

The effects of metal surface geometry on the formation of uranium hydride.

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Abstract

The present work examines the effect of surface geometry on the reaction between hydrogen gas and uranium metal, forming uranium hydride (UH_3), a pyrophoric compound of significance to the civil nuclear industry. Hydride formation was initiated on uranium samples that had been patterned with a focused ion beam instrument to form surface arrays of triangular prisms and pillars with differing apex angles. Post reaction analysis indicated preferential hydride formation at the apex of these features. Additionally, once hydride formation had commenced the observed growth rate on the prisms appeared to accelerate in comparison to the rate exhibited on the [Agreed, apologies for the poor wording structure] surrounding surface.

Key words: uranium, hydride, geometry, local strain distribution.

Introduction

Under favourable conditions¹, uranium and hydrogen react to form uranium hydride (UH₃); a fine black dispersive powder that is potentially pyrophoric in air [1]. The uranium-hydrogen reaction usually commences after a period of induction followed by nucleation of individual nuclei specifically located at sites on the metal surface which favour diffusional transport of hydrogen through the overlying uranium oxide layer to the metal (referred to as spot locations) [2,3]. If enough hydrogen is available to sustain the reaction, spot locations will grow laterally (parallel to the metal surface) and eventually coalesce to form a continuous layer across the entire surface of the metal. As the reaction progresses, the reaction front at the metal-hydride interface will propagate into the metal as a ‘contracting envelope’ function, before entirely converting all available uranium metal to hydride [4,5]. The kinetics, mechanisms and morphology of both the initial and bulk reaction are considered to be dependent on principally two controls; the environmental conditions in which the metal exists (e.g. temperature, hydrogen pressure and purity) [6,7] and secondly the metallurgical characteristics of the uranium itself (e.g. inclusions, oxide layer thickness and grain boundaries) [2,3,7,8]. In addition, the rates and thermodynamics of the bulk U-H₂ reaction have been thoroughly researched in the literature across a range of temperatures and pressures. For example, hydride formation rates on electrically heated uranium wires exposed to a fixed volume of hydrogen, showed a rate increase with temperature up to 225°C, after which the rate decreased again as the reverse de-hydriding reaction increasingly competed [9][10]. Furthermore, using automated gas buret techniques, it was determined that the uranium-hydrogen reaction exhibits a decreasing pressure dependence with increasing hydrogen pressure, which will eventually

¹ Temperatures of 0-500°C and hydrogen pressures of 0.001-100 bar [9].

become independent once the hydrogen pressure exceeds the absorption equilibrium pressure [10,6]. The theory of why this behaviour is observed has not yet been determined [11]. However, the initial stages of the reaction namely, during and immediately after the induction period are still poorly defined [5,12].

It is generally accepted that the preliminary stages of the U-H₂ reaction are surface mediated [10,13,14]. In practice, a surface passivation layer (SPL) consisting of oxides, hydroxides and water, ubiquitously covers the surface of the uranium metal [10]. This acts as a barrier for hydrogen diffusion to the metal [15], but at points where the SPL is weakest e.g. oxide fractures, a direct and preferred route for hydrogen migration, dissociation and chemisorption at the metal surface is provided [16]. Furthermore, the barrier provided by the SPL will also behave as a confining layer to encourage hydrogen accumulation at the metal-SPL interface. Hydrogen atoms diffusing through weaknesses in the oxide layer are forced to dissolve into the metal rather than laterally along the metal/oxide interface, as adjacent substitution sites are occupied by oxygen atoms. In time, the hydrogen concentration will exceed that required to saturate the metal and begin UH₃ nucleation [10]. The rate of uranium hydride formation has been observed as a decelerating parabolic curve, transforming to an 'S' shaped curve at lower temperatures [12,17]. The initial time delay preceding the reaction observed in the latter scenario is named the induction period and at low temperatures (up to 225°C), this time period is considered as the rate limiting step of the U-H₂ reaction. The delay in the reaction is attributed to the time it takes for hydrogen to diffuse through the SPL and into the metal, up to the point of visible UH₃ nucleation [12].

To assist our understanding of the early U-H₂ reaction, recent investigations have focused on factors influencing the initial spot sites of UH₃ nucleation, as these locations exhibit reduced induction periods in comparison to the bulk metal [7]. For example, impurities in the hydrogen gas such as O₂ and CO, or preparation techniques using Ga (as found in this investigation),

have been observed to prolong the induction period for UH_3 nucleation [10,17,18]. These species may reduce the diffusion of hydrogen through the SPL by preferentially occupying sorption and dissociation sites, consequently adding to the effect of the SPL [8]. Alternatively, the SPL may emulate heterogeneities found on the metal surface, weakening and fracturing the layer to create direct hydrogen diffusion pathways to the metal, thereby decreasing the induction period [7]. Such heterogeneities may include mechanically damaged locations e.g. scratches [3], inclusion particles [2,3], and grain boundaries [4,7]. In this study, the effects of uranium surface topography have been examined; these have only been briefly mentioned previously in the literature but have practical implications [12].

For instance, in the civil nuclear industry, intermediate level wastes (ILW) containing metallic uranium are encapsulated in grout and stored in stainless steel canisters for long term (in excess of 100 years) storage [19]. In open environmental systems, i.e. where oxygen and water vapour are present, neither UH_3 nor H_2 are observed as persistent products of uranium corrosion [20]. Instead, oxide formation acts as the dominant corrosion mechanism [21]. However, in physically confined conditions where uranium is detained in spaces which are designed to limit the transport of gaseous species inside and outside the system, UH_3 may form [19,22]. This may be particularly the case of uranium which is in contact with water-filled grout pores, together with other reactive, hydrogen generating metals/alloys like aluminium or Magnox. If this scenario were to occur, the subsequent transport and handling of such material will support a greater risk of a thermal transient event (due to the pyrophoric nature of the UH_3) than if it were not there.

