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

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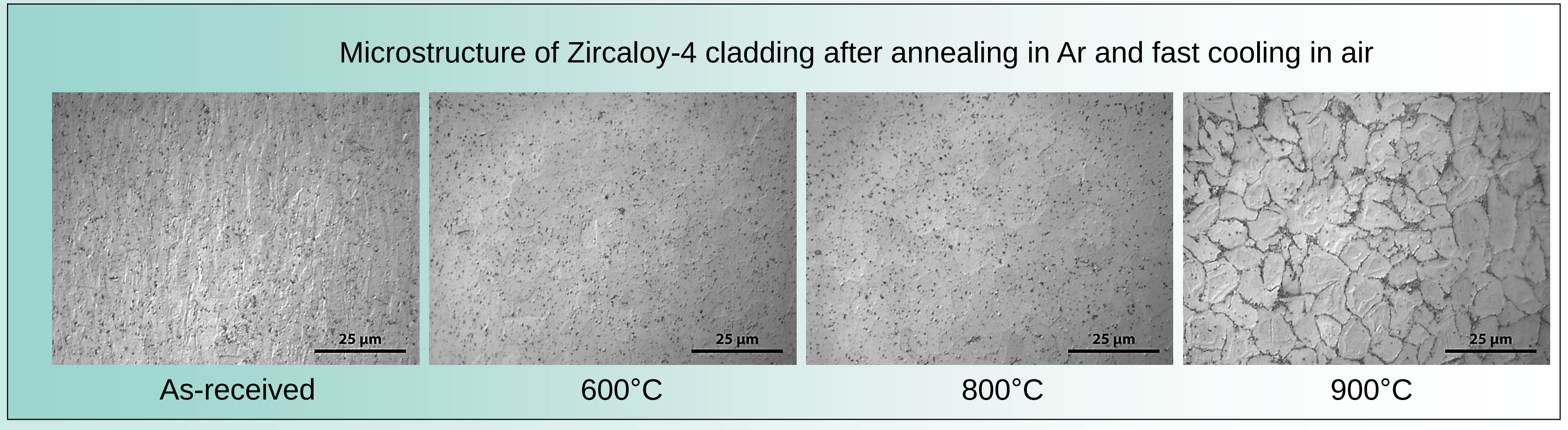
Introduction

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 describe hydrogen uptake within the LOCA interval. The problem is sophisticated 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 the series of single rod hydrogenation tests was performed at KIT in framework of the new QUENCH-LOCA programme.

