



# The effect of thermal pre-treatments on the nucleation of uranium hydride



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## ARTICLE INFO

### Article history:

Received 28 January 2016

Received in revised form 18 May 2016

Accepted 24 May 2016

Available online 5 June 2016

### Classification codes:

A8160 corrosion, oxidation and surface treatment

A8265N other gas-surface interactions

### Keywords:

Actinide alloys and compounds

Metal hydrides

Gas–solid reactions

Corrosion

## ABSTRACT

Uranium hydriding experiments are reported in which samples experienced a single thermal cycle within the range of 35 °C to 75 °C, before undergoing reaction with hydrogen at a pressure of 110 mbar. Under equivalent reaction conditions, elevated nucleation kinetics were observed for samples that had been thermally cycled prior to hydrogen exposure, as compared to samples that had not been cycled. These observations have been rationalised in terms of two alternative hypotheses based on i) the anisotropic thermal expansion of uranium leading to disruption of the surface uranium oxide overlayer during cooling of the experimental samples or ii) differing levels of water present on the oxide overlayer following pre-treatment.

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## 1. Introduction

Clean uranium will readily react with hydrogen to form uranium hydride, a finely divided, black powder which is highly reactive and pyrophoric under atmospheric conditions [1]. Therefore, there are considerable technical and safety issues that arise due to the formation of uranium hydride.

The uranium–hydrogen reaction can typically be characterised by four distinct stages; an induction stage (no measurable reaction), a growth stage (discrete hydride sites initiate and grow), the bulk reaction stage (coalescence of these discrete sites into a continuous hydride layer that then grows into the bulk) and the termination stage (total consumption of either the metal or gas). Of these, the bulk reaction stage has been studied in detail and the associated kinetics and rates of reaction have been well defined [2–5]. In contrast, the parameters affecting the induction and early growth stages have received relatively little attention. Specifically, the length of this induction period has been shown to depend on a variety of different factors, these include the characteristics of the surface uranium oxide layer present on the uranium metal [6–9] and the presence of gaseous impurity species in the hydrogen [10–12]. Furthermore, the early stages of hydride reaction

site initiation and growth have also been studied in relation to properties of the uranium metal, e.g. the presence of alloying elements [13–15] or defect sites such as grain boundaries, scratches, inclusion (carbide) particles, and crystal twins [8,16–25].

Under most practical conditions, a surface layer, consisting of oxides, hydroxides and carbides, covers the surface of bulk uranium samples [11]. It was first noted by Spedding et al. [6] that the removal of such an overlayer caused a decrease in the length of the observed hydriding induction period. On the other hand, Owen and Scudamore [7] reported that longer exposure times to air prior to exposure to hydrogen resulted in a generally less reactive surface characterised by longer induction times and fewer hydride reaction sites initiated after any given time. Subsequently, Harker [9] carried out a study in which the influence of the mean thickness of oxygen-grown  $\text{UO}_{2+x}$  films on the magnitude of the initiation times of uranium hydride sites was investigated, demonstrating a correlation between overlayer thickness and the initiation time observed for hydride reaction sites.

To develop an understanding of the initial stages of the uranium hydriding reaction it is necessary to study the intrinsic factors influencing the induction and growth kinetics of reaction sites. Previously, Bazley et al. [26] demonstrated that using a controlled sample preparation and drying pre-treatment (75 °C, 16 h, in vacuo), minimised the observed variability in induction behaviour for a series of experiments in which samples were reacted at a temperature that was either equal to or higher than the pre-treatment temperature of 75 °C. The effect of

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the heating treatment was attributed to the partial removal of water from the surface of the samples studied.

Using a similar approach to Bazley et al. reproducible measurements of hydride site initiation and growth behaviour have been made. However this current study has explored the influence that a cycled thermal pre-treatment has upon the initiation and growth kinetics of uranium hydride sites.

## 2. Experimental

### 2.1. Sample preparation

All depleted uranium samples used in this study were obtained from cold-rolled stock and measured approximately 12.7 mm × 12.7 mm × 1.5 mm. The carbon content of the samples was <100 ppm. Sample preparation was carried out as previously reported [26], i.e. visible surface oxide was removed from all surfaces by mechanical abrasion to 600 grit (equivalent to a 15 μm finish), before the sample was transferred into a stainless steel reaction cell incorporating a window allowing one face of the sample to be observed. The cell was evacuated precisely 25 min after polishing of the final (observable) face of the sample was completed, typically reaching ~10<sup>-7</sup> Torr within 4 h.

### 2.2. Heating pre-treatment

Samples then underwent one of five pre-treatments, while being maintained under a dynamic vacuum, as summarised in Table 1. Standard samples underwent a single pre-treatment stage consisting of heating (16 h) at either 38, 58 or 75 °C (i.e. Pre-treatments 1–3 in Table 1). Additional samples underwent a two stage pre-treatment consisting of heating at 77 °C for 16 h (Stage 1), followed by cooling to either 57 or 35 °C (Stage 2) and are thus described as thermally cycled (i.e. Pre-treatments 4–5 in Table 1). Fig. 1 presents plots of reaction cell temperature and pressure for a standard pre-treatment at 38 °C (Fig. 1.a) and a thermally cycled sample, i.e. heated to 77 °C then cooled to 35 °C (Fig. 1.b). These two thermal treatments illustrate the two extremes of the conditions investigated in the present study and correspond to Pre-treatments 1 and 5, as given in Table 1, respectively.