Uranium present in such ILW has usually undergone some degree of mechanical processing e.g. decanning from Magnox cladding through dyes, which may result in the uranium exhibiting an irregular, striated topographical surface at multiple scale lengths; micrometers to millimetres [19]. Hence, the purpose of this study was to artificially create regions of

topographical variation on a flat uranium surface to examine the effects of H_2 exposure influenced by topographic anomalies. We have used focused ion beam (FIB) milling to generate arrays of triangular prisms and conical pillars as our topographic anomalies. The location and rate at which hydride formed on these structures were compared to the surrounding flat uranium surface. Using D_2 as a more reliable tracer than H_2 (this was repeated on three samples with incrementally greater quantities of D_2), permitted successive samples to generate a time (and uptake) resolved sequence. Magnetic sector secondary ion mass spectrometry (SIMS), secondary electron microscope (SEM) and FIB imaging were used to identify and locate uranium deuteride (UD_3) sites formed across the surface of the metal. Hereafter we will refer to the deuteride as hydride, assuming that they exhibit identical chemical behaviour.

Experimental

Three uranium metal samples, originating from the same unirradiated Magnox fuel ‘penny’, were all prepared using the same method. Each sample was initially mechanically abraded using water and sequentially finer grades of SiC grit grinding paper to a 4000 grade. After this, the samples were immediately rinsed and cleaned with acetone and methanol for 5 minutes in an ultrasonic bath. A Helios Nanolab 600i combined electron and ion dual beam system was then used to mill an array of four triangular prisms with apex angles of 17° , 28° , 34° and 45° approximately into the surface of the metal. A spacing of 20-40 μm between structures was selected to prevent the possibility of deposition on adjacent prisms during etching (pre-corroded prisms are displayed in Figure 1(a-e)). Each triangular prism was initially milled as a cuboid using a bitmap function with the focused ion beam (FIB) at a beam current of 20 nA and energy of 20 kV. The cuboids were then etched at 2.7 pA, 16 kV using grazing angles of 5° , 10° , 15° and 20° respectively to form the triangular prisms. Each prism was approximately 30 μm in horizontal length.

After prism development, a 2kV etch using a beam current of 6.6 nA was performed for 30 seconds at a magnification which covered $300\text{ }\mu\text{m}^2$ over the entire area of the prisms, pillars and surrounding surface to remove the majority of the gallium implanted into the metal during milling [23,24]. This step proved to be extremely important, as gallium ion implantation was observed in precursory experiments to significantly increase the induction period for the onset of UD_3 formation in areas treated by the FIB. Therefore to contrast the UD_3 induction period and formation on the flat surface versus the prisms, this step was necessary. However, this treatment does not remove all gallium (as seen later in Figure 4), and therefore UD_3 nucleation on the prisms was only compared to nucleation sites on the immediately adjacent flat areas and not the entire surface of the metal.

After the samples were prepared using the ion beam, the samples were removed from the dual beam and left in air to oxidise for 2 hours, allowing a relatively uniform layer of oxide to form across the metal surface, including the pillars and prisms. Each sample was then reacted separately with D_2 in a specialist gas rig system. To do this, the 316 stainless steel cell containing the sample was evacuated to $\sim 5 \times 10^{-9}$ bar and heated to 220°C for 1.5 hours using a clam shell furnace before a fixed pressure of D_2 (0.5 bar) was exposed to the entire surface area of the sample. Precursor tests were conducted to verify that D_2 leakage was below detectable levels. Therefore, a recorded drop in pressure during D_2 exposure of the metal was assumed to result from UD_3 formation. Knowing the volume of the reaction cell the recorded pressure drop could be converted to mols D_2 consumption. To examine the progressive stages of the U- D_2 reaction, each sample was allowed to react with incrementally more D_2 ; 12, 22, and $30\text{ }\mu\text{mol}$.

To compare the hydriding behaviour of different surface topographies and irregularities, an array of pillars was milled from a sample surface which was later reacted with $12\text{ }\mu\text{mol}$ of D_2 .

The pillars were constructed using circular bitmap functions with a FIB instrument at a beam current of 20 nA and 20 kV accelerating voltage. The pillar array underwent exactly the same ion beam treatment as the prisms to remove excess Ga. Pre-corroded pillars are displayed in Figure 1(f-j) and each pillar was approximately 32 μm from base to tip and the angle at the tip of each pillar $\sim 18^\circ$.

Post reaction analysis of the reacted samples was performed using the Helios nanolab instrument. To confirm the presence of UD_3 on the surface of the metal, a magnetic sector secondary ion mass spectrometer (SIMS) was used in positive ion mode to provide analysis. The mass peaks at 238.15, 240.18, 242.14, 253.92, 255.92, 261.8, 269.64 and 271.6 Daltons were identified as best reflecting the developed U^+ , UD^+ , UD_2^+ , UO^+ , UOD^+ , UC_2^+ , UO_2^+ and UO_2D^+ ions and clusters respectively (Figure 2).

Results

Examination of the prism arrays after D_2 exposure showed, as expected, a gradual increase in the volume of UD_3 formed with increasing durations of D_2 exposure (Figure 3). The local area surrounding the prism sites displayed considerably fewer UD_3 spot sites in comparison to the bulk surface of the metal (Figure 4(a)); attributed to the residual influence of gallium ion implantation after the low kV FIB cleaning etch. These areas are presumed to have comparable concentrations of Ga to the prisms and pillars since they were only contaminated by brief FIB imaging rather than extended milling or etching. Therefore, for the remainder of this article, these flat locations will be used for comparison against the irregularly structured arrays.

