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Review

A review of uranium corrosion by hydrogen and the formation of uranium hydride

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ABSTRACT

Uranium hydride (UH₃) is the direct product of the reaction between uranium metal and gaseous hydrogen. In the context of uranium storage, this corrosion reaction is considered deleterious, not just because the structure of the metal may become significantly degraded but also because the resulting hydride is pyrophoric and therefore potentially flammable in air if present in significant quantity. The current review draws from the literature surrounding the uranium-hydrogen system accrued over a 70-year period, providing a comprehensive assessment of what is known about hydride formation, decomposition and oxidation in the context of uranium storage applications.

1. Approaches for research on uranium-hydride (UH₃)

Under the correct conditions, uranium and hydrogen readily combine to form a metal hydride (UH₃) in which the metal is transformed from an elemental to trivalent state and the hydrogen becomes chemically entrapped at high elemental density. Historically this reaction between metallic uranium and hydrogen gas (Eq. (1)) has been investigated from two different angles. Firstly, hydrogen corrosion of the metal and secondly, chemical storage of hydrogen, with historically, the former being the prime motivation for research.

\[ 2U + 3H₂ \leftrightarrow 2UH₃ \]  

1.1. Corrosion

When uranium is corroded by hydrogen, the formation of UH₃ results in the physical disintegration of the parent metal. Given that sufficient hydrogen is available, the reaction can be self-propagating [1,2] and occurs at a rate up to four orders of magnitude faster under similar conditions than the rate of uranium oxidation [3]. Such corrosion is deleterious regardless of the storage scenario and the resulting hydride is pyrophoric, which further adds to operational safety issues surrounding corrosion [4]. Accordingly, the prevention of metallic uranium corrosion by hydrogen is a key objective within the nuclear industry worldwide.

1.2. UH₃ potential uses and applications

The hydriding reaction (Eq. (1)) is reversible as the UH₃ decomposes upon heating to uranium metal and H₂ (as discussed in greater detail in Section 5). Thus, uranium can act as an efficient chemical storage material for hydrogen, holding up to almost twice the weight of the gas per unit volume as hydrogen in its liquid form [5]. From a hydrogen storage perspective, it is desirable for the reaction to be optimised in terms of speed, efficacy and repeatability [6,7]. Most recent research has demonstrated uranium as having good long-term performance as a chemical medium for the storage of hydrogen, with the added operational benefits of low hydrogen equilibrium pressure for absorption, low thermal mass and higher thermal conductivity in comparison to other chemical compounds and metals used for storage [8]. Uranium can, therefore, be used as an efficient hydrogen storage material [9] and is often the favoured storage medium for tritium handling facilities [5,10].

These two opposing drivers for research have resulted in a good but not comprehensive understanding of the U + H₂ system. More recently, the reactor research community has added to the list of interested parties for UH₃ research, investigating it as a candidate fuel material for future small modular nuclear reactors (SMRs) [11]. Such SMR concepts harness the effectiveness of H₂ as a neutron moderator with the fact it is evolved from UH₃ at high temperatures. This relationship between temperature and H₂ release creates a feedback loop (charge-discharge...
2. Fundamental properties

A large density difference exists between the hydride and the precursor metal (Table 1), meaning that UH3 is a non-protective, auto-brecciating reaction product. In such cases the hydride generally appears in a voluminous, finely divided black powder with high surface area [13] and like its particulate metallic counterpart, is highly reactive and pyrophoric under atmospheric conditions [14–16]. However, it is conceivable that this powder could be sintered to produce a near 100% density material [17] or to prepare monolithic hydride by other more advanced methods (e.g. reactive sputtering).

2.1. Crystallographic structure

Two phases of UH3 are known; α-UH3 and β-UH3 (Table 1) [20]. In both phases, each uranium atom is surrounded by 12 equidistant hydrogen atoms around the UII lie on: ± (0,u, ± 2u), ± (1/2, ± 2u,1/2+u) where u = 0:155. All α-UH3 has been observed to possess a primitive cubic lattice (Pm3n) with 8 uranium atoms per unit cell, of dimension 6.151 ± 0.001 Å for UH3 and 6.627 ± 0.001 Å for UD3, with the atomic position of the hydrogen atoms as y = 0.155 ± 0.016 Å and z = 0.303 ± 0.002 Å and deuterium y = 0.1556 ± 0.006 Å and z = 0.3041 ± 0.006 Å [21]. By simple calculation using the data from Table 1, it can be seen that the density of U but not β-UH3, allowing α-UH3 to form via spinodal decomposition in a hydrogen saturated metal to then act as nucleation sites for subsequent β-UH3 formation [28].

