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The effect of sample preparation on uranium hydriding

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ABSTRACT

The influence of sample cleaning preparation on the early stages of uranium hydriding has been examined, by using four identical samples but concurrently prepared using four different methods. The samples were reacted together in the same corrosion cell to ensure identical exposure conditions. From the analysis, it was found that the hydride nucleation rate was proportional to the level of strain exhibiting higher number density for the more strained surfaces. Additionally, microstructure of the metal plays a secondary role regarding initial hydrogen attack on the highly strained surfaces yet starts to dominate the system while moving to more pristine samples.

1. Introduction

Radioactive intermediate level wastes arising from the UK civil nuclear programme, including reactive metals such as uranium metal and Magnox cladding have continually been accumulating for up to 60 years. Due to the constantly increasing amount of this material, there is an urgency to underpin the safety of the oldest wastes by better understanding their physicochemical state. This knowledge also supports future retrieval and repackaging of selected wastes, better preparing them for long-term storage and disposal. Uranium hydride (UH_3) formation is a potential yet unwanted corrosion occurrence indirectly resulting from wet oxidation [1]. The highly unstable nature of UH_3 when exposed to air [2] raises serious environmental and technical challenges with respect to the safe handling and treatment of these by-products should they have formed.

From the literature [3], it is well known that the uranium-hydrogen reaction can be divided into four distinct stages:

i) An induction period where initial hydrogen adsorption occurs. This period extends from the time of hydrogen exposure to when the first nuclei appear on the metal surface.
ii) A nucleation and growth period where discrete UH_3 sites begin to form and grow (Accelerating stage).
iii) A bulk reaction where coalescence of the hydride sites results in a homogeneous reaction front moving into the surface (Linear stage).
iv) A termination period where complete transformation of the metal to UH_3 is observed (Decelerating stage).

It has been observed that the initial transformation of uranium to UH_3 occurs in a spot-wise manner and usually at preferred locations on the metal surface which encourage physi-sorption, dissociation and diffusion of hydrogen gas (H_2) [4]. These are referred to as low energy diffusion and trapping sites.

There have been many studies concentrated on deriving the uranium-hydrogen reaction rates under various environmental conditions, therefore the linear stage of the reaction has been thoroughly studies [5–14]. However, the initial reaction phase, where rates are accelerating rapidly is far more complex due to the many factors effecting hydride spot initiation and growth [4,15–23]. It has thus proven much more challenging to examine. According to the literature, common parameters such as the induction period, the nucleation rate, the hydride growth and the location of the hydrides are influenced by a number of factors [4,15–23]. To initiate the uranium-hydrogen reaction, hydrogen has to diffuse through a naturally occurring oxide layer covering the metal surface and nucleate at the metal-oxide interface [24]. The induction period is extended with increasing oxide thickness [19]. Additionally, the purity and stoichiometry of the growing oxide controls the initiation time and

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the nucleation density of the hydrides [19]. This is because impurities are considered to block potential sorption sites and diffusion pathways to the metal [19]. The purity of the reactant gas was also found to prolong the induction period owing to the competition of impurity entities (O_2, H_2O, N_2, CO_2 etc.) with H_2 on the available sorption sites [16]. Another important factor, which effects the early hydriding stage, is the reactant gas pressure and temperature [3]. Elevated pressures and temperatures were found to shorten the induction time [3]. However, the temperature effect is far more pronounced providing that the experiment temperature is close to where maximum hydriding rates are observed ($T = 160–250\,^{\circ}C$) and hydrogen is abundant in the system [15]. The nucleation density, which is defined as the number of growing nuclei per mm^2, is finite for every sample and depends on the solubility of hydrogen in uranium and the metal microstructure [15]. Since the diffusivity of hydrogen is enhanced with increased temperature, it is expected that higher temperatures will increase the nucleation rate providing there is a constant H_2 supply [15]. Indeed, experiments by Scott et al. [20] demonstrated very significant nucleation rates at the highest temperature range for hydriding, forming chains of hydride rather than individual spots.

