

# Imaging of Hydrogen in Zirconium Alloy with Secondary Ion Mass Spectrometry (SIMS) : Time of Flight and Quadrupole SIMS Methods

N. Mine<sup>1</sup>, S. Portier<sup>1</sup>, J-P. Barnes<sup>2</sup> and M. Martin<sup>1</sup>

<sup>1</sup> Hot Laboratory division, Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland

<sup>2</sup> CEA, LETI, MINATEC Campus, 17 rue des Martyrs, F38054 Grenoble, Cedex 9, France.

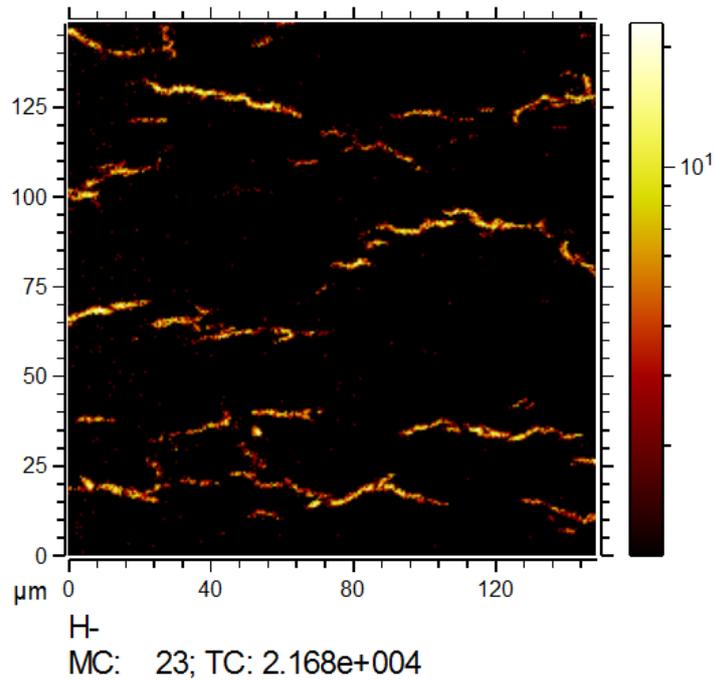
Although hydrogen can be detected easily in Secondary Ion Mass Spectrometry, its source must be well identified compared to various contaminations. Characterization of hydrogen in metals requires local information, which motivates the development of imaging methods. In this work, we investigated Zircaloy-4 and Zircaloy-2 cladding specimens (typically used for nuclear fuel cladding) hydrogenated in a Sievert apparatus. The hydrogen content varies from 130 to 600 wppm locally (heterogeneously distributed in the cladding).

Processes were developed on a quadrupole SIMS with gallium depth profiling (Atomika 4000, Munich Germany)[1] and a dual beam ToF-SIMS V (IONTOF GmbH, Münster Germany). In order to observe the hydride precipitates in SIMS from the polished surfaces, cesium sputtering is used to improve the secondary ion yield of H<sup>-</sup>, coupled to a high brightness imaging source for analysis (gallium or bismuth cluster source on the Quadrupole and Time of Flight SIMS respectively). The solutions applied to improve the secondary ion dynamic range are described. The hydrides have been clearly identified (see figure 1 and 2). These results can be correlated with other microscopy methods (BSE, SEM...). Both instruments permit to monitor hydride precipitates with sub-micrometer spatial resolution (about 500 nm). We discuss the resolution limiting factors for hydrogen imaging using both instruments.

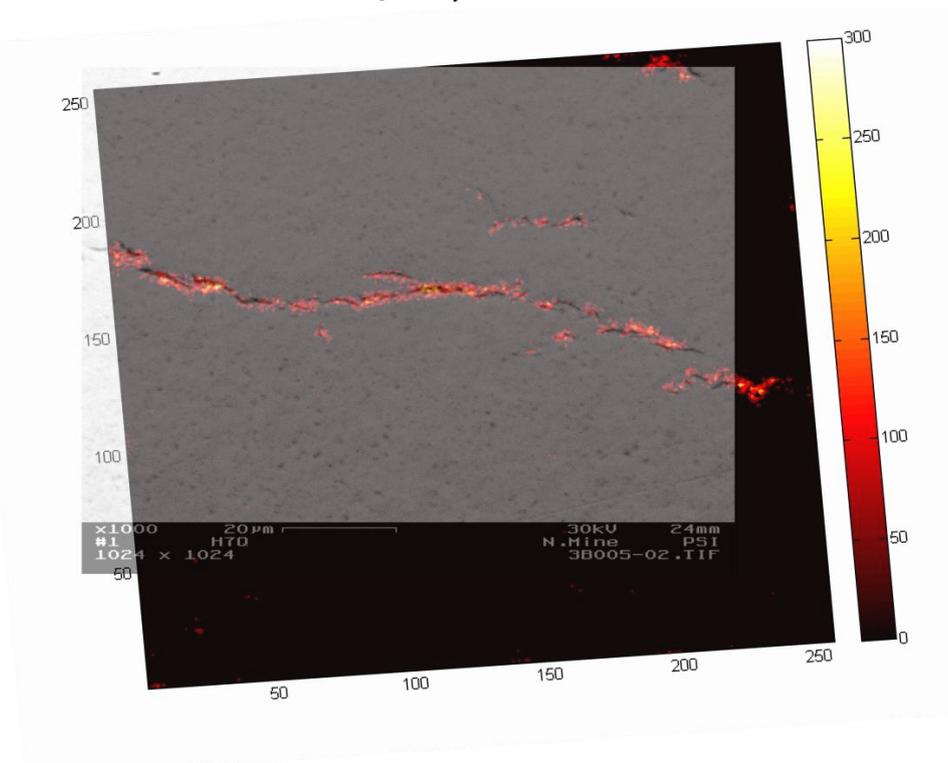
From XRD experiments, we know that the major hydride phase is the  $\delta$ -phase (ZrH<sub>1.66</sub>). Using the latter assumption, the hydrogen content can be approximated by integrating the H<sup>-</sup> intensity (and normalizing by the analysis area). The H<sup>-</sup> useful yield in a wide precipitate serves as a reference/standard. This hydrogen content is compared to values measured with other techniques (BSE, hot gas extraction). Finally, the correlation between the secondary phase particles (SPP : Ni, Cr, Fe, ...) and the hydrides has also been investigated using ToF-SIMS[2].

[1] N. Mine, S. Portier and M. Martin, Conference Proceedings SIMS XIX (2013), accepted in *Surface and Interface Analysis*, DOI 10.1002/sia.5466

[2] The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 290605 (PSIFELLOW/COFUND).



*Fig.1 Secondary ion (SI) image of the hydride precipitates obtained from ToF-SIMS dual beam depth profiling with 25 keV  $\text{Bi}_3^+$  analysis and 2keV  $\text{Cs}^+$  erosion*



*Fig. 2 Superposition of a SEM-BSE image with the SI image obtained using the Atomika 4000 Quadrupole SIMS. The hydride precipitate image is obtained from the 25 keV gallium primary ion depth profile of a 12 keV cesium pre-sputtered area.*