Structural deformation of metallic uranium surrounding hydride growth sites

Christopher P. Jones [a],*, Thomas B. Scott [a], James R. Petherbridge [b]

[a] Interface Analysis Centre, University of Bristol, 121 St Michael's Hill, Bristol BS2 8BS, UK
[b] AWE, Aldermaston, Reading, Berkshire RG7 4PR, UK

ARTICLE INFO

ABSTRACT

Electron backscatter diffraction (EBSD) was utilised to probe the microstructure of uranium metal in the vicinity of surface corrosion pits, resulting from hydrogen exposure (5×10^4 Pa, at 240 °C). Microstructural analysis of the surface revealed a subtle increase of grain orientation variation for grains at the border of the hydride growths. Cross sectional analysis, at pit sites, revealed significant microstructure deformation in the form of crystal twinning and micro-cracking beneath the surface. These observations provide qualitative evidence that local stress intensities generated as a consequence of hydride growth and confinement, were sufficient to cause deformation within the parent metal.

Crown Copyright © 2015 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Uranium is vulnerable to corrosion by environmental gases that may lead to material degradation, shortened lifetimes, alteration of mechanical properties and ultimately material failure. This is particularly apparent in the case of corrosion by hydrogen where the primary reaction product, hydride (UH_3), is both pyrophoric and has significantly lower density than the metal at room temperature (10.95 g cm^{-3} and 19.1 g cm^{-3}, respectively). Consequently, a fundamental understanding of the corrosion process at all stages is of critical importance.

Typically, it is observed that, at a given temperature, the reaction proceeds when the metal is exposed to H_2 at a pressure which exceeds the equilibrium pressure of the metal hydride (UH_3). This leads to a direct solid–gas interaction in which the metal is converted to the hydride. Initial reaction takes the form of discrete hydride nucleation sites forming across the metal surface [1,2]. With continued corrosion these sites are reported to grow and ultimately coalesce, forming an encompassing film of hydride, prone to spallation as a fine pyrophoric powder [3–5]. The arising powder has been characterised as UH_3 using X-ray photoelectron spectroscopy [6] and X-ray diffraction [3].

Many published studies have primarily focused on measuring the kinetics of the reaction, i.e. the rate at which reaction sites nucleate or the overall rate of reaction [2,7–17]. However, advances in surface analysis techniques have allowed the influence of bulk and surface properties of uranium metal to be investigated. Thus, hydride site initiation has been correlated with metallic defect sites such as grain boundaries, scratches, inclusion (carbide) particles, and crystal twins [1,5,6,18–26].

Indeed, previous studies reported by the current authors have indicated that material in which there is a high surface concentration of carbide inclusion particles (i.e. 575 inclusions per mm^2 for uranium with a carbon concentration of 600 ppm) exhibit a marked preference for hydride forming reactions to occur at these inclusion sites [19]. However, in the case of high purity uranium in which the surface concentration of inclusion sites is much lower (i.e. ~20 inclusions per mm^2 for material with a carbon content of <100 ppm) nucleation of hydride formation sites is predominantly observed at metal grain boundaries [1,24]. These observations would seem to suggest that inclusions provide a more favourable location for hydride reaction to initiate, as compared to metal grain boundaries, and that the latter only become significant when the former are present at very low concentrations.

Such observations are consistent, to some extent, with a model in which the surface oxide layer present on the uranium metal surface presents a barrier that hydrogen must breach in order to reach the underlying metal [4,27]. For instance, inclusions exposed at the metal surface interrupt the overlying uranium oxide layer and could thus provide express pathways for hydrogen diffusion, as suggested by Harker et al. [19]. However, the precise causes for the preferential hydride nucleation observed at inclusions and grain boundaries are still to be discerned.

Although a number of studies have been reported [11–13,15], the exact details of the mechanism by which a hydride reaction site

grows into the surrounding uranium metal still remains uncertain. What is clear is that once a hydride reaction site has nucleated and expanded to such an extent that the surface oxide layer is breached, the growth rate of the site increases dramatically. Partially, this is ascribed to the diffusion of hydrogen through the hydride at an established reaction site being far more rapid than the diffusion through the surface oxide layer (as required for the nucleation of a new site).

In conclusion, it can be stated that, a number of outstanding questions remain related to the underlying causes of the reported preferential hydride site growth at metal grain boundaries and inclusion particles. In addition, the mechanism by which these sites grow is still yet to be fully understood. Therefore, the primary goal of the current research was to provide a better understanding of the initial stages of hydrogen corrosion on uranium surfaces by identifying and investigating any structural changes occurring in the metal surrounding hydride growth sites. Specifically, the following work investigated how the stresses generated by hydride growth are accommodated by the surrounding microstructure of the metal, both at the metal surface and within the bulk. This was achieved using new focused ion beam (FIB) surface preparation techniques suitable for successful EBSD analysis of large scale (>10 μm) hydride growths. The as received samples were annealed in order to promote both grain growth and the relaxation of the residual internal stresses present in the material, thereby generating a cleaner, simpler, microstructure prior to hydriding. Also, it should be noted that in order to minimise the possible influence of carbide inclusions on observed hydride site nucleation the current work used uranium material with a low carbon content (<100 ppm).

