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Quantification of dislocations densities in zirconium hydride by X-ray line profile analysis

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ABSTRACT

Zirconium-based components in nuclear power plants are embrittled by precipitates of δ zirconium hydride, which involves a martensitic-type transformation of the hexagonal α-Zr lattice into the face-centered cubic Zr sublattice of the hydride. As a result, the hydride precipitates have a complex and heavily distorted internal structure that manifests as broad peaks in X-ray diffraction experiments. By a detailed analysis of the peak widths measured for different crystal planes we have found that most of this broadening is the result of dislocations. The analysis also showed that δ-hydride has very anisotropic mechanical elastic properties, in agreement with ab-initio simulations presented in the literature.

Provided with this peak-broadening model, we have quantified dislocation densities within δ-hydrides precipitated in several Zr alloys, by analyzing previously published X-ray diffraction experiments performed at three synchrotron X-ray sources. The specimens investigated correspond to components affected by different hydride embrittling processes, namely: (i) samples from various components, charged in the laboratory with H contents in the ~250 wt ppm range, (ii) laboratory-produced hydride blisters in Zr2.5%Nb pressure tubes; and (iii) Zircaloy-4 specimens machined from cooling channels of Atucha I nuclear power plant after 10 years in-service, containing ~140 wt ppm of equivalent H content and subjected to an estimated fast neutron fluence of ~10^{22} neutrons/cm^2. Results show that dislocations densities in the δ-hydrides are large (5–20 × 10^{15} cm^{-2}) and vary among the different specimens. We also found that dislocations densities in the hydride are proportional to the fraction of hydrides already formed in the matrix, which was interpreted as the effect of matrix hardness in the precipitate structure.

1. Introduction

Zirconium alloys are widely used in the nuclear industry due to their low neutron absorption, good mechanical properties and corrosion resistance at operation temperatures. Zr alloys are embrittled by H absorbed in-service, which precipitates as a brittle hydride phase. Hydride embrittlement may occur mainly through three mechanisms:

i) At relatively low H concentrations (<1200 wt ppm H), small hydride precipitates reduce the overall strength of these alloys, with the impact on mechanical properties being highly dependent on the size, shape and orientation of the precipitates. A ductile-brittle transition is observed in Zircaloy-4 when the H content is higher than a critical value which depends on the alloy microstructure [1,2].
ii) In thermal gradients H concentrates at cold regions, forming hydride rims or blisters, i.e., macroscopic regions with very high H content (~12000–16000 wt ppm H). This affects the long term storage of spent fuel from nuclear power plants [3], and it has produced the failure of pressure tubes in the past [4].
iii) Over long operational periods, stressed components such as pressure tubes or welded parts may suffer from Delayed Hydride Cracking [5], a failure mechanism where crack growth occurs by repeated precipitation and fracture of small hydrides at the crack tip [6].

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In all of these situations H precipitates as δ-hydride (ZrH_x with $1.6 < x < 1.64$ at room temperature), one of the four compound phases found in the Zr–H system, which has a density ~17% lighter than pure Zr [7]. δ-phase precipitates appear as plateletes to the optical microscope, but at higher magnification these platelets are observed to be in fact composed by clusters of smaller sword-like hydrides [8]. The δ hydride is a *defected* structure in which the protons occupy approximately ¾ of the available tetrahedral interstitial sites of a face-centered cubic Zr sub-lattice with an almost constant lattice parameter for the full range of H composition (~4.779 Å at room temperature) [9–12]. Understanding the mechanical response and eventual fracture of embedded δ-hydride precipitates due to applied loads is essential to model, and eventually mitigate embrittlement [13]. This requires knowledge of the elastic constants and active modes for plastic deformation of the δ-hydride. Also central to all models is a quantification of the stress state and plastic deformation within and around the hydride precipitates that results from accommodation of the localized volume change involved in the phase transformation (α-$Zr + xH \rightarrow$ δ-ZrH_x). Large uncertainties still exist in the literature about these basic aspects of hydride deformation, mainly due to the experimental difficulties associated to investigate the mechanical response of such small precipitates embedded within the bulk Zr matrix.

So, information about the elastic constants and deformation modes has been obtained from tests performed on bulk, homogeneous, crack-free hydrides produced from pure Zr in a modified Sieverts apparatus [14–17] and, more recently, also from Zr2.5%Nb [18]. Microscopic observations after indentation tests [19] and after compression tests [15], show that plastic deformation of δ-hydride involves both slip and twinning. Slip on the {111}<110> system is the dominant deformation mechanism for as-produced single-phase bulk δ-hydride between room temperature and 250 °C [15,19]. Dislocation lines and twin bands on a {110} twin plane are readily observed in TEM images as intrinsic defects in the as-produced bulk material [19].