On comparison of the prisms with different pitches, it was observed that when reacted with increasingly more D_2 , the lowest angled (most pointed) prism tips commenced UD_3 nucleation faster than the high angled prisms, i.e. the induction period increased as the prism pitches verged towards a flat surface (Figure 3). For example, after 12 μmol of D_2 uptake, only the 17°

prism tip had undergone transformation to UD_3 and in this case, UD_3 growth was sufficient to cause significant rupture of the protective uranium oxide layer (Figure 3(ai)). Some slight indication of UD_3 initiation was also observed on the 28° and 45° angled prism surfaces at this stage. Upon exposure to greater amounts of D_2 , however, the 45° angled prism was the last to initiate UD_3 nucleation out of the four samples. In comparison to the prisms, the surrounding flat surface exhibited small 2-3 μm diameter spots beneath the oxide layer with a number density of ~ 137 spots per $100 \mu\text{m}^2$ (Figure 4(b)).

The pillars also present on this sample ($12 \mu\text{mol D}_2$) showed evidence of UD_3 formation (Figure 5). Figure 5(b-d) exhibits the pillars observed to be most affected by UD_3 . In all cases, the apex was the preferred location of nucleation, demonstrated by the vertical fracturing and eruption of UD_3 . However not all pillars exhibited this behaviour, with the majority not being effected at all, indicating that the geometry may not be the only factor influencing hydride formation.

After reaction with $22 \mu\text{mol}$ of D_2 (Figure 4), both the 17° and 28° angled uranium prisms had completely transformed into UD_3 and in the process had breached the surficial oxide layer (Figure 3(aiii) and (biii)). The latter prism exhibited a greater volume of UD_3 due to greater uranium availability in the body of the prism. Some fracturing of the 34° prism oxide layer was also observed at this stage of the reaction, attributed to the strain induced by the growing UD_3 beneath the oxide layer, although limited swelling was evident. Swelling may be reduced at these sites in comparison to a flat surface, because the geometry of the prism initially accommodates higher volumes of outward-growing UD_3 in comparison to a flat surface (i.e. more 'free' volume per unit surface area). No, or very limited evidence of UD_3 formation could be observed on the 45° prism, after exposure to $22 \mu\text{mol D}_2$. After exposure to the same amount of D_2 ($22 \mu\text{mol}$) the adjacent flat surface, exhibited UD_3 growths of 5-15 μm diameter, with a number density of 84 per $100 \mu\text{m}^2$ and evidence of some spots merging to make larger 20-25 μm diameter compound

growths. Some UD_3 sites had grown sufficiently to initiate rupturing of the overlying oxide layer. When sectioned (not shown), these sites were always located at single or multiple particle inclusion sites. Similarly behaved UD_3 sites not investigated by FIB sectioning also showed evidence of nucleation occurring at inclusion particles, as particles were often visible near the surface of the hydride.

By 30 μmol of D_2 sample uptake, all the prisms had progressed to the bulk reaction stage of UD_3 formation, indicated by fractured UD_3 erupting from each prism trench. The adjacent flat surface displayed a significant coverage of hydride (a spatial number density of 11 spots per $100 \mu\text{m}^2$), but the spots were generally confined beneath the oxide layer. Although extensive oxide fracturing was evident, the nature of these UD_3 sites lacked the eruptive nature exhibited by the UD_3 sites located over the prisms.

Discussion

The purpose of this study was to further expand our knowledge of the variables that exert influence over hydride nucleation and growth rates by comparing the length of the induction period (and therefore comparative initial rates) of UD_3 formation on a mechanically abraded smooth surface to an area of controlled topographical irregularity. The results presented here are a strong indication that the geometry of the prisms and pillars influences UD_3 formation. Firstly, it was observed that the induction period decreased with increasing pitch of the prism sides (as they became more pointed). Secondly, the UD_3 that nucleated on the prisms grew more rapidly and consequently ruptured through the oxide layer earlier than the UD_3 sites located on the adjacent smooth surface. It is believed that this behaviour was influenced by two factors: the high reactive surface area to metal volume ratio of the prisms and pillars compared to the flat surface, and the properties of the oxide layer (SPL) at such sharply angled locations.

In context of the current work, the apexes of the prisms and pillar structures represent zones of relatively high surface area to volume ratio because the bulk uranium metal is exposed to the D_2 gas via multiple metal surfaces, albeit overlaid by the SPL. For example, assuming a geometrically symmetrical prism structure, the surface area to volume ratio to a $5\mu m$ depth can be calculated. For each prism with apex angles of 17° , 28° , 34° and 45° , the surface area to volume ratios are 2.8:1, 1.7:1, 1.4:1 and 1.1:1. In comparison, for a relatively flat abraded surface with the same surface area as the 17° prism, a ratio of 0.2:1 is calculated.

Figure 6 presents a schematic diagram of an exaggerated deuterium accumulation beneath the SPL in different geometric scenarios. This model assumes a uniform stoichiometry and oxide thickness across the surface of all the prisms and, when exposed to an ample supply of D_2 , the diffusional flux of D_2 through the SPL is equal at all points on the surface, resulting in a linear diffusional flux. In addition, the geometric scenario is assumed not to provide any additional low energy diffusion pathways for deuterium (e.g. inclusions or grain boundaries). According to these assumptions, at any one time the depth and concentration of the diffused deuterium atoms into the metal would be equal at all points at the surface owing to a linear diffusive flux, except at the tips of the prisms represented by the red square in Figure 6. The concentration would be significantly greater at these locations, attributable to a large hemispherical flux in addition to the linear diffusional flux i.e. the prism tip is being attacked from two sides instead of just one, as for the rest of the surface. Provided that enough deuterium is available, the deuterium is forced to concentrate at a greater rate here, where the confluence of two diffusional fronts meet, than at the adjacent flat surfaces, causing saturation and UD_3 nucleation. This effect is greater in steeper sided geometries, as the faces accommodating diffusion are closer together and hence accumulation and concentration of deuterium is enhanced. On a flat surface, the accumulation of deuterium beneath the SPL would be equal across the whole surface.

