

## Hydride Formation and Deformation Mechanisms in Commercially Pure Titanium

Stoichko Antonov<sup>1\*</sup>, Qing Tan<sup>2</sup> and Baptiste Gault<sup>2,3</sup>

<sup>1</sup>. National Energy Technology Laboratory, Albany, OR, United States.

<sup>2</sup>. Max-Planck-Institut für Eisenforschung GmbH, Dusseldorf, Germany.

<sup>3</sup>. Imperial College London, London, United Kingdom.

\* Corresponding author: Stoichko.Antonov@netl.doe.gov

Due to the excellent strength-to-weight ratio and corrosion resistance, titanium and its alloys are important structural materials for applications in the aerospace and biomedical industries [1]. The excellent corrosion resistance of commercially pure (CP), hexagonal close-packed (hcp)  $\alpha$ -titanium makes it an attractive material for components subjected to a variety of aggressive environments, e.g., sea water, bodily tissue and fluids, and other aqueous solutions [2]. Titanium, however, has a high affinity for hydrogen, making it highly susceptible to hydride-associated failures due to stress corrosion cracking of CP titanium [3]. In these alloys, a sufficiently high trace level of  $\beta$ -stabilizing elements can lead to the retention of a low volume fraction of  $\beta$ -phase, in the form of small (~hundreds of nm) discrete precipitates typically located at triple points and grain boundaries across the microstructure. The hydrogen solubility in the  $\beta$  phase is ~200x higher than that in  $\alpha$ -Ti at room temperature [4], which can cause increased hydrogen concentrations in  $\alpha$  phase that are sufficiently high to cause hydride formation.

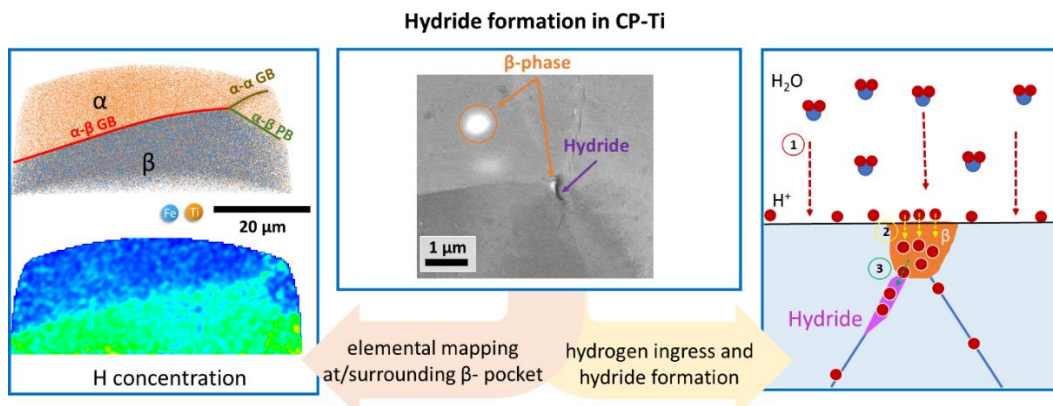
One of the challenges in studying hydrogen and hydride behavior in CP titanium, and other Ti-based alloys, is the facile formation and dissolution of new hydrides during the preparation of specimens [5]. The difficulty in preparing hydride-free metallographic specimens makes it somewhat ambiguous to discern the underpinning mechanisms of hydride formation and deformation behavior in Ti alloys post-microstructural manipulation, e.g. deformation of the sample. For instance, whether these preparation-induced hydrides exhibit the same properties as those formed in bulk samples during H-charging, and whether post-deformation sample preparation alters the pre-existing hydrides-matrix deformation structure and interaction, remain open questions. In this research, we employ state-of-the-art methods to unveil some of the mechanisms behind hydride formation and deformation to understand the hydrogen embrittlement of  $\alpha$ -Ti alloys.

First, cryogenic sample preparation via focused ion beam (FIB) for atom probe tomography (APT) was used to analyze the elemental segregation of H and trace elements to  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  grain and phase boundaries near the  $\beta$  precipitates in a Grade 2 CP-Ti, Figure 1. The preliminary findings show that H and Fe exhibit the same partitioning to  $\beta$  behavior, as well as segregation to the  $\alpha/\alpha$  grain boundary, but not the  $\alpha$ - $\beta$  phase boundary. We propose that the formation of hydrides in Grade 2 CP-Ti is associated to the ingress of H from discrete  $\beta$  precipitates, which are stabilized mainly by Fe impurity, and subsequent interaction of H with the  $\alpha$  phase at the  $\alpha$ - $\beta$  boundaries. As such, trace  $\beta$  stabilizing elements play a crucial, yet indirect, role for hydrogen embrittlement by increasing the number fraction of  $\beta$  phase and thus the hydride nucleation sites. These findings are crucial in light of the increasing importance of recycling of titanium alloys, where there can be concerns around the progressive accumulation of impurities (Fe in this case) that cannot be removed by vacuum metallurgy.