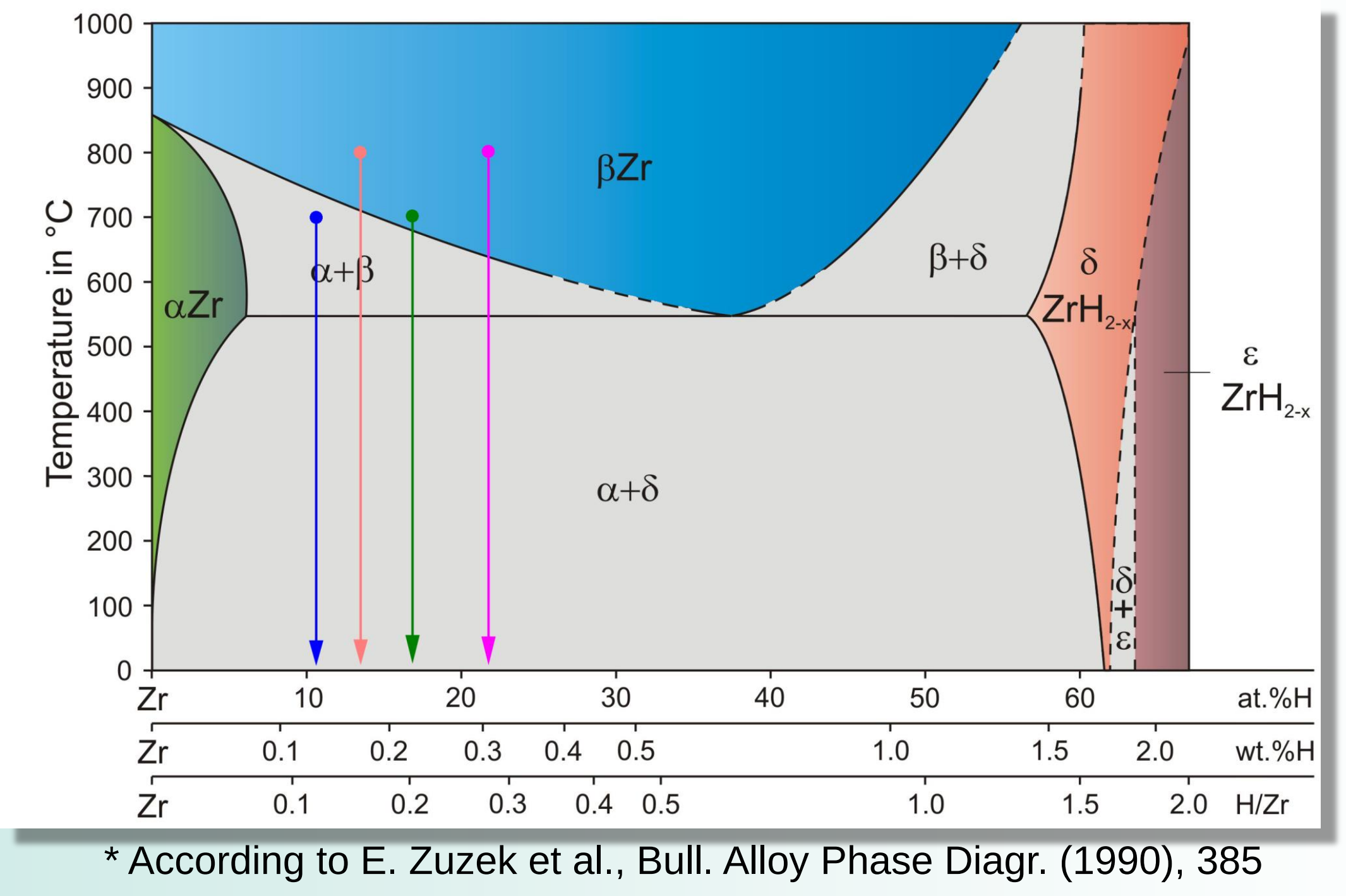
Metallography and SEM investigations

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



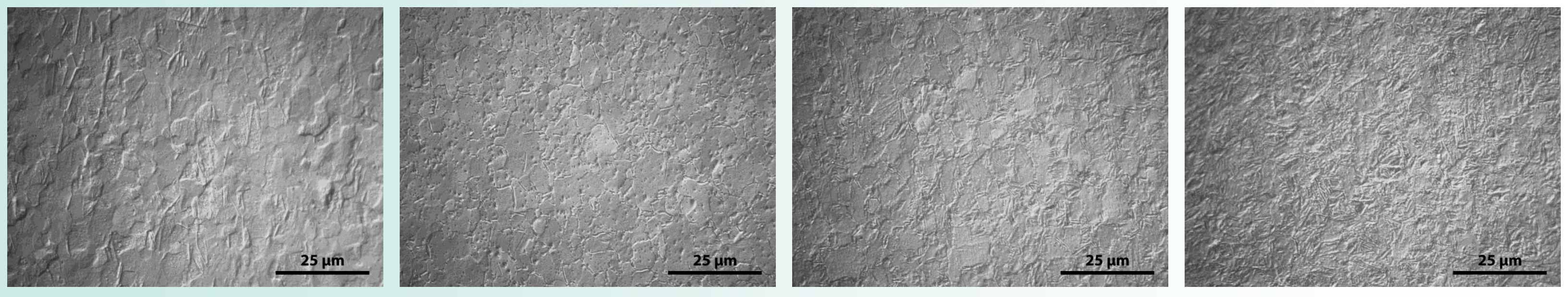
As-received 600°C 800°C 900°C