It should also not be forgotten that the transformation of U to UD_3 results in a 1.75 times volume expansion. Bearing in mind that the metal at the tip of the prism is in tension and the overlying oxide is in compression, the UD_3 nucleating at the prism tips would be expected to rupture the oxide rapidly to expose the fresh UD_3 beneath, as shown in Figure 3. The subsequent growth rate of further UD_3 at these sites would then be expected to increase as UD_3 is reportedly a significantly better diffusion medium for D than the oxide [15]. Matured nucleation sites at these locations in comparison to the nucleation sites existing on the flat surface may be direct evidence for this.

In reality, the diffusion of deuterium through the oxide layer could not be said to be equal across the surface of the samples in this study. It is possible that grain boundaries, crystal twins and inclusion particles were present in the manufactured prism structures resulting in uneven oxide growth. These factors could not be controlled during the experiment, but the likelihood of them occurring decreased with the smaller angled and thus smaller volume prisms, which were the first to exhibit UD_3 formation and with repetition of experiments. However, the early nucleation of UD_3 on the 45° angled prism after 12 μmol uptake D_2 may be attributed to one of these factors (Figure 3(dii)).

In the present work, the extent of oxide layer development was controlled, but the nature of the growth at angled locations may have also contributed to UD_3 nucleation at the prism and pillar tips. As mentioned in the introduction, the integrity and thickness of the SPL largely contributes to the length of the induction period prior to the onset of hydride formation. Like uranium hydride, uranium oxides form at the metal oxide interface via an anionic diffusion mechanism and due to the geometry, thicknesses of oxide are probably greater at the tips of the prisms [15,25]. In controlled conditions on a smooth surface, oxide formation begins and grows at an initially parabolic and then linear rate whilst the oxide layer increases in thickness. Depending on the conditions of growth, compressional stresses from the uranium on the new voluminous

oxide at the metal-oxide interface will enhance strain in the overlying growing oxide layer. This is relieved by fracturing and spallation of the old oxide at the oxide-gas interface or part way through the oxide, termed ‘break away’ behaviour [15]. The magnitude of this effect is dependent on the oxidation rate and purity of the oxide and uranium [15,26,27]. The oxide then remains at a relatively constant thickness and linear rate of growth across the surface. SIMS depth profiling determined there was approximately 116 nm of uranium oxide on the smooth uranium surfaces (not shown), and the oxide can therefore be assumed to be in the linear stage of growth [22].

At the prism apexes formed in these experiments, the oxide thickness and integrity could be slightly altered by the geometry. In order to validate contributory mechanisms for the observed hydride formation behaviour, Finite Element (FE) modelling at the same scale was performed in order to determine the stress state of the metal resulting from the corrosion process. The FE model incorporated both the surface oxide layer and the underlying metal structure as shown in Figure 7. The output of the analyses was focused on the deformation of the metal using simulated heating to induce differential stresses between the oxide and metal. A 2D plane stress analysis revealed that the metal at the tips of the pillars is in tension relative to the rest of the structures and irrespective of the modelled oxide thickness.

This observation tallies well with numerous previous studies that have indicated that localised strain effects in the metal may be significant for promoting hydride formation and have recently been discussed in detail by Loui [28]. For example, recent density functional theory modelling studies by Taylor and Lillard [29] have investigated the interatomic penetration of hydrogen into uranium surfaces. Their study suggested that lattice diffusion of hydrogen into a defect-free metal surface is energetically unfavourable and diffusion was significantly lower than experimentally determined values. Subsequently, by varying the model lattice strain from compressive to tensile, it was theoretically determined that diffusion became significantly

enhanced and comparable to experimental studies [30–32]. Our modelling shows that such stress fields are likely to occur at the apex of our prisms and pillars, where hydrogen is accordingly expected to accumulate preferentially. Further work by Taylor and Lillard [33] has provided additional evidence in support of microstructure and stress as being truly important for controlling the location facilitating hydride formation on uranium surfaces. Their calculations demonstrated that the formation of UH_3 would become more energetically favourable in locations where the lattice could more readily expand to accommodate interstitial hydrogen i.e. surfaces, grain boundaries, vacancies and void spaces.

The FE model analysis showed that the oxide in these tip zones was under elevated compressional stress. It is possible that the geometric effects also caused accelerated oxide growth at the tips of the prisms and therefore fracturing and ‘break away’ behaviour would occur more readily. Consequently extensive oxide fracturing provided more low energy pathways for deuterium to reach the metal, instigating UD_3 nucleation. Heating of the sample during the experimental procedure may have also induced further oxide growth and fracturing by differential thermal expansion of adjacent crystals, however the heating was performed slowly under vacuum conditions (5×10^{-10} bar) and according to previous electron back scatter detection measurements on the same material which revealed grain sizes of 20-100 μm in diameter, the prisms would only have been sculpted over one or maximum two crystal grains of uranium. This effect was therefore considered fairly negligible considering the number of samples tested and demonstrating similar behaviour, although obviously cannot be ignored.

Comparatively rapid hydride development at the apexes of geometric irregularities such as prisms or pillars can be attributed to a combination of both the high reactive surface area to volume ratio and also the combination of compressional stress developing in the oxide and tension in the uranium metal prior to D_2 exposure.

These observations are significant, as they may partially explain other favourable hydride nucleation sites. For example, Scott et al., [7] observed that some grain boundary locations were preferred hydride nucleation sites over others. Furthermore, grain boundaries running at low angles relative to the surface were expected to favour hydride nucleation over high angled grain boundaries owing to a greater surface area of atomic order at the metal surface, assuming that the crystal orientation at the surface favoured chemisorption [7]. It is proposed here that the geometry of such low angled grain boundaries also provides high surface area to metal volume ratios for the formation of uranium hydride, in comparison to high angled grain boundaries oriented more perpendicular to the uranium surface (Figure 8(a)). The high reactive surface area does not necessarily require direct exposure to the reactive gas, but could also occur at low energy diffusion pathways such as grain boundaries. For example, both the oxide covered uranium surface and the grain boundary provide hydrogen diffusion pathways and constricting boundaries, thereby concentrating hydrogen at the acute angled apex (identified by the red dot in Figure 8(a)).