Then, *in-situ* synchrotron-based high-energy X-ray diffraction (HE-XRD) was used to investigate the deformation mechanisms and interactions between hydrides and the parent  $\alpha$ -Ti matrix in the H-charged

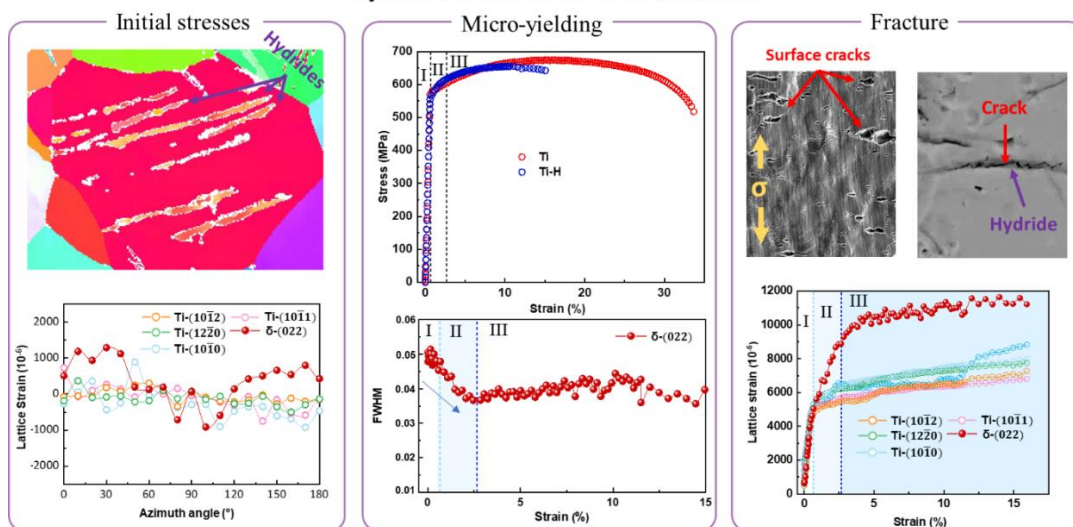
Grade 2 CP-Ti, Figure 2. The formed hydrides have a platelet morphology with orientation relationship of  $(0001)_\alpha // (001)_\delta$  and  $[1\bar{2}10]_\alpha // [110]_\delta$ , and a habit plane of  $(2\bar{2}0)_\delta // (01\bar{1}0)_\alpha$ . The HE-XRD results show that high internal and interphase stresses were generated within and around hydrides due to the volume expansion induced by the  $\alpha$ -Ti to  $\delta$ -hydride phase transformation. The initially wide dispersion of the d-spacings of the hydrides significantly contributed to the diffraction peak broadening, in contrast to expected common knowledge that it is caused by the grain size and dislocations. During deformation, the hydrides exhibit a typical high strength but brittle secondary phase behavior, which undertakes more elastic strain than the matrix after the matrix yields and is the location where cracks are first generated. In contrast to first principle calculations [5] and hydride deformation studies in zirconium [6], phase transformation to other hydride phases was not observed during the deformation.

This study on the formation and deformation mechanism of hydrides in pure titanium provides insight into the hydride deformation behavior and hydrogen embrittlement in titanium, and some of the findings are also likely applicable to zirconium alloys. Cryogenic sample preparation and *in situ* analysis methods can overcome the challenges related to the hydrogen ingress and hydride formation during sample preparation of  $\alpha$ -Ti alloys and are likely the way forward to collecting high fidelity data that enables understanding of hydrogen embrittlement of Ti and other environmentally sensitive materials [7].



**Figure 1.** Atom probe analysis of the grain and phase boundary elemental segregation and a proposed mechanism for the ingress of H and subsequent  $\text{TiH}_x$  formation in Grade 2 CP-Ti.

## Hydride deformation in titanium



**Figure 2.** Hydride-formation induced interphase stresses and subsequent deformation behavior as studied by *in situ* HE-XRD.

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