However, the results on bulk hydrides cannot be directly extrapolated to characterize the response of small hydride precipitates to external loads because of the constraining effect of the metal matrix. Fracture always precedes any measureable plastic deformation in tensile tests of bulk pure δ-hydride. On the other hand, recent in-situ synchrotron X-ray diffraction experiments during mechanical testing have revealed the details of the elastic and plastic response of the hydride precipitates in uniaxial tests in Zircaloy-2 [20] and in Zircaloy-4 [21]; and in notched CT specimens [22,23]. There is still no agreement about the interpretation of the response of hydride precipitates to uniaxial loads.

From the information reported for bulk δ-hydrides we can assume that plastic deformation of the hydride precipitate in αZr results mainly from slip. Hence, the plastic response and eventual fracture of hydride precipitates to applied loads would be greatly dependent on the dislocation density within the hydride prior to the test. High dislocations densities have been reported in TEM observations of δ-hydride precipitates embedded in Zr2.5%Nb [8] and in Zircaloy-4 [24,25]. In the latter case, dislocation densities within hydride precipitates have been estimated to be $\sim 1.1–1.5 \times 10^{15}\ m^{-2}$ for Zircaloy-4 containing ~1000–2000 wt ppm H, both from TEM observations [24] and from neutron diffraction peak profile analysis [25].

Here we present measurements of dislocation densities within hydride precipitates present in specimens affected by different hydride embrittling processes, namely: (i) samples from various components, charged in the laboratory with H contents in the <300 wt ppm range, (ii) laboratory-produced hydride blisters in Zr2.5%Nb pressure tubes; and (iii) Zircaloy-4 specimens machined from cooling channels of Atucha I nuclear power plant after 10 years in-service, containing ~140 wt ppm of equivalent H content and subjected to an estimated fast neutron fluence of $\sim 10^{22}$ neutrons/cm^2. The wide variety of specimens investigated allowed an estimation of the range of dislocations densities existing on the hydrides present in typical nuclear components.

Dislocation densities were obtained through a detailed qualitative and quantitative analysis of peak shape measured for different hydride reflections in synchrotron X-rays diffraction experiments. The dependence of peak width on crystal reflection was interpreted in terms of the results obtained from fitting of the experimental diffractograms by the convolutional multiple whole profile (CMWP) procedure [26,27]. This model gives as output a theoretical diffractogram which can be directly compared to the experimental one, where different contributions to the peak shape are included: instrumental broadening, particle size, dislocation density with the corresponding contrast factors and planar defects as twinning and stacking faults.

This paper is organized as follows. Section 2 gives a brief description of the different samples investigated, and the synchrotron X-ray diffraction facilities used to test them. Section 3 presents a thorough qualitative and quantitative study of the characteristic dependence observed for the physical broadening of δ hydride lines (δ-{*hkl*}) on the inverse of the interplanar distance ($K = 1/d_{hkl}$). Section 4 presents the line profile analysis for the specimens, which provides information on the accumulation of plastic deformation within δ-hydride precipitates as a response to neutron irradiation, microstructure and compositional variations at the time of precipitation. Section 5 discusses the present findings in terms of existing knowledge about the plastic deformation of δ-hydride precipitates.

2. Samples and testing

The diffraction experiments analyzed here were performed over the last six years at three synchrotron X-ray facilities in USA and Brazil. Those experiments were originally devised to characterize other aspects of hydride precipitates, and their findings have been published elsewhere [28]. Those studies were based on the analysis of the position and intensity of the observed diffraction peaks, but over the years it became clear that δ-hydride peaks were considerable wider than α-Zr peaks, and presented a very characteristic pattern on reflection index. This is exemplified in Fig. 1, showing a detail of a diffractogram registered for a hydride blister, at a location where the volume fractions of α-Zr and δ-hydride were nearly equal. The δ-(220) and δ-(200) peaks are considerably wider than the α-(11–20) and α-(10–11) peaks, respectively, even when the instrumental resolution is almost identical, due to the close proximity between the α and δ peaks displayed in the figure. This motivated a thorough analysis of peak width, in order to extract some additional information from those past experiments.

The experiments analyzed in this work were chosen because they represent examples for several of the hydride degradation mechanisms mentioned in the Introduction; but also because they provide an insight on how plastic deformation of the δ-hydride precipitate depends on neutron irradiation, and on the microstructure and hydride concentration of the Zr-alloy. The chemical compositions of the specimens studied here and the synchrotron beamlines used for testing are listed in Table 1. In the section below, we provide only a brief account about specimen preparation and experimental methods for the different specimens, and the reader is referred to the original papers for additional information.

2.1. Hydride blisters in Zr2.5%Nb pressure tubes

A hydride blister was grown on a coupon machined from a