Microstructure and Mechanical Properties of Zircaloy-4 Cladding Hydrogenated at Temperatures Typical for LOCA Conditions

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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 due to secondary hydriding very high local hydrogen concentrations can be reached, which can lead to a cladding destruction. Though a lot of investigations on the hydrogen embrittlement were performed there were no attempts to absorb hydrogen uptake within the LOCA interval. The problem is complicated since typical LOCA temperatures are close to phase transformation point and hydrogen itself can decrease α – β transition boundary. With aim to investigate the Zircaloy-4 behaviour under these conditions some series of single rod hydrogenation tests was performed at KIT in framework of the new QUENCH LOCA-programme.

Metallography and SEM investigations

**Microstructure of Zircaloy-4 cladding after annealing in Ar and fast cooling in air**

Absorbed hydrogen decreases the temperature level of phase transformation between α- and β-Zr. According to the Z-H phase diagram the temperature boundary of transformation decreases practically linearly from 880°C to 550°C with increase of hydrogen content from 0 to 7500 ppm. The quick cool-down from temperatures above this boundary zone, finally the typical Widmanstätten pattern and hydrides should precipitate already at quite low hydrogen content. However, no "macroscopic" hydrides were detected by means of optical microscopy, only high magnification SEM observations reveal presumable submicroscopic hydrides.

The XRD-analysis has showed the presence of α-, β-, ψ- phases of zirconium hydrides in 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". In contrast to well predictable stress-strain behaviour of texturized material after annealing, an addition of hydrogen immediately drop down the material plasticity. Even the lowest time hydrogenation leads to brittle fracture of tube. The ultimate strain and ultimate stress depend mainly on hydrogen content and moderately on the annealing temperatures. Because carried out SEM observations gave not enough information on the hydride structure and distribution, further detailed TEM investigation should be performed in order to determination of location, dimensions, morphology and orientation of nano-scale hydrides. This data is necessary for understanding of the cladding embrittlement mechanism after accident under LOCA conditions.

**Tensile test at room temperature**

As-received Zircaloy-4 tube showed approximately 13% of true strain and 750 MPa of ultimate stress. Annealing during 20 minutes at 850°C assures to the reduction of maximal true strain down to 600 MPa. True strain at rupture has risen up to almost 30%, which is normal for annealed Zircaloy-4. As soon as hydrogen was absorbed, it has lead to an immediate impact on mechanical properties. Just 750 ppm absorbed at 700°C reduces drastically the plasticity. The rupture was in all cases brittle. In extreme cases at the maximum detected level of picked-up hydrogen of 4500 ppm the maximal strain was only 1%. In the case of 800° and 900°C the alloy still retained less not 4.5% with a little higher level of true stress because lower solubility of hydrogen at higher temperature according to Sievert's law for Zr.

**Microhardness test**

Microhardness tests of annealed (left-hand figure) and hydrogenated (right-hand figure) specimens were carried out. The heat treatment lead to immediate decrease in microhardness in comparison to as-received state with minimal value at 850°C. Slight hardening emerged as quenching from β-phase at 900° and 1050°C was possible. In all cases annealing causes material softening in comparison to as-received state.

Hydrogen causes material hardening with increasing content so that level of 3000 ppm hydrogen gives microhardness value comparable with as-received state and it continues increasing further in direct relation to hydrogen content.

**X-Ray diffraction analysis**

Increase of hydrogen content leads to shift of the first and the most intensive peak (200) and raise of γ(311) intensity. Фα phase only peaks corresponding to (211) and (311) were stable. The peak (211) appears as a single-peak only after 3000 ppm H. Further increase of hydrogen content hasn't led to formation of new peaks but to redistribution of the intensities of the already existing ones. At extremely high hydrogen content values above 3000 ppm the peak of 8 zirconium hydride becomes dominant.

Conclusions

Absorbed hydrogen decreases the temperature level of phase transformation between α- and β-Zr. According to the Z-H phase diagram the temperature boundary of transformation decreases practically linearly from 880°C to 550°C with increase of hydrogen content from 0 to 7500 ppm. The quick cool-down from temperatures above this boundary zone, finally the typical Widmanstätten pattern and hydrides should precipitate already at quite low hydrogen content. However, no "macroscopic" hydrides were detected by means of optical microscopy, only high magnification SEM observations reveal presumable submicroscopic hydrides.