Likewise, impurities common in uranium such as carbo-nitride and carbide particle inclusions have been shown to promote surface hydride initiation in the metal around their margins. This behaviour may in part be attributed to fracturing in the oxide as a result of differential thermal expansion between the three phases: inclusion, metal and oxide [34]. If this is assumed to be the case, then again a high reactive surface area to metal volume ratio is created between the oxide (at the metal surface) and inclusion margin (identified by the red dot in Figure 8(b)). This effect would be further enhanced with clusters of adjoining inclusion particles, which are common in uranium used in the UK first-generation nuclear reactors (i.e. Magnox). For the inclusions there are many factors possibly at play to promote UD_3 formation. Here we suggest with evidence that geometry is one of them.

Conclusion

The work presented here highlights the importance of surface topography on the hydride formation behaviour of uranium. Geometric irregularities in the surface of the metal in the form of prisms and pillars (few 10s of μm in length) were constructed using FIB methods and then corroded in different quantities of deuterium gas (12-30 μmol) at a constant temperature of 220°C and pressure (0.5 bar). Prisms with steeper sides were observed to nucleate UD_3 earlier than those with more gently sloping sides, which was attributed to the locally increased surface area to volume ratio, possibly assisted by deleterious alterations of the oxide at these locations. A consequence of this behaviour was that the UD_3 prematurely ruptured the surface oxide layer and subsequently exhibited rapid growth rates. This has important implications for the nuclear industry, as processed uranium arising from fuel decladding is morphologically irregular and mechanically strained, which may make it more susceptible to hydride formation and corrosion in general, than previously estimated from tests on flat (e.g. abraded) samples. As a result, hydride formation rates derived from experiments using abraded or polished uranium coupons may be considered as underestimates when predicting hydride development in ILW packages containing uranium metal.

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Figure captions

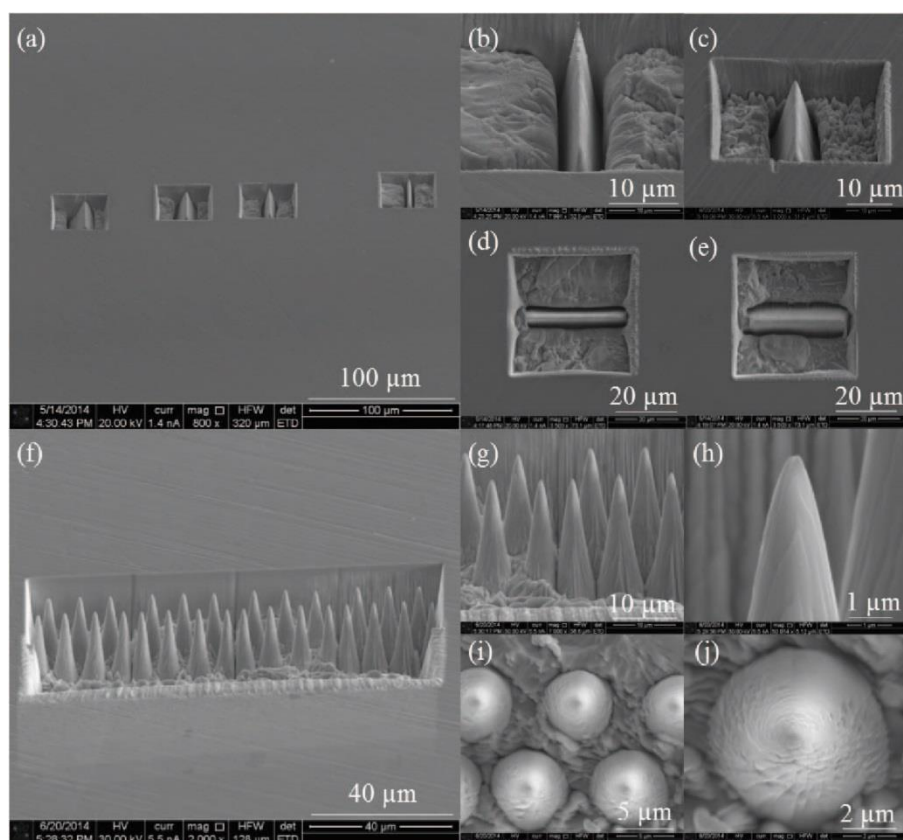


Figure 1. SEM images of the triangular prisms and pillars before exposure to deuterium gas. (a) Displays all four prisms against the comparatively flat mechanically abraded surface (4000 grit) and (b-e) shows the geometry of typical 17° and 28° angled prisms. All prisms are typically ~30 μm in length and increase in width from ~10-20 μm corresponding to the increase in angle, 17°-45°. (f) Exhibits the entire array of the pillars and (g-j) the surface of the pillars. Each pillar is approximately 32 μm in height, 7 μm in base diameter, with apex angles of ~18°.