2.1.1. α-UH3

The following sections of this review examine the published literature which describes the physical and chemical properties of UH3, first focusing on the properties of the material, then the formation reaction, and finally the interaction between UH3 with its surrounding environment. This understanding is applicable across the spectrum of uses, with greatest importance for safe uranium storage.

2.1.2. β-UH3

Like with the α-phase, β-UH3 has been observed to possess a primitive cubic lattice (Pm3n) with 8 uranium atoms per unit cell, of dimension 6.643 ± 0.001 Å for UH3 and 6.627 ± 0.001 Å for UD3, with the atomic position of the hydrogen atoms as y = 0.155 ± 0.016 Å and z = 0.303 ± 0.002 Å and deuterium y = 0.1556 ± 0.006 Å and z = 0.3041 ± 0.006 Å [21]. By simple calculation using the data from Table 1, it can be seen that α-UH3 holds ≈ 1.01 times as much H2 as β-UH3 per unit volume. Also, according to theoretical data, α-UH3 contracts with applied pressure by 0.25 A²/GPa for low-pressure regimes [29] while for β-UH3 and for applied pressures up to 29 GPa a more modest 13% contraction may be observed [30].

The activation energy for the diffusion of hydrogen or deuterium into, α-UH3 and β-UH3 were found to be 35.1 ± 3.8 kJ mol⁻¹ and 37.2 ± 3.8 kJ mol⁻¹ respectively, for temperatures > 370 K [21]. Below room temperature, hydrogen readily exchanges between solid adsorbed H2 and the UH3 [31]. The rate of exchange between gas and solid, for environments of 70–700 kPa H2 between 25–400 °C, has been found to be controlled by the rate of hydrogen transport within ~ 0.7 μm diameter hydride particles [12].

At 100 °C, α-UH3 has been recorded as co-existing in a stable state with the β-phase but is totally converted to β-UH3 upon heating to 250 °C [20,26]. This is accompanied by a 1.7% volume expansion due to the density difference. The opposite transformation was not witnessed when the conditions were reversed [20,27]. Thus, the hydriding temperature and any thermal excursions that occur during confinement directly influence the form of the hydrogen corrosion product that persists. The heat of formation of UH3 and UD3 measured at 25 °C (i.e. a
combination of $\alpha$-UH$_3$ [20] and $\beta$-UH$_3$ have been recorded as $-127.0$ kJ mol$^{-1}$ and $-129.8$ kJ mol$^{-1}$ respectively, [25] and in both isotopic forms the formation is notably exothermic. Work looking at the H$_2$ exchange with UD$_3$ found the free energy difference between the two phases to be small [31], and that the H$_2$ in UH$_3$ has been observed to readily exchange with D$_2$ at, and below, room temperature [12].

2.2. UH$_3$ morphology

Due to the pyrophoric nature of UH$_3$ when exposed to the air, direct characterisation is challenging, especially when a high surface area and mass of hydride exists. Safe handling within non-specialist laboratories is only possible when small masses of material are used i.e. isolated mass of hydride exists. Safe handling within non-specialist laboratories is challenging, especially when a high surface area and surface area of uranium hydride that could form in any given storage environment.

To produce metal powders of high surface area for subsequent oxidation corrosion experiments [13,32-34] hydriding-dehydriding cycles are used as a method for disintegrating precursor metal blocks. If this cycle is repeated numerous times, the mean particle size of the material is found to approach a constant value (Fig. 2) [34]. This is reflected in the reaction kinetics as shown in Fig. 3 and it has been observed that after six cycles, the reaction kinetics remain the same providing the reaction conditions remain the same [7]. In the first couple of cycles, the hydriding step has been reported to yield a U/H ratio which is less than three indicating the reaction may be initially non-stoichiometric or incomplete but normalizes after the third cycle [35].