Equilibrium phase diagram of Zr-H system*



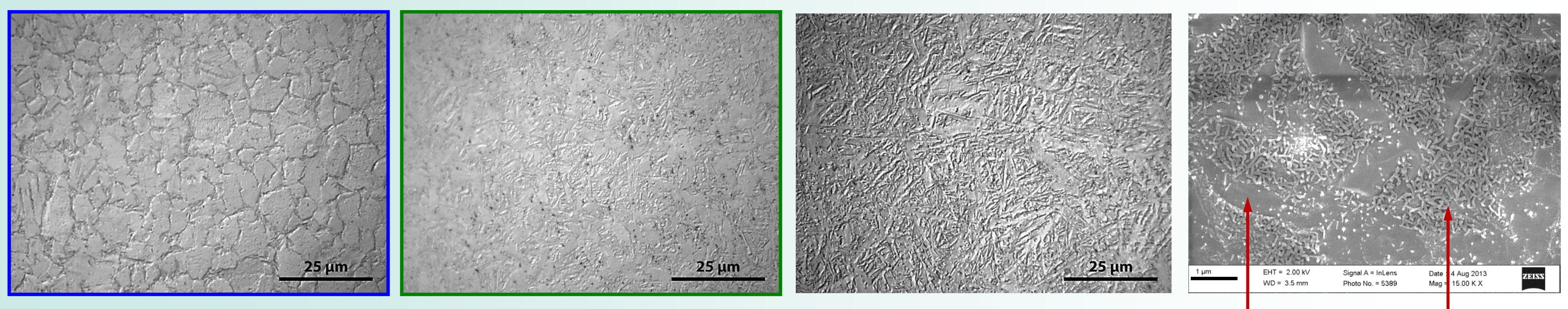
* According to E. Zuzek et al., Bull. Alloy Phase Diagr. (1990), 385

Hydrogenation of Zircaloy-4 cladding *at 600°C* in Ar+H_2 mixture and fast cooling in air