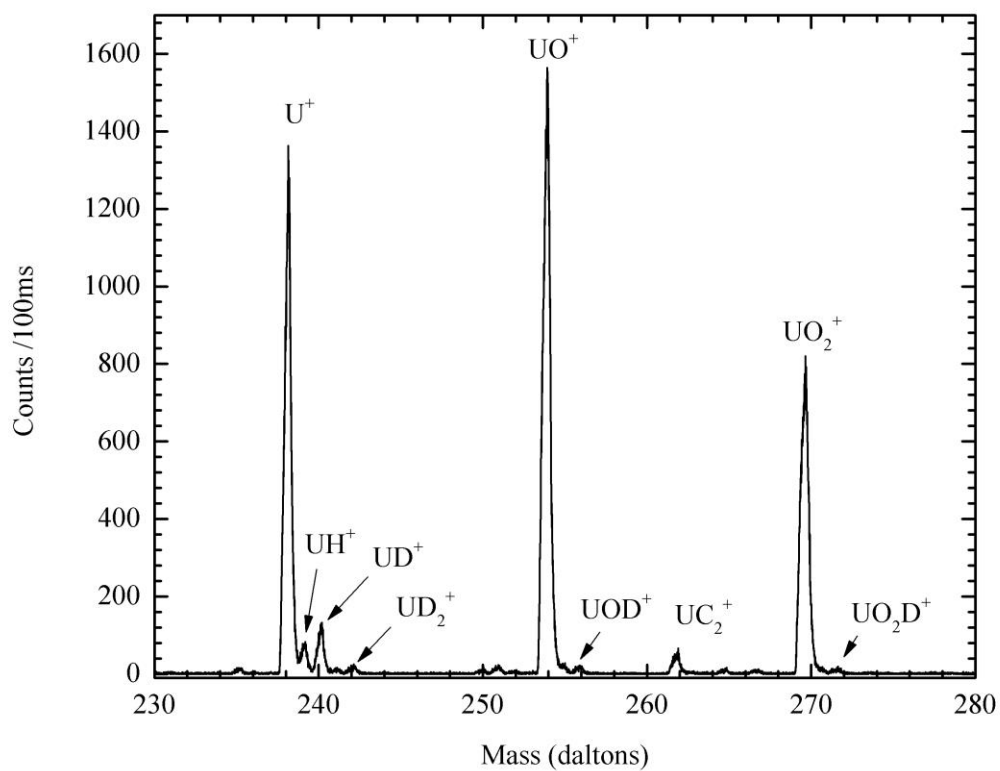


Figure 2. Positive secondary ion mass (SIMS) spectrum recorded over a $425 \mu\text{m}^2$ area using a 3 nA current over a region of the flat uranium surface of the $12 \mu\text{mol D}_2$ reacted sample. The resolution of the scan was too low for identification of individual isotopes of uranium metal.

Moles of D₂ reacted

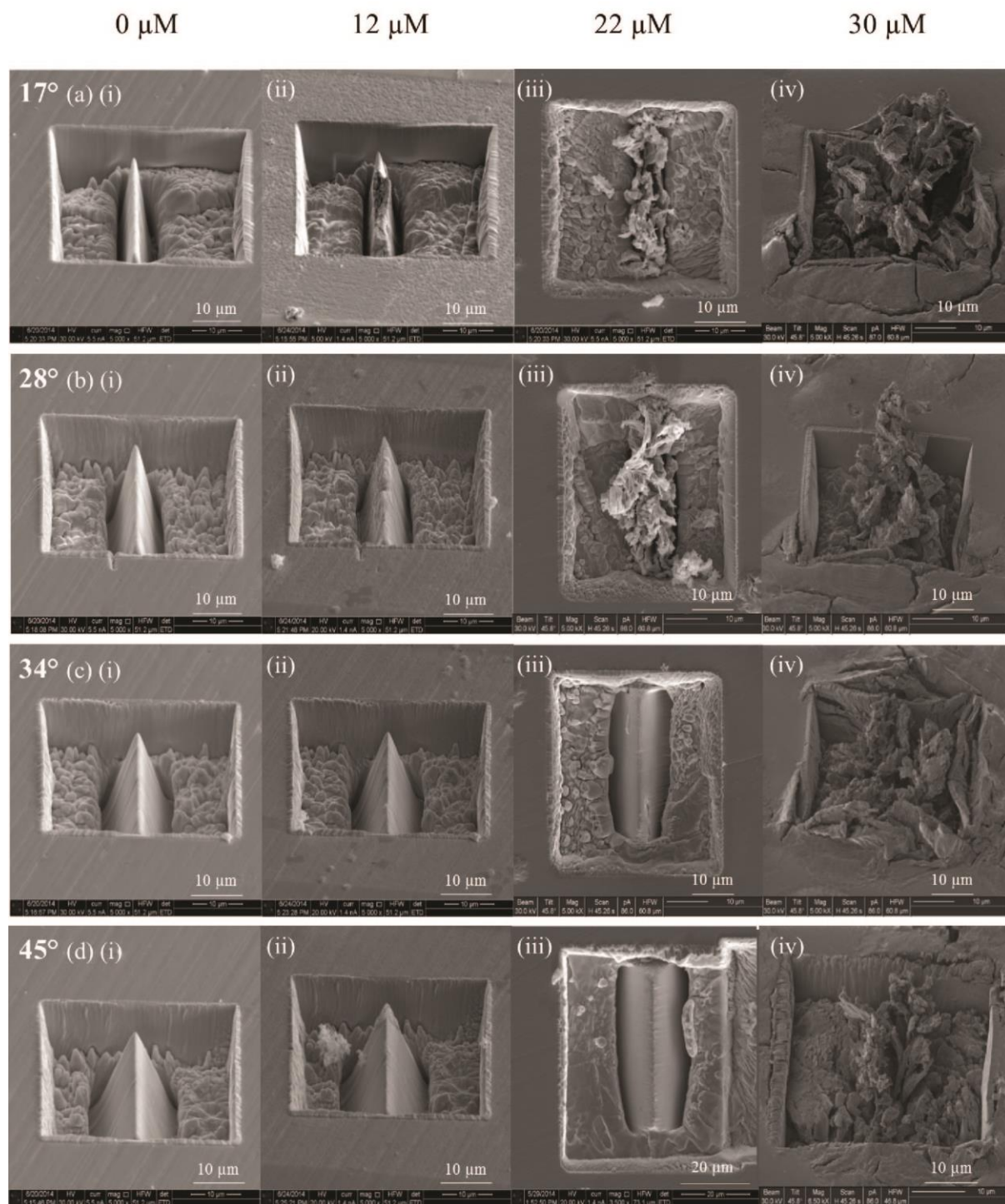


Figure 3. Images of the 17° (a), 28° (b), 34° (c) and 45° (d) prisms before (i) and after reaction with 12 (ii), 22 (iii) and 30 μ mol (iv) of D₂ gas.

