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Microstructure characterization of a hydride blister in Zircaloy-4 by EBSD and TEM

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ABSTRACT

This paper presents a detailed microstructural characterization by EBSD and TEM techniques of a hydride blister grown on a Zircaloy-4 plate. The hydrides formed are found to be of δ-type, and exhibit an increasing volume fraction from alloy matrix, across matrix-blister boundary, and into the blister. The microstructure of the blister mainly consists of δ-hydride platelets, however there is still un-transformed α-Zr phase inside the blister. The orientation relationship between the hydride and alloy matrix has been analyzed. In addition to the commonly observed $(0001)_{\alpha-Zr}//\{111\}_{\delta}$ orientation relationship, we found hydrides with a secondary $(0001)_{\alpha-Zr}//(100)_{\delta}$ orientation relationship. A correlation was drawn between the formation of hydrides with the two orientation relationships and the parent grain orientation. TEM observation revealed the distribution of the remnant α-Zr phase inside the blister, which had either a nodular shape or appeared as thin nano-sized layers among the hydride platelets. The microstructure of the hydrides has been characterized by HRTEM, exhibiting a uniform atomic structure with high dislocation density. Lastly, δ-hydride embryos obeying the primary orientation relationship were found within untransformed α-grains, indicating a consistent nucleation mechanism during blister growth.

1. Introduction

Zirconium (Zr) alloys have been extensively used in nuclear reactors as core structural materials. Due to direct contact with cooling water and the subsequent corrosion reaction, hydrogen ingress is inevitable for Zr alloys, which eventually results in hydride precipitation once the hydrogen solubility is exceeded. Such brittle hydrides are sources of crack nucleation and a potential cause of failure of Zr alloy components in nuclear reactors. In some extreme conditions macroscopic hydride blisters can develop on the surface of the Zr-alloy, which was first recognized in 1983 due to the failure of a pressure tube in a CANDU nuclear reactor [1]. Ever since, numerous studies have been carried out to grow blisters on Zr-alloys to simulate the impact of different possible in-service behaviors [2–6]. The transformation of α-Zr to hydride involves a large volume expansion, of about 17% per unit cell of Zr, therefore cracks are ubiquitously present inside the blister, which can potentially lead to stress concentrations in the alloy matrix and hence crack propagation through the mechanism known as delayed hydride cracking (DHC) [7].

To address the discrepancies of several theoretical studies that calculate the misfit stress field within and around blisters [8–10], the texture and phase constitution of a blister grown in a Zr-2.5Nb alloy were studied by a high spatial resolution synchrotron X-ray technique [11]. It was reported that there was at least 20% α-Zr remnant in the blister, in addition to the dominating δ-hydride phase.

The δ-hydride, $ZrH_{1.67}$, has a disordered fcc lattice of the CaF_2 crystal structure and with a lattice spacing of 4.778 Å [12]. TEM characterization has shown that the precipitation of δ-hydride from α-Zr typically obeys the following orientation relationship (OR) [13]:

$$(0001)_{\alpha-Zr}//(111)_{\delta},\ \left[11\bar{2}\,0\right]_{\alpha-Zr}//\left[1\bar{1}\,0\right]_{\delta}.$$

By using this OR, the texture of δ-hydrides in a blister were predicted based on the texture of the parent α-Zr in a Zr-2.5Nb alloy; a good correlation has been found between the experimental and predicted hydride pole figures [11]. However, there are

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a number of questions that remain. Firstly, not all the maxima observed in the (001) experimental pole figure [11] were reproduced in the calculated pole figure, which suggests the existence of another OR for hydride formation inside the blister. Secondly, the morphology and distribution of the remnant α-Zr remain to be characterized by microscopy.

Due to the challenges of preparing samples from the brittle hydride blister, there has been no prior detailed electron microscopy characterization on its microstructure. There have however been extensive TEM and SEM studies of small volume fractions of hydrides within zirconium matrices [14–26]. Exclusively, previous EBSD studies done on δ-hydrides forming either intra- or intergranularly in Zr alloys demonstrate the well known $(0001)_{\alpha-Zr} or (10\bar{1}\,7)_{\alpha-Zr}//(111)_{\delta}$ OR [20–26]. However, there were a few studies reporting the occurrence of a much less common $(0001)_{\alpha-Zr}//(100)_{\delta}$ OR. One study found its existence in a Zr-1Nb alloy in-between hydrides formed on or near a twin and the twin's α parent grain [21]; another study reported particle like hydrides formed with this second OR during *in situ* TEM straining of a hydrided Zircaloy-2 sample [27]. This same secondary $(0001)_{\alpha-Zr}//(100)_{\delta}$ OR was suggested to explain the discrepancy between observed and predicted textures in a blister [11], and our preliminary results have suggested that it in fact makes a significant contribution to the texture development of hydrides forming a blister [28].