2. Experimental

2.1. Initial surface preparation and subsequent formation of hydrides

Sample coupons (10 mm square, ~1 mm thick) were obtained from rolled depleted uranium feedstock with a grain size of ~15 μm. Chemical analysis of samples from the same source [28] yielded impurity levels for carbon, aluminium, iron, silicon and chromium of ~50, 22, ~5, ~2 and ~2 ppm (by weight), respectively. These samples were annealed under UHV conditions (<1 × 10^{-4} Pa) at 550 °C for 9 days in order to minimise residual internal stresses and promote grain growth. The annealing of the high purity metal was invoked to provide a material with few crystalline defects and low residual stress upon which to observe orientation changes induced by controlled hydride growth. The samples were prepared in the open laboratory by wet mechanical polishing. Samples were sequentially abraded using Buehler SiC paper of increasingly fine grade to P4000 grit, producing a 2–3 μm surface finish. Samples were then lapped using 1 μm diamond paste in an argon filled glovebox, rinsed and washed clean using research grade ethanol prior to electropolishing. The aim of the electropolishing step was to remove the majority of surface topographical anomalies, such as microscratches, thus reducing the number of possible preferential nucleation sites. The process used an electrolyte solution consisting of a 10:6:6 ratio by volume of research grade ethanol, orthophosphoric acid (85%) and ethylene glycol, respectively. The electrolyte was contained within a stainless steel beaker (acting as a cathode) and a variable voltage was applied to maintain a current of 0.2 A. The samples were electropolished for 5 min, rinsed in absolute ethanol, passivated by a short immersion (2–3 s) in the unbiased electrolyte, rinsed again in ethanol then air dried using a blower system.

The samples were then immediately gasket-sealed into a half-inch diameter stainless steel Swagelok vacuum cell with built-in thermocouple. The cell was evacuated to a pressure lower than 5 × 10^{-4} Pa and subsequently heated to (and maintained at) 75 °C for 12 h duration to drive off adsorbed water from the sample surface. The cell was then heated to the desired reaction temperature of 240 °C where it was maintained for 2 h to reach thermal equilibrium, and drive off any residual surface adsorbed water, prior to the introduction of hydrogen gas. Purified hydrogen (from a lanthanum–nickel hydride bed) was added to the reaction cell and a section of the rig (72.6 cm^3 total volume) at a pressure of 5 × 10^4 Pa. Upon sealing this volume, the gas pressure was monitored to observe the onset of hydride formation and halted (by evacuation of gas via a rotary pump) after a 500–1500 Pa drop was recorded, equivalent to reaction of approximately 1% of the sample. Samples were then allowed to cool to room temperature under UHV conditions before precursory analysis.

Microscopy confirmed that the resulting samples had undergone limited hydride formation with a low number (<30) of hydride nucleation sites observed across the entirety of the coupon's surface. The fully formed hydrides were observed to range in surface diameter from 35 μm to 120 μm (Fig. 1). Assuming that the growth sites all share a similar growth rate, the observed range in hydride size indicates that the growths did not initiate simultaneously during the hydrogen exposure.

2.2. Mechanical cross-section and preparation for EBSD analysis

EBSD analysis of the hydride inclusions was conducted both at the surface of the uranium and on a mechanically prepared cross-section through the hydride (and surrounding metal). For surface investigation of the metal microstructure, electropolishing (30–60 s duration) was conducted following the procedure described in Section 2.1. This etched ~10 nm of material, removing any surface formed oxide layer whilst leaving the morphology of the hydride growth sites ostensibly unaltered. The resulting sample surface was uniformly smooth, enabling microstructural characterisation via EBSD analysis to be performed.

However, the use of EBSD to probe the sub-surface metal surrounding the hydride growth sites required sufficient sample material to be removed in order for the backscattered electrons to reach the detector without reabsorption. This was achieved by first mechanically sectioning a hydride coupon adjacent to a hydride site. The cut surface was then gradually abraded back, using P1200 grade SiC paper, until the hydride site was intersected. For both the sample surface (in the case of lateral growth investigation) and the cross-section face (for a vertical, subsurface, investigation), the uranium metal adjacent to the hydride growth site was prepared for EBSD analysis via the same process described in Section 2.1, culminating in electrochemical etching. Fig. 2 shows a hydride crater after electropolishing the newly exposed face. The metal grains surrounding the pit are clearly visible from the SEM image due to differential channelling contrast caused by variation in crystallographic orientation.

For detailed subsurface investigation of the uranium metal in the immediate vicinity of the hydride growths, focussed ion beam (FIB) milling was required because the electropolishing process had preferentially etched the fine features from the hydride–metal boundary (regions of high localised current density are generated around protruding artefacts on the sample surface). FIB milling was performed using a FEI FIB-201 with a liquid gallium ion source operating at 30 kV with the maximum available probe current (11 nA), and the beam skimming at 90° to the exposed surface. This produced a high quality surface for EBSD analysis, albeit in a limited area adjacent to the hydride growth.