### 2.3. Hydriding

Hydrogen exposure was carried out using the procedure previously described [26], i.e. under a constant hydrogen pressure of 110 ± 10 mbar supplied from a LaNi<sub>5</sub>H<sub>x</sub> bed. The initiation time of an individual hydride reaction site (i.e. the *n*<sup>th</sup> site) was defined as the time of the first image captured in which the site was visible (diameter greater than 30 μm), i.e. *t<sub>n</sub>*. Thus, the total number of visible hydride sites (*N*) was measured as a function of time. From this, the induction time of an experiment was defined as the time at which the first site became visible on the sample surface, i.e. *t<sub>1</sub>*.

Following the conclusion of the experiment, the radial growth rate (*V<sub>r</sub>*) was determined for a given site using the final site radius and the site growth duration (e.g. for the *n*<sup>th</sup> site, total hydrogen exposure time minus *t<sub>n</sub>*). For each experiment, a mean site radial growth rate was determined using measurements from a number of sites (typically

~20). This was achieved by either determining the gradient of a linear fit to a plot of site radii versus time or from the mean of the individual site growth velocities.

## 3. Results

### 3.1. Nucleation behaviour

The nucleation behaviour of uranium hydride sites is depicted by the profiles shown in Figs. 2 and 3, which plot the variation in the number of reaction sites (*N*) visible on the sample as a function of time (*t*). The nucleation profiles can be described by the power-like trend discussed previously by Bazley et al. [26], although there are significant differences between the initiation behaviours of the thermally cycled and standard samples.

Thermally cycled samples were found to display significantly enhanced nucleation kinetics compared to standard samples reacted at equivalent temperatures. To demonstrate that the enhancement observed was not a consequence of experimental variance, duplicate experiments were performed. It was found that although some variance in initiation behaviour was apparent between nominally identical experiments the enhancement observed for the thermally cycled samples was far greater than the experimental variance. In addition, duplicate experiments were found to yield consistent *N* vs *t* profiles.

Fig. 2 presents the nucleation profiles for the thermally cycled and standard samples reacted at a nominal temperature of 35 °C. The thermally cycled samples exhibited faster nucleation kinetics than the standard samples, with both a shorter time to the onset of reaction (i.e. induction time *t<sub>1</sub>*) and a higher rate of subsequent reaction site initiation. The induction time is particularly helpful in demonstrating the difference between thermally cycled and standard samples reacted at 35 °C. The first site appeared on the thermally cycled samples after 950 and 2273 s, whereas the onset of reaction on the standard samples was significantly longer (i.e. 16,769 and 28,528 s). It is also evident from Fig. 2 that cooling from a pre-treatment temperature of 77 °C to a reaction temperature of 35 °C results in an *N* vs *t* curve that is similar to that obtained for a standard pre-treatment at 75 °C.

Further initiation profiles are presented in Fig. 3 depicting the behaviour of standard and cycled samples reacted at a nominal temperature of 58 °C that corroborate the enhanced initiation kinetics of uranium hydride reaction sites on thermally cycled samples. The time to the initiation of the first site (*t<sub>1</sub>*) for the thermally cycled samples being 1146 s and 3190 s, whereas the standard samples initiated the first site after 6813 s and 11,572 s.

The difference in *t<sub>1</sub>* times between the samples reacted at a nominal temperature of 58 °C (i.e. 58 °C for standard and 57 °C for cycled pre-treatments) is less marked than that exhibited for samples reacted at a nominal temperature of 35 °C (i.e. 38 °C standard and 35 °C cycled). This observation may indicate that hydride site initiation behaviour could be influenced by the temperature range over which the sample is thermally cycled (i.e. thermally cycled samples heated to 77 °C and reacted at either 35 °C or 57 °C experience drops in temperature prior to reaction of 42 °C and 20 °C, respectively).

### 3.2. Hydride site radial growth rate (*V<sub>r</sub>*)

The radial growth velocity (*V<sub>r</sub>*) of uranium hydride sites has been determined for the cycled and standard samples reacted at nominal temperatures of both 35 °C and 58 °C. It has been observed in these experiments that thermal cycling does not influence the growth rate of reaction sites. For example, Fig. 4 presents measurements of the final measured radii of a number of hydride reaction sites plotted as a function of sites growth duration. Data is presented for two samples reacted at a nominal temperature of 58 °C, one a standard sample and the other thermally cycled. Mean site growth rates have been determined, from the gradient of linear variation in radii as a function of site

**Table 1**

Summary of heating pre-treatments undertaken. Samples were maintained under dynamic vacuum during all stages of treatment.

Pre-treatment	Description	Stage 1	Stage 2
1	Standard	Hold at 38 °C for 16 h	
2	Standard	Hold at 58 °C for 16 h	
3	Standard	Hold at 75 °C for 16 h	
4	Thermally cycled	Hold at 77 °C for 16 h	Cool to 57 °C over 3 h
5	Thermally cycled	Hold at 77 °C for 16 h	Cool to 35 °C over 6 h

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