In this study we use advanced EBSD and TEM techniques to characterize the microstructure of a blister grown on a Zircaloy-4 specimen. Through EBSD mapping of the blister microstructure and a parent grain reconstruction algorithm, we have successfully reconstructed the α parent grains from the hydrides and remaining α-Zr in a Zircaloy-4 alloy, demonstrating the presence of both previously reported ORs. The results obtained provide an improved understanding of the mechanism of blister formation and growth in Zr alloys.

2. Materials

A Zircaloy-4 sample (22 mm × 23 mm x 4 mm in thickness) was hydrided in a Sievert-type device at 425 °C and 11.2 × 10^3 Pa of hydrogen. A palladium film was previously deposited on the surface to assure hydrogen ingress until a surface hydride concentration of 610 wt ppm was achieved. Further heat treatment at 480 °C for 24 h produced a homogeneous hydride distribution and a hydrogen concentration of 395 wt ppm according to the solvus measured by Kearns [29]. The palladium and hydride layers that remained after this annealing were removed by mechanical polishing, followed by etching in a solution of 45 ml HNO_3, 45 ml H_2O, 6 ml HF. Then, the sample was machined to a circular shape.

Finally a blister was grown on the sample surface, along the normal direction (ND) of the plate. The experimental device used was similar to that described in a previous work [30]. The sample was placed over an aluminum block heated in an electrical furnace up to 425 °C for 29 days. A thermal gradient was obtained by pressing an aluminum cold finger on the upper surface of the sample. The contact area was 5 mm in diameter. After blister formation, the sample was cooled in the furnace.

3. Sample preparation

The hydride blister is inherently brittle, contains large macroscopic cracks, and there is only a limited volume fraction present; this presents big challenges for electron microscopy sample preparation. Firstly, small rectangular bars containing the blister were cut using a Struers Accutom-5 with a 150 μm thick diamond blade. Sections were cut containing the blister and matrix, with either the Zircaloy-4 plate TD or RD directions normal to the section surface; we will term these TD-normal and RD-normal samples.

Some sections were prepared for EBSD characterization, by firstly grinding with sandpaper up to 2000 grit, then applying one more step of attack polishing with a dilute solution of HF combined with 0.05 μm colloidal silica suspension to make a mirror-like surface finish. The final step consisted of a 30s chemical etching in a solution of 10% HF, 45% HNO_3, and 45% distilled water. Fig. 1 shows an image of the prepared TD-normal specimen taken using a Keyence VHX-5000 optical microscope. The blister area is outlined; a large crack can clearly be seen to have grown into the material.

To prepare for TEM viewing, the cross section area was first reduced to 2 × 2 mm along the ND direction, removing from the alloy matrix side. Then the small bar containing the sectioned blister volume was embedded in a copper tube of 3 mm diameter with epoxy. Slices of 500 μm thickness were then cut from the filled tube, which provided samples containing the blister area with TD-normal. The thicknesses of the 500 μm slices was then reduced to around 70 μm by mechanical grinding. By embedding the sample within the copper tube, it was possible to maintain the brittle blister area intact during this process. Conventional twin-jet electro-polishing cannot be applied because of the different polishing rate between alloy matrix and hydride blister. Therefore, ion milling was used to prepare an electron transparent area within the blister from the embedded sample, using Ar ions in a Gatan PIPS II machine. The PIPS II is equipped with two Penning ion guns with 500 μm beam size and adjustable sample stage to align the blister area for milling. The rough milling was done at 4 keV, 6° tilt angle till the blister area developed optically observable serrated edges. Then the final milling consisted of two steps of first 0.5 keV and then 0.2 keV fine milling at 5° tilt angle for 10 min each. It has been proved that such low energy millings can significantly reduce the defects and artifacts induced by ions at higher energy [31]. This method successfully allowed preparation of TEM samples with a large thin area in the blister, suitable for conventional bright field & dark field (BF & DF) and HRTEM imaging.

The EBSD measurements were carried out with a Bruker detector and ESPIRIT software on an FEI NanoSEM. The specimens were mounted onto a 70° pre-tilt holder, and the microscope used an accelerating voltage of 20 kV and 15 mm working distance. Multiple maps were acquired for both TD and RD normal samples; in the alloy matrix, in the matrix-blister transition region, and within the blister. This allowed observation of the hydride microstructure and characterization of ORs between hydrides and parent α grains. TEM characterization was carried out with a FEI Tecnai Osiris S/TEM, operated at 200 kV.

4. Results

4.1. EBSD results for TD-normal sample

In order to survey the distribution characteristics of hydrides from the alloy matrix, across the blister boundary and into the blister, a large EBSD map was acquired on the sample with TD normal. Fig. 2 (a) shows the EBSD map of grains colored according to their orientations. From the (0002) α-Zr pole figure, shown in Fig. 2 (c), the grains with their prism planes' normal close to the sample normal are of green and blue color while the grains that have their basal plane normal close to the surface normal are of yellow, pink and red color. The phase map is shown in Fig. 2 (b); all the hydrides are indexed as δ-hydrides. It can be seen that hydrides distribute non-uniformly as thin platelets in the alloy matrix, elongated along the RD direction. The volume fraction of hydrides