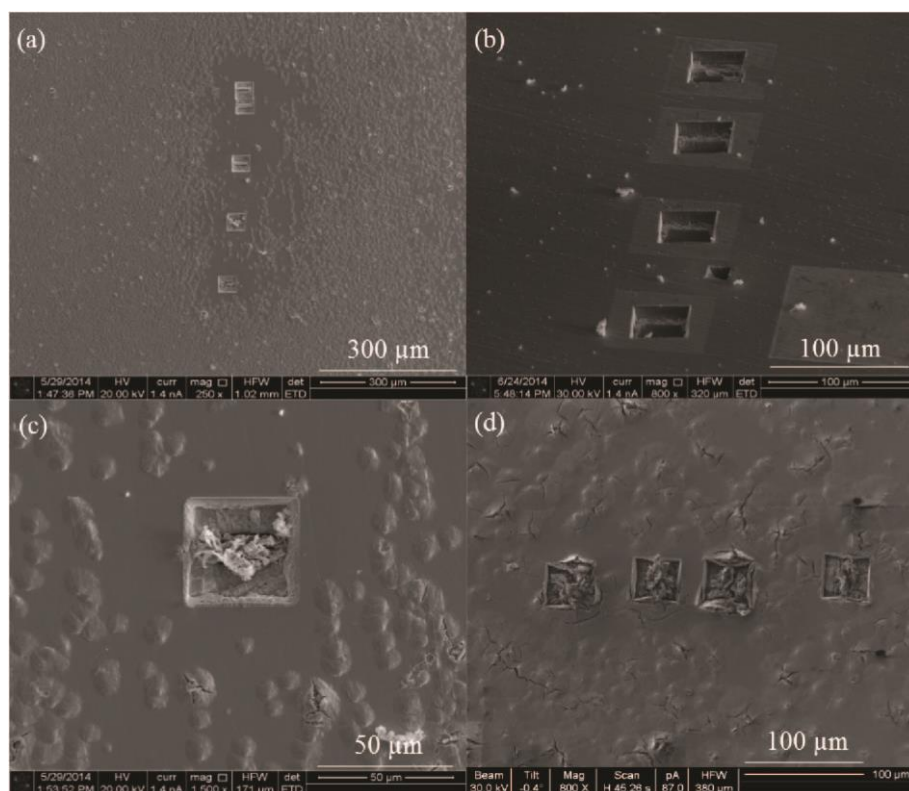


Figure 4. Image (a) shows the typical characteristics of the flat surface area surrounding the prisms, which was also effected by gallium ion implantation (22 μmol sample). (b) to (d) are the observed surfaces in these locations after reaction with 12, 22 and 30 μmol of D₂ respectively.

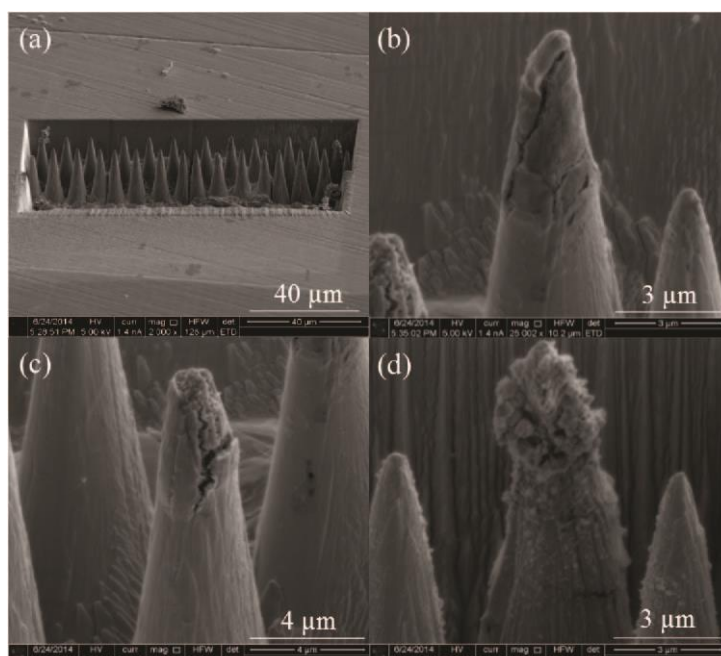


Figure 5. SEM images of the pillars after reacting with 12 μmol of D₂. (a) Shows the entire array and (b) to (d) individual pillars that have commenced UD₃ nucleation.