Fig. 4 shows secondary electron (SE) images of a uranium powder that has been prepared by six hydriding-dehydriding cycles followed by a period of controlled oxidation (in H$_2$O vapour and O$_2$ gas), after which the material was allowed to stabilize in air before being loaded into a focused ion beam (FIB) instrument for imaging [13]. The reaction product is angular in appearance with the individual particles appearing lozenge-shaped, or as elongate cuboids with a roughened exterior. The size ranges from $15 \pm 10 \mu m \times 5 \pm 2 \mu m$. This reaction product matches the description given by other investigators for uranium subjected to 50 hydride-dehydride cycles, followed by several hours of air exposure. They describe the final product as cylindrical or ‘wire’ like, possessing branching thread-like extensions 0.01–1 μm thick [7].

Imaging at higher magnification identified the oxide grown from the particles as having a stacked plate-like character (Fig. 5). These appear to fracture creating an oxide spall ranging from micron to sub-micron in size. Fig. 6 shows a cross-section through a post-reaction uranium particulate. The morphology of the surface oxide is variable, reflecting the underlying particulate shape. The thickness is uneven reflecting the ease with which the oxide can spall due to the lack of lateral retention. Despite the uneven appearance, there does appear to be a consistent base thickness of oxide surrounding the particle. This suggests corrosion of uranium produces a fine material which could subsequently be easily disseminated if released.

The average surface area of the material shown in Figs. 4–6 along with similarly prepared samples from other studies performed by the authors [13] were determined via Brunauer–Emmett–Teller (BET) analysis using nitrogen gas and gave a result of $= 0.72$ m$^2$ g$^{-1}$, with a standard deviation = 0.45 m$^2$ g$^{-1}$. This compares well with the spread of other data available in the literature for hydrided and dehydrided uranium metal powder where recorded results ranged from 0.33 to 3.62 m$^2$ g$^{-1}$ [14,34,36–38], implying that the result for both hydrided or dehydrided metal is very similar. Indeed, due to the volatility of the reaction product, few studies have achieved a direct measurement of hydride without some degree of oxidation. Results from assorted uranium corrosion products (oxidised hydride, fuel, oxidised metal) are far more varied, ranging from 0.5 to 1.04 m$^2$ g$^{-1}$ [14,39]; 2–12.9 m$^2$ g$^{-1}$ [32,34,40] even as high as 30 m$^2$ g$^{-1}$ [38], suggesting different levels of oxide spallation and break-up for the recorded surface area values.

For the use of hydride as a possible SMR fuel material, this research

![Fig. 2](image-url)  
Fig. 2. Showing the change in particle size for uranium and uranium hydride (UH$_3$) powder after successive hydriding-dehydriding sessions at (a) 100 °C and (b) 320 °C. The arrows signify the sequence of the reactions with A → B → C indicating the Hydriding → Dehydriding → Hydriding step. Graph adapted from [39] and reproduced from reference [102].
is useful in predicting the through life particle size and surface area of over multiple cycles of hydrogenation and dehydrogenation.

3. The U + H₂ reaction

The initial development of hydride on lightly oxidised metallic surfaces is, for many binary metal-hydrogen systems, characterised by the appearance of growing hydride “spots” on the metallic surface [1,2,41–45]. For a hydride spot to nucleate the flux of hydrogen to the metal surface must exceed that which is diffusing into the bulk metal to allow saturation to occur [3,46]. As both increase exponentially with temperature, the nucleation rate may be slowed if the gas pressure is inadequate [46]. The number density of the hydride spots is finite and dependent on the solubility of H₂ and the microstructure of the metal [42]. Provided that there is sufficient hydrogen to allow continued reaction, the nucleation centres tend to grow radially and eventually merge to form a continuous hydride layer at the metal surface. This then thickens by the so-called ‘shrinking core’ morphology to ultimately consume the whole sample [47,48]. For the bulk hydriding stage and over a wide range of temperatures (25–500 °C) the activation energies (Eₐ’s) have been given a range from 23.2–39 kJ mol⁻¹ [7,28,41,49–54]. From the data four stages have been associated with the uranium-hydrogen reaction [55]:

1. An induction period. Under normal conditions, the metal surface is covered with a surface passivation layer (SPL) of oxides, hydroxides, oxycarbides and water [46] which acts as a barrier to hydrogen diffusion [56] and also removes dissociation sites [57].

2. Nucleation and growth of discrete UH₃ sites. This occurs at the point or points where the SPL has failed. Initial hydrogen attack is termed as ‘nucleation’. This expression is broadly accepted due to the almost hemispherical way that the sites spread on the metal surface [1]; however, UH₃ has also been observed in strip-type [58] or filiform-like morphologies [59].