780 wppm H 1400 wppm H 2000 wppm H 3490 wppm H

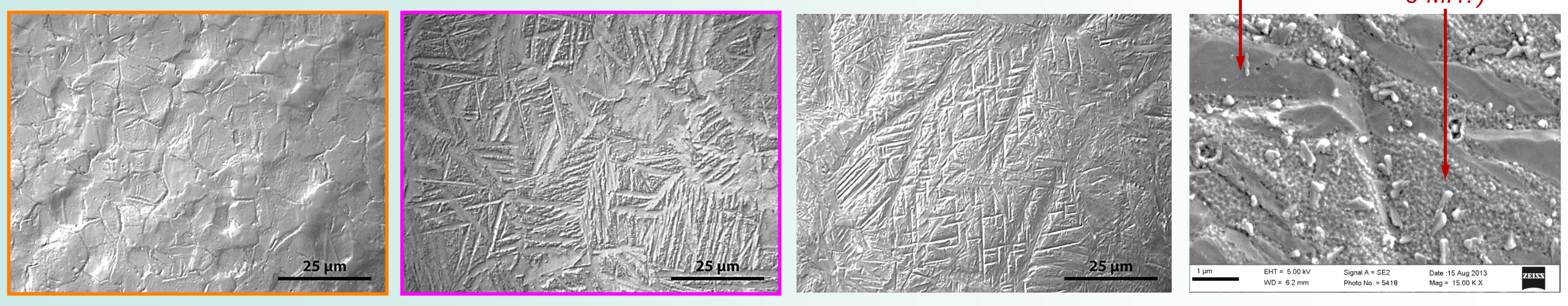
Hydrogenation of Zircaloy-4 *at 700°C*



1330 wppm H 2250 wppm H 4760 wppm H REM: 4760 wppm H

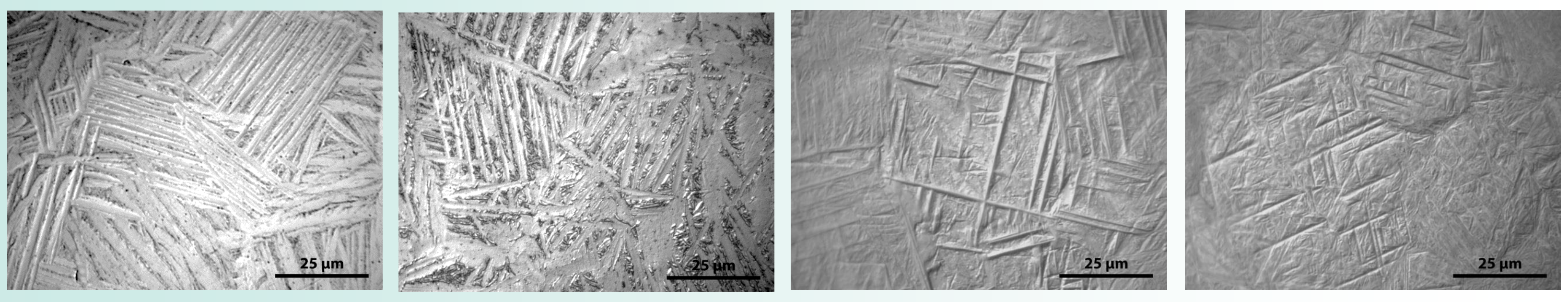
α-Zr (with γ-MH?) *α-Zr (with δ-MH?)*

Hydrogenation of Zircaloy-4 *at 800°C*



1790 wppm H 3060 wppm H 8600 wppm H REM: 8600 wppm H

Hydrogenation of Zircaloy-4 *at 900°C*

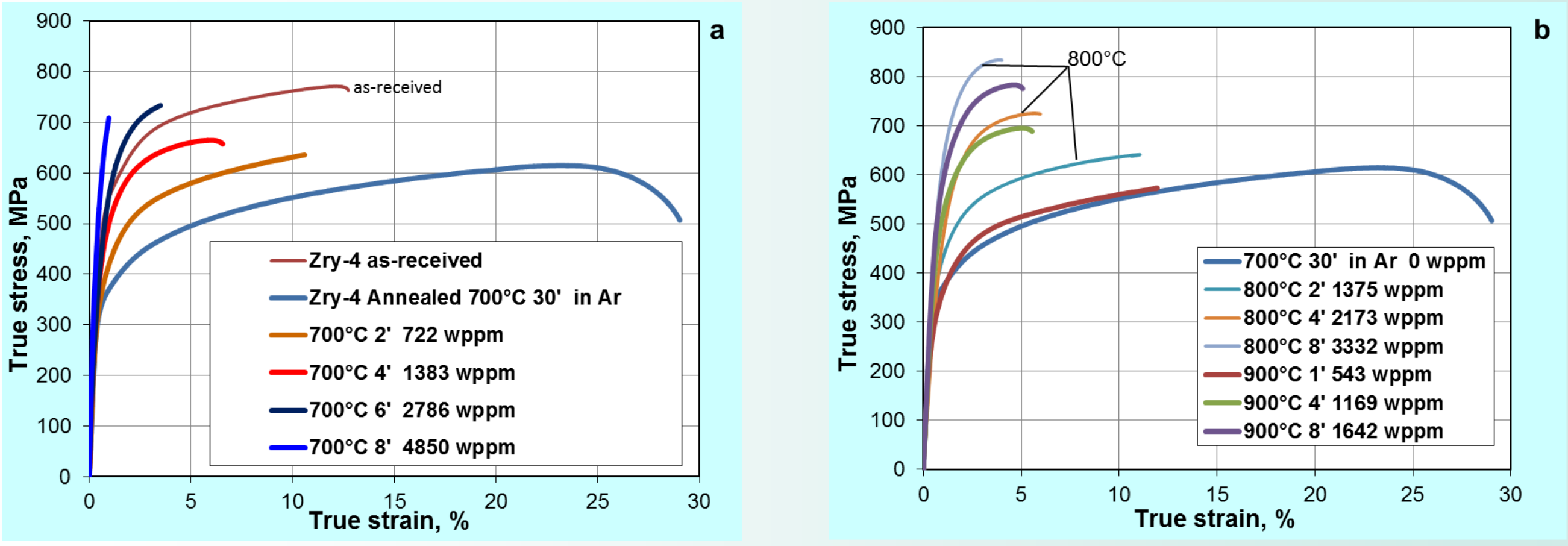


880 wppm H 1500 wppm H 2000 wppm H 6700 wppm H

The as-received sample was highly texturized. 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 µm) and after phase transition relative large linear regions (30-50 µm) of same oriented sub-grains are forming.