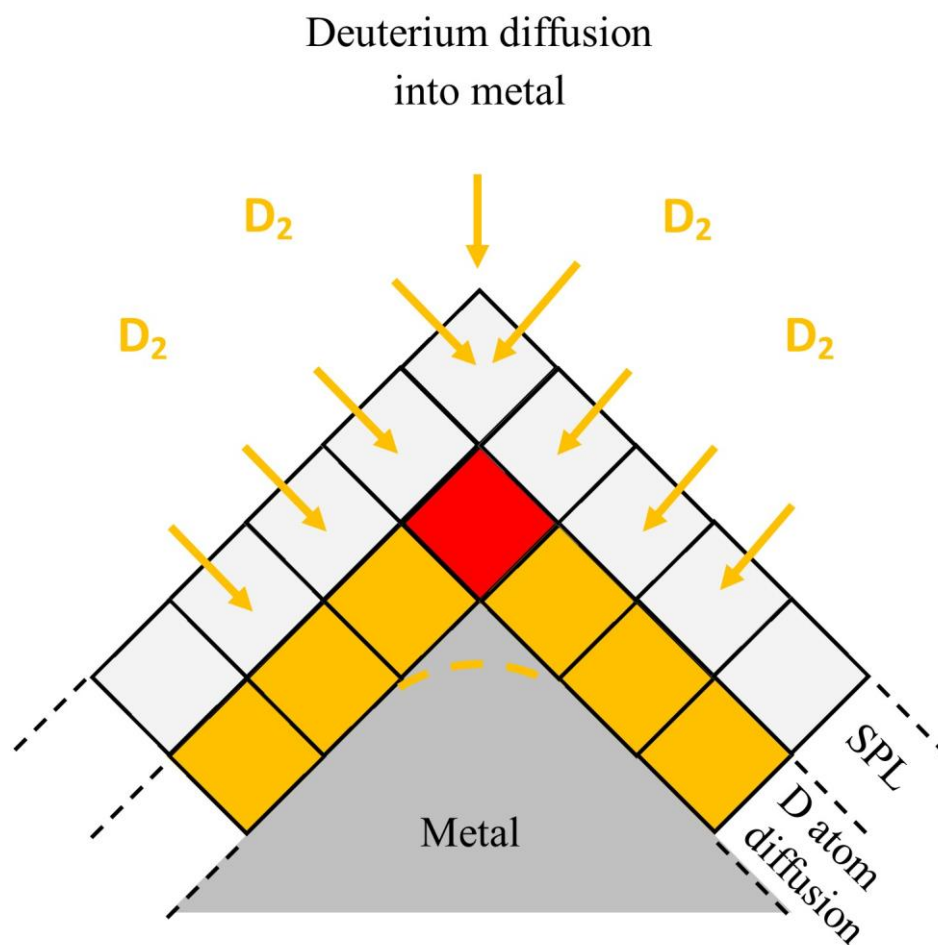


Figure 6. Schematic diagram of the idealised deuterium diffusion beneath the SPL layer.

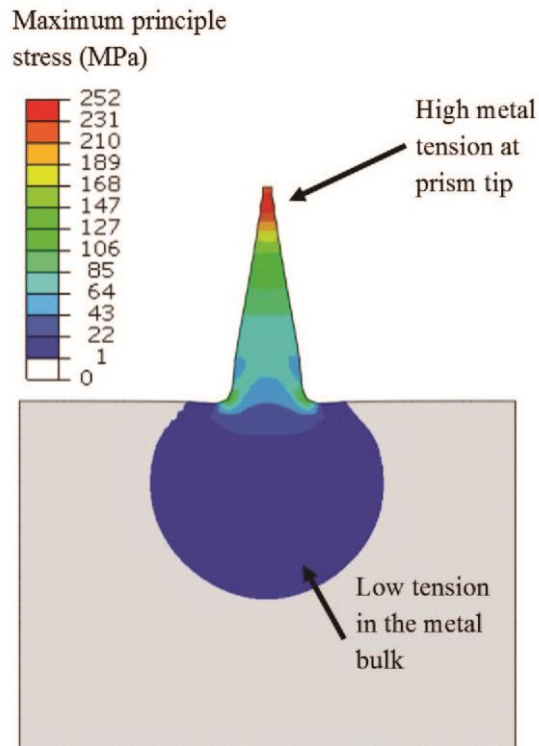


Figure 7. Finite element modelling showing the distribution of tensile stresses induced from the loading of a uniform oxide growth. The scale is represented in maximum principle stress (MPa); the red end of the colour spectrum indicates zones of high and blue low tensile stresses.

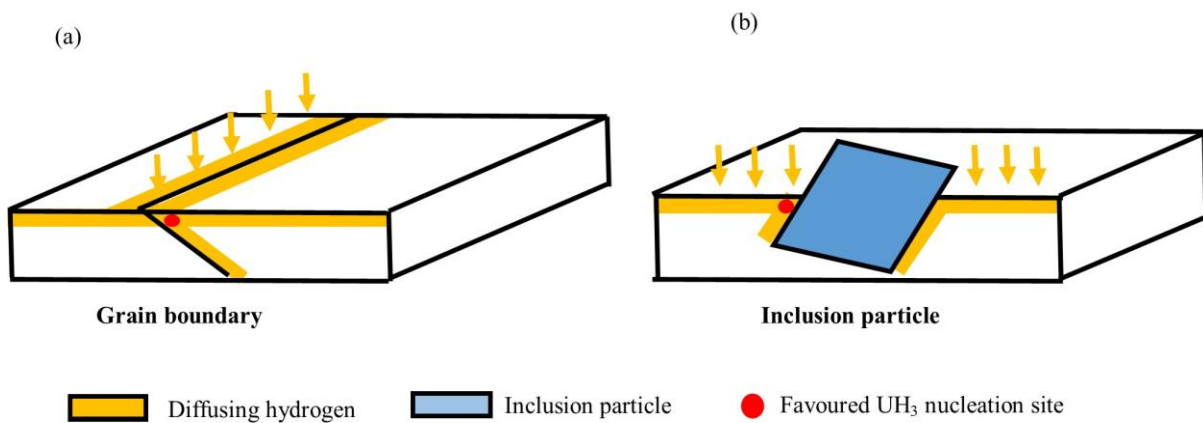


Figure 8. Schematic diagrams of exaggerated deuterium diffusion in (a) low angle grain boundary and (b) inclusion particle scenario.

Highlights:

- Geometrical prisms and pillar arrays were ion beam milled onto a uranium surface
- The influence of surface topography on uranium corrosion by hydrogen is demonstrated
- Prisms and pillars with low angled asperities were observed to nucleate hydride earlier than those with high angled
- Reactivity was attributed to the locally increased surface area to volume ratio and enhanced metal strain.
- Hydride formation rates derived from experiments using smooth uranium surfaces may be considered as underestimates for the reactivity of real wastes.