3. Bulk reaction. This occurs when the discrete reaction locations coalesce to form a homogeneous reaction front. The transition may be delayed or even not observed depending on the gas purity [43], temperature regime [60] and geometry of the reacting sample [42].

4. Total conversion of bulk metal to UH₃. The progression of the hydride reaction front into the metal continues until total consumption occurs, and the reaction slows and eventually ceases.

These stages are highlighted in Fig. 7 which shows the idealised pressure decrease of hydrogen over time due to reaction with a uranium metal powder at 320 °C. The duration of these stages depends on the form of the uranium metal, (i.e. powder or a solid) as kinetics differ depending on the surface area to volume ratio [46,51]. The size and shape of the metal not only affect the reactive surface area [61], but also affect the heat release [62], accelerating temperatures away from isothermal conditions [63], and reducing or even removing the induction time [61]. Hence, the formation of UH₃ would appear to be a simple process. However, in practice, the situation is much more complex. Therefore, it is the factors controlling the induction period and initial nucleation and growth site formation which ultimately determine the fate of uranium metal in a hydrogen environment. In the early hydriding stage, the reaction is considered to be controlled by two
main factors: the environmental conditions surrounding the metal (temperature, hydrogen purity and pressure) [24,64,65] and the characteristics of the metal surface and its oxide [66], which is now be explored further.

3.1. The induction period

The generally accepted view is that hydride nucleation and the subsequent growth of nucleated material is preceded by a period in which hydrogen penetrates the SPL [42,55,56]. Previous work has shown that the duration of this ‘induction’ period is dependent on several factors, namely, oxide thickness, oxide heterogeneity, degree of surface hydroxylation, abundances of impurity phases in the metal, such as carbides and the purity of the H2 gas.

When hydrogen permeates the oxide layer, it begins to build-up at the oxide-metal interface. The mechanism for H2 permeation and diffusion has not yet been clarified and could vary depending on the oxide stoichiometry. When the concentration of hydrogen in the metal at this interface exceeds the hydride solubility limit (a temperature-dependent parameter) the gas-solid hydriding reaction takes place. Overall, the hydrogen concentration in the metal near the oxide-metal interface is governed by the net difference in the abundance of incoming H atoms passing the oxide-metal boundary, relative to the abundance of the outgoing H atoms diffusing into the bulk of the metal.

Thus, for oxide-coated uranium, the physical build-up of hydrogen at the oxide-metal interface prior to the hydride forming reaction can be described by the following sequence of elementary steps [67] (highlighted in Fig. 8):

1. **Surface Sorption:** Physisorption of H2 at the oxide surface, followed by either diffusion or dissociative chemisorption of two H atoms and/or ions.
2. **Permeation:** Surface to subsurface penetration and diffusion of hydrogen through the oxide layer coating the uranium metal. This may occur as: molecular H2 or via a dissociative chemisorption step to atomic or ionic H.
3. **Concentration:** Build-up of H atoms at the oxide-metal interface, towards the hydride solubility limit leading to reaction.

The model of Cohen et al. [68], defined the first two steps of this process (surface sorption and permeation) using a combination of diffusion- and surface-related properties. The sorption step of the hydriding process was described as a function of two temperature-dependent surface sorption related parameters of the oxide film, namely: its H2 surface sticking property and desorption rate constant. The permeation step was described as a function of two diffusion related parameters of the oxide film: its thickness and its diffusion rate constant [68]. The induction period and the initiation of hydride nucleation sites are interlinked, as the former relates to the ease with which H2 can access the metal, and the latter highlights the first point of attack on the metal surface. The factors controlling these processes (induction period, initiation of hydride sites and hydride location) are discussed below.

3.1.1. Hydrogen purity

If the H2 gas to which the uranium is exposed is contaminated with impurity gases such as O2, H2O or air, the observed induction period is increased and the reaction rate suppressed [43,69]. This is ascribed to either enhancement of the SPL by further oxidation or leading to competition for surface sorption sites with the impurity gases [41,46]. Impurities can also potentially saturate the oxide, blocking diffusion pathways [70]. If the impurity is oxygen or water, there is also a competing anion for reaction with the uranium [37]. Many experimental failures in reproducing the uranium-hydrogen reaction are a result of contamination, usually the result of ingress of atmospheric gas (O2 contamination).

3.1.2. The oxide

The primary natural barrier that uranium has against its external environment is its oxide layer which covers the metal surface. The strong affinity of uranium for oxygen is widely