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The effect of work-hardening and thermal annealing on the early stages of the uranium-hydrogen corrosion reaction

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ABSTRACT

The characteristics of hydride formation on metallic U at the early stages were investigated for three differently treated samples. The first sample reacted in its as-received state, the second was thermally annealed and the third sample underwent cold work-hardening prior to reaction with deuterium. From the analysis, the vacuum heat-treated sample was found to be more resilient to hydriding at the nucleation and growth stage, exhibiting a reduced number of nucleation points when compared to the as-cast uranium. The work-hardened sample was observed to be more susceptible to H_2 corrosion, displaying very dissimilar hydriding behaviour when compared to the other.

1. Introduction

Hydrogen corrosion of metallic U may occur during various stages of the nuclear fuel cycle, however, it is predominantly observed to occur during waste disposal [1–3]. The formed corrosion product, uranium hydride (UH_3), is a highly pyrophoric and unstable substance and, therefore, classed as a potential hazard due to the potential for enhanced radionuclide release and dispersion of gas/solid fission products arising from the spent nuclear fuel (SNF) material (fire, smoke containing fission products, etc.) [4,5]. The reaction can be described by four distinct stages:

i. The induction period (Initial hydrogen adsorption).
ii. The nucleation and growth period (Discrete UH_3 sites form and grow).
iii. The bulk reaction period (Adjoining UH_3 sites create a reaction front that engulfs the surface and progresses inwards consuming the U metal).
iv. The termination period (Complete transformation of U to UH_3).

Prior to the bulk reaction stage, the rate of which is mainly governed by the conditions of the surrounding environment [6–15], the nucleation and growth stage occurs in a spot-wise manner where hydrides begin to form and grow at certain regions of the metal surface [16]. These regions are assumed to act as low energy points where hydrogen molecules can quickly and easily physi-sorb, chemisorb, dissociate and reach the metal surface to react [16]. The nucleation and growth period is rapid and far more complex than any other stage of the uranium-hydrogen system. There are a number of factors controlling the nucleation rate and density of the UH_3 formation, along with the topography and morphological characteristics of the hydrides [16–26]. Increasing oxide thickness has a diminishing effect on the hydride nucleation rate and density [21]. However, this results in larger and more developed hydrides [21]. An impure reactant gas (H_2, D_2, etc.) would eventually cause the nucleation number density to shrink, owing to the competition between hydrogen and other diffusing entities (CO, O_2, N_2, H_2O) on the existing sorption sites [18]. Saturation of the available sorption sites for hydrogen may appear if the level of surface and/or oxide impurities prior to the reaction is significant [21]. The pressure and temperature of the reaction determine the flux of hydrogen (H_2) from the gas phase to the metal [27]. Thus, the rate of nucleation will increase exponentially with temperature up to the maximum value where hydriding is conceivable ($\sim$260 °C), provided that H_2 pressure is adequate [27]. However, the nucleation number density is finite for certain conditions, since the solubility of hydrogen in uranium is solely controlled by temperature and metal microstructure [17]. Temperature may also affect the location of hydriding initiation and growth to a certain extent [22,28,29]. Working on early stage hydriding of a well-annealed depleted uranium sample at the high-temperature regime ($\geq$240 °C), Scott et al. [22] found that hydrides nucleated mainly across high misorientation angle grain and twin boundaries, forming chains instead of distinct spots [22].

The surface characteristics, including the metal microstructure, play the most dominant role with respect to the location of hydriding initiation and the overall hydriding behaviour at the early reaction stage [20,22]. Strain on the surface manifested as scratching lines, or a work-

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hardened layer, is either a result of mechanical abrasion during experimental preparation or as a result of stripping off coating material, such as Magnox from a spent nuclear fuel rod, in a real-world scenario. Surface strain typically affects the hydriding behaviour and morphology of the hydrides [30,31]. Very recent work by Banos et al. [30], working on natural uranium samples prepared using mechanical abrasion, revealed that it is the level of surface strain that controls hydriding parameters such as nucleation rate, density and location of the hydrides. Additionally, for chemically etched and strain-free surfaces, the microstructure was deduced to control the population and location of surface-formed hydrides [30]. Complementary work on natural uranium, by employing electron back-scattered diffraction (EBSD) to map a partially hydrided uranium surface, was undertaken to evaluate and quantify the effect of the various characteristics of metal microstructure on UH_3 site initiation [32]. From analysis of the electropolished and partially hydrided surface, it was established that more than 90% of the observed UH_3 sites formed around grain and twin boundaries [32]. From both these works, it was concluded that when a work-hardened layer is present on the surface, discontinuities in the microstructure which are also reflected as discontinuities in the superficial oxide, act as preferential sites for UH_3 nucleation and growth [30,32]. However, for a more pristine surface, it is the metal microstructure and grain/twin boundaries, which exert a greater control on the abundance and location of the forming hydrides [30,32]. Therefore, if the grain boundary length is diminished (grain growth) and the level of internal stresses are reduced (annealing), it is expected that a pristine surface will exhibit fewer preferential points for successful initial hydrogen attack. Likewise, on a surface with a well-developed work-hardened layer, surface strain and an increased grain boundary length, developed through slip twinning, is expected to strongly influence early hydriding behaviour.