The metal microstructure plays a key role on the nucleation number density and location of hydride growth [18,20]. Dislocations such as crystallographic slipping planes and twins formed through the fabrication process, along with grain boundaries, provide low energy locations for hydride nucleation and growth [18]. It has been documented that the microstructure of the metal surface is sometimes reflected in the growing oxide; therefore strained or disrupted regions in the metal will appear as discontinued areas on the oxide surface due to the unevenness of the growing oxide [18,25]. In addition, different oxidation rates have been recorded between metal grains with different crystal direction [25]. The heterogeneity of the oxide thickness leads to induced stress in-between the oxide boundary interface [18]. A similar effect has also been observed at the perimeter of inclusion sites, with an additional source of strain for these areas coming from the different thermal expansion (considerably higher melting point of carbide phases) between the inclusion (UC, UCN and UC_2) and the metal [26]. Thus, it is expected that grain and twin boundaries along with inclusions and other strained regions will be reflected as areas of oxide disruption. Discontinuities in the oxide facilitate hydrogen ingress to the metal, thus promoting on-site nucleation [18]. The above considerations lead to the assumption that a pristine and strain-free surface with large crystallographic grains will provide fewer points of initial hydrogen attack when compared to a strained surface exhibiting small grains, providing both have similar average oxide thickness. Indeed, grain and twin boundaries [15,20,24,27–29] have been identified as early nucleation and growth sites by some investigators and inclusions were also reported as initiation locations by others [4,18,28,30,31].

It is believed that the interplay of the above factors control the very early hydriding behaviour of uranium metal. Previous studies in the literature have provided indications that strain in the metal or oxide may encourage early initiation of hydride growth [32] but none has yet provided substantial and definitive proof [4,18]. Following this hypothesis, it was decided to examine the influence of sample cleaning preparation, thus the effect of the conditions at the surface, on uranium hydriding at the early stage. Sample preparations involving mechanical abrasion will cause a work-hardened layer to form in the outermost region of the metal surface [24]. The thickness of this layer will depend on the level of the grinding medium used and the mechanical force applied during abrasion [24]. As an alternative, chemically driven processes, which involve metal removal by means of acid dissolution or electrochemically driven anodic dissolution, may produce near pristine surfaces [22,28]. Nevertheless, surface features such as inclusion particles are significantly disturbed [22] and the composition of the growing oxide may be altered [28]. Little attention has been given by investigators on this matter, despite the numerous different sample preparation techniques been employed by various groups prior to the hydriding reaction [4,17,19,20,22,28,30,33]. Table 1 summarises the experimental conditions previously used in the available published literature for the uranium-hydrogen reaction. To compare between studies, information such as sample origin, hydriding conditions and cleaning preparation in addition to post-reaction surface examination are included in the table. It is evident that despite similar experimental conditions (temperature and pressure) [17,20,22,24,30,33], the growth behaviour of UH_3 differs between research groups, which may be attributable in part, to the sample preparation procedure. Of course, subtle dissimilarities in the metal microstructure [4,22,28,30] or the grown oxide [4,19,28] may also be responsible for these discrepancies. In an effort to isolate and focus on the effect of cleaning preparation on uranium hydriding behaviour, four identical samples originating from the same metal coupon were concurrently prepared using four different methods. These samples were reacted together simultaneously such that the temperature, hydrogen exposure time and pressure were identical for each sample, therefore the only variables effecting the hydriding reaction was the condition of the metal surface i.e. level of strain and oxide thickness.

2. Experimental

2.1. Sample characterisation

Unirradiated natural uranium prepared for Magnox fuel was used for the study. The traditional casting method for Magnox-uranium production was to β-quench the cast uranium rods by heating to 660–700 °C and rapidly cooling to room temperature. Electron back-scattered diffraction (EBSD) analysis on the uranium showed a randomly oriented microstructure with multiple grains exhibiting a linear variation in size (Fig. 1). Grain texture indicates plastic deformation as a result of stresses developed during the fabrication process. The anisotropic thermal properties of uranium combined with the manufacturing process will have caused considerable internal stresses, this is demonstrated by the existence of multiple slip planes, and twin boundaries throughout the crystallographic structure (Fig. 2a). The samples exhibited a high carbon content with an average of 1045 inclusions per mm^2 on the polished surfaces (Fig. 2b). Inclusions, usually carbides, of various shapes (X-shaped, H-shaped, cuboid) and sizes (2.5–17 μm in dia.) were spread homogeneously on the surface. Four samples of the same weight and surface area (0.45 g, $\sim 0.8\,cm^2$) were cut from the same uranium penny using a Struers Accutom cutting machine. This process was expected to induce some localised surficial strain at the cut surface from mechanical disruption caused by the cutting blade.

2.2. Surface preparation

After cutting, the four square-shaped samples were mechanically abraded on all sides to a 2–3 μm surface finish (P4000) using silicon carbide papers and water as a lubricant. The samples were then cleaned with water to remove excess debris and four different cleaning preparation methods were employed:

2.2.1. Coarsely finished sample

This sample was stored in an inert atmosphere (Ar-filled glovebox) whilst the other three preparations were employed. When the others were near completion a final re-abrasion to a 2–3 μm finish was achieved.