Hydrogen changes the appearance of microstructural pattern cardinally. Hydrogen content lower than 1800 wppm is characterised by α-Zr grains with broad grain boundaries.

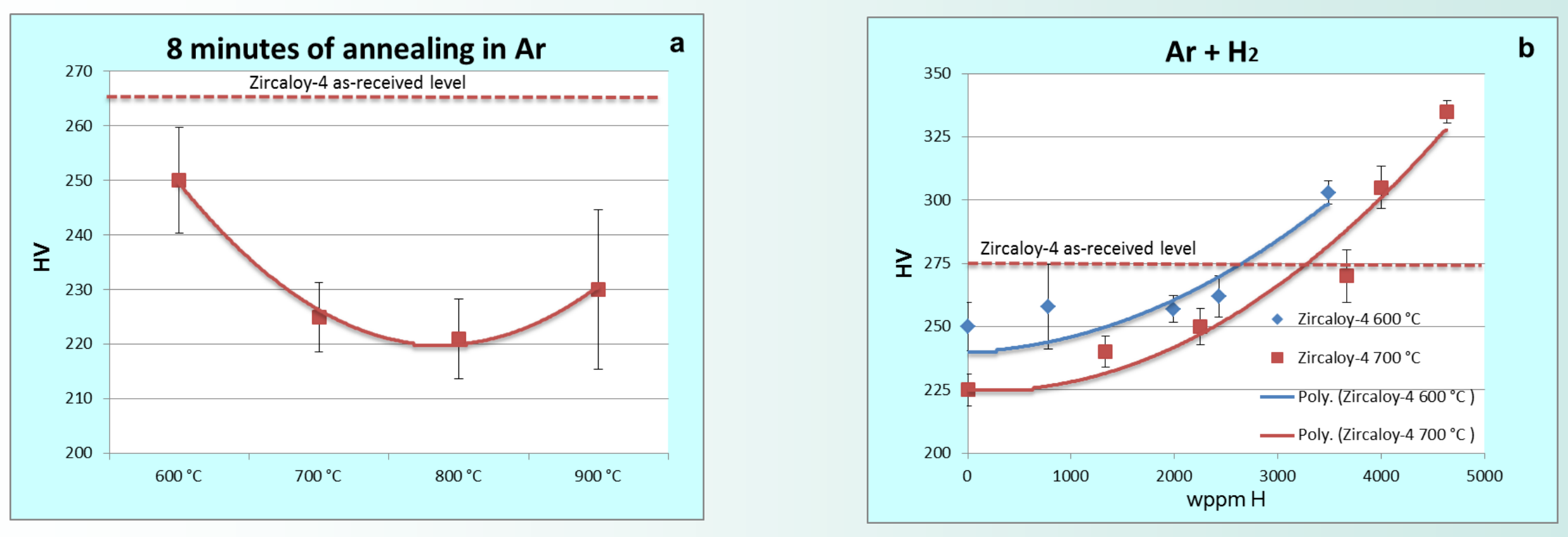
Tensile test at room temperature



As-received Zircaloy-4 tube showed approximately 13% of true strain and 750 MPa of ultimate stress. Annealing during 30 minutes 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 normal for annealed Zircaloy-4.

As soon as hydrogen was absorbed, it has had an immediate impact on mechanical properties. Just 700 wppm 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 4850 wppm the maximal strain was only 1%. In the case of 800°C and 900°C the plasticity of alloy still remained not less than 4-5% with a little higher level of true stress because lower solubility of hydrogen at higher temperature according to Sieverts's law for Zr.

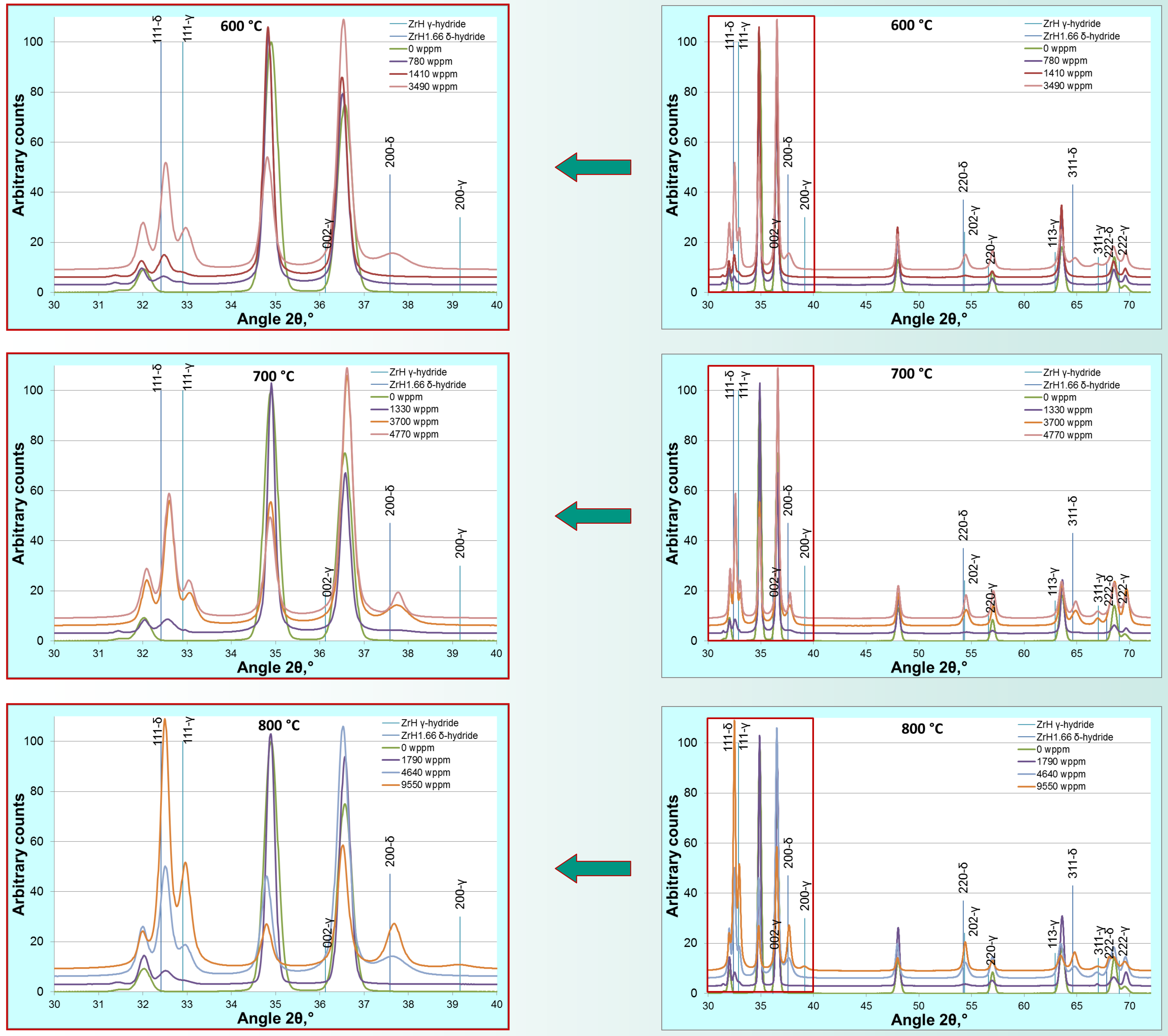
Microhardness test



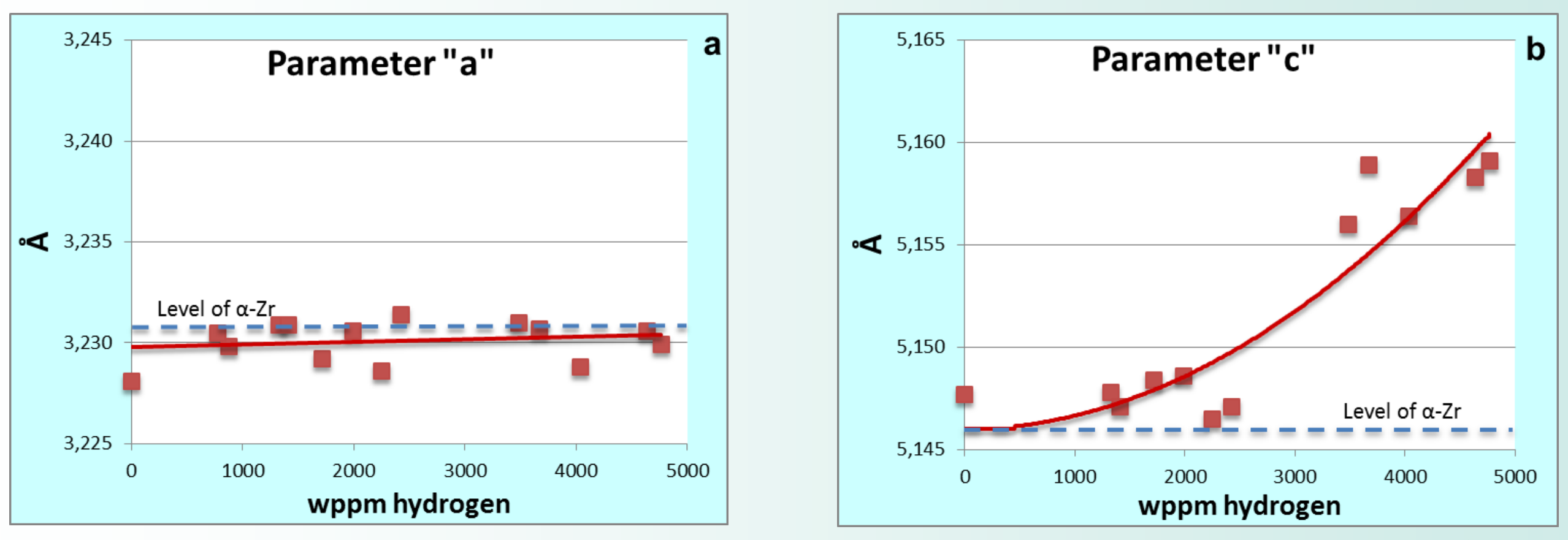
Microhardness tests of annealed (left-hand figure) and hydrogenated (right-hand figure) samples were carried out. The heat treatment led to immediate decrease in microhardness in comparison to as-received state with minimal value at 800°C. Slight hardening emerged as quenching from β-phase at 900 and 1000°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 wppm 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 origination of the first and the most intensive peak δ{111} and then δ{200} and raise of γ{311} intensity. For γ-phase only peaks corresponding to {111} and {311} were visible. The peak γ{111} appears as a single peak only after 3000 wppm H. Further increase of hydrogen content hasn't led to formation of new peaks but to redistribution of the intensities of the already existed ones. At extreme high hydrogen content values above 8000 wppm the peak of the δ zirconium hydride becomes dominant.



Not all absorbed hydrogen was consumed for formation of hydrides during the cool-down. A shift up to -0.1° between the XRD pattern obtained from the as-received specimen and the specimen from the hydrogen enriched zone was observed. This indicates that the crystal lattice is distorted by hydrogen, which is at least partially dissolved in the α-Zr lattice (with content up to 400 wppm). Lattice parameters changed differently: whereas the parameter "a" was constant, the parameter "c" increased continuously with increase of hydrogen content at least until 5000 wppm.

Conclusions

Absorbed hydrogen decreases the temperature level of phase transformation between α- and β-Zr. According to the Zr-H phase diagram the temperature boundary of transformation decreases practically linearly from 860°C to 550°C with increase of hydrogen content from 0 to 7000 wppm. The quick cool-down from temperatures above this boundary forms 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 submicroscale hydrides.

The XRD-analysis has showed the presence of γ-, δ-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 dropped down the material plasticity. Even the lowest time period of hydrogenation leads to brittle fracture of tube. The ultimate strain and ultimate stress depend mainly on hydrogen content and moderately on the annealing temperature.

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.