This work was focused on comparing and evaluating the early hydriding characteristics of three samples that have undergone various treatments prior to reaction, to create comparable differences in surface strain. To achieve this, the first uranium sample was reacted in its as-received state (as-cast), while the second sample was thermally annealed to relieve strain imbued during fabrication, whilst also encouraging grain growth. The third sample was deliberately cold-work polished to induce a superficial work-hardened layer of significant thickness. All three samples were loaded into the same cell and reacted together to ensure identical reaction conditions.

2. Experimental

2.1. Sample characterisation

Unirradiated natural uranium metal, prepared as fuel rod material for Magnox reactors, and used in previous works [30,32], was used for the study. Table 1 displays the composition of the metal, as determined by energy dispersive X-ray (EDX) analysis. The main impurities in the metal were C, N, O, Al, Si and Fe. C, N and O impurities were considered as over-estimated owing to (a) carbon deposition from residual hydrocarbon disintegration by the action of the electron beam and (b) the ubiquitous presence of a surface oxide film, and (c) amplification of the signal coming from the low mass elements (over the heavy elements), for low accelerating voltages [33–35]. Preliminary scanning electron microscopy (SEM) inspection of the surface revealed carbides and carbo-nitrides of varied morphology. The samples exhibited a high carbon content with approximately 820 ± 270 carbides/mm^2 on the polished surface; the mean diameter of the carbides was estimated to be 7 ± 4 μm (Fig. 1a). The carbide number density was found to change across the samples, with regions close to the edge of the original fuel bar exhibiting a higher number density than regions corresponding to the centre-line. This variation is generally well accepted to occur as an unavoidable part of the fabrication process.

Table 1
Level of impurities detected through energy dispersive X-ray (EDX) analysis of Magnox-U. 1.

Element	*Impurity level in (wt%)*
U	88.15 ± 1.32
C	12.37 ± 0.81
N	1.94 ± 0.20
O	1.73 ± 0.87
Al	0.20 ± 0.06
Si	0.06 ± 0.04
Fe	0.00 ± 0.37

Metal grains with linear variation in size and random orientation were developed during the initial casting and subsequent β-quenching of the material. This fabrication process also resulted in internal stress development which was manifested as multiple slip planes and twin boundaries between the grains (Fig. 1b). Three square samples of the same weight, shape and surface area (~0.45 g, 4.6 × 4.6 × 2 mm) were cut from the virgin Magnox-U metal by employing a Struers accutom cutting machine. This process was expected to cause some surface mechanical disruption to the cut surfaces of the samples.

2.2. Sample treatment

Following mechanical sectioning, three distinct treatment methods were employed to induce different levels of internal and external strain on the surface.

Sample 1: As-cast uranium. The first sample was used in its as received state (as-cast uranium).

Sample 2: Thermally annealed uranium. The second sample was loaded into a stainless steel cell with silver-coated copper gasket seal and heat-treated under high vacuum (5×10^{-7} mbar or 5×10^{-5} Pa) at 550 °C for 140 h. Following annealing, the cell was left to cool to ambient temperature under vacuum over a 20 h period. The annealing encouraged grain growth and recrystallisation, which has been found to initiate at temperatures as low as 450 °C [19]. This heat treatment also led to relief of residual mechanical strain present as a result of the manufacturing process [19].

Sample 3: Work-hardened uranium. The final sample underwent cold work-hardening using Buehler silicon carbide grit papers to produce a coarse finish (P320, 46 μm) followed by finer finish (P600–P1200) to produce a work-hardened layer of significant thickness (3–6 μm, Fig. 2b). Fig. 2a & b present focused ion beam (FIB) cross-sectional views of the as-cast uranium and the work-hardened sample. It is evident that the thickness of the disrupted layer owing to mechanical damage is increasing while the level of strain along this layer is multiplied.

Fig. 3a–c show the EBSD maps of each sample surface. To produce a surface pristine enough for EBSD mapping, the samples were mechanically polished down to a ¼-μm surface finish and electrochemically etched, using a solution containing a 10:6:6 (volume ratio) mixture of ethylene glycol, orthophosphoric acid and absolute ethanol, with an applied voltage of 10–11 V and a flowing current of ~0.1 A for less than 1 min. Consequently, the samples were loaded separately into the FIB and the surface was sputtered using a beam current of 2700 pA for ~10 min at an incident angle of 7° to the surface, in order to reveal the metal microstructure. On the as-received sample (Fig. 3a), multiple grains and twin boundaries of various sizes were clearly identified. Fig. 3b presents the EBSD map of the thermally annealed sample. It is evident that some grain growth has occurred on the surface, along with considerable strain relief, manifested as a reduction in the density of crystal twins present. The work-hardened surface exhibited a greater number density of twin boundaries when compared to the other two surfaces, along with significant damage leading to splitting of the large grains to smaller sub-grains (Fig. 3c). Fig. 4 demonstrates the spread of the grain size (in area fraction) for all three mapped surfaces. From the figure, it can be seen the as-cast uranium surface exhibits grains of