2250 wppm H led to formation of distinct (200) β peak. Hydrogenation during 360 s (3700 wppm H) at 1000 K showed more pronounced hydride peaks (200) β , (220) β , (311) β . The peak (222) β induced the left asymmetry of α -Zr peak (112) α -Zr. For γ -phase only the most intensive hydride peak corresponding to (111) γ was visible. Further increase of hydrogen content did not lead to formation of new peaks but to an increase in the already existing hydride peaks as a example Zircaloy-4 containing 4760 wppm H.

At the same time a redistribution of relative intensities of α -Zr peaks was observed (right-hand figure), which has shown that texture change took place during hydrogenation. After hydrogenation main zirconium line intensities (100) α , (002) α , (101) α changed significantly. In particular after hydrogenation during 360 s at 1000 K (2700 wppm H) peaks (002) α -Zr and (101) α -Zr have exchanged their intensities. So the peak (002) α -Zr became 50% and (101) α -Zr raised up to 100%. In turn the intensity of (100) α -Zr increased gradually with the time of hydrogenation and hydrogen content. Further hydrogenation did not lead to any further changes in relative intensities of α -Zr peaks. No doubt that crystal lattice will tend to change its high-energy textured state towards low-energy equilibrium annealed state. As it can be seen in the right-hand figure, all line intensities moved to their table values of an annealed material.

Hexagonal lattice parameter analysis



Analysis of α -Zr hexagonal close packed lattice parameters "a" and "c" by means of two independent methods has showed complicated behaviour of zirconium lattice after hydrogenation. The parameter "a" was about 3.2307 \pm 0.0005 Å at all obtained hydrogen content levels (left-hand chart). This level is equal to as-received material. The parameter "c" increases continuously from 5.146 (0 wppm H as-received) to 5.160 Å (4000 wppm H) and further hydrogenation degrees (right-hand chart). Due to this increase the c/a-ratio and elementary volume also increased.

The explanation of lattice embrittlement

The lattice of Zr consists of atomic layers. And it is common knowledge that the atoms in layers are closely packed in comparison to distance between layers. Every Zr atom has 4 free electrons to maintain lattice integrity. In the presence of hydrogen free electrons used to build a chemical bond between Zr and H to build a zirconium hydride. In this case rests of free electrons must be regrouped between atoms to compensate the repulsion force. The most interesting feature that hydrogen can build only one bond with subsequent electron charge redistribution. So the decohesion theory of hydrogen embrittlement is applicable in the case of Zirconium and his alloys.

As a result:

- 1) Loss of plasticity because of lack of free electrons.
- 2) Decrease the strength of atomic bonds (decohesion) between Zr atomic layers \rightarrow lower energy to form a new surface.
- 3) 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).

Cohesion scheme



Decoherence scheme



Conclusions

- A lot of optical microscopy data showed, it is impossible to distinguish hydrides from another elements of structure, especially at low hydrogen content level. High magnification SEM observations reveal hydrides at high hydrogen content level. Fracture surface analysis showed that even at lowest obtained hydrogen content the fracture was of mixed type with signs of plasticity. With increasing hydrogen content there was a transition to a brittle flake-like structure with the rests of the α -Zr needles.
- Tensile tests showed that hydrogen content has a significant impact on mechanical properties, especially on the strain to rupture.
- Microhardness tests showed a relationship between hydrogen hardening, annealing softening and hardening due to $\beta \rightarrow \alpha$ transformation during the cooling phase.
- The XRD analysis showed the presence of γ , δ -phases of zirconium hydride in all of performed experiments. 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".
- Because carried out observations have proved only the presence of hydrides and gave not enough information on the hydride structure and distribution, further detailed EBSD and TEM investigations should be performed in order to determine the location, morphology and orientation of hydrides and to separate them from other structural features.
- The performed experiments can explain the absence of macroscopic hydrides in QUENCH-LOCA experiments. The increased brittleness of some zirconium claddings after QUENCH-LOCA tests could be caused by submicro-scaled hydrides which are distributed in the bulk of material.
- The proposed scheme of the decohesion mechanism helps to understand the embrittlement of zirconium and other hydride forming alloys. The fact of the increase of the lattice parameter "c" allows to suggest that the decohesion mechanism attributed to increased internal stresses due to hydrogen atoms inside the lattice could be responsible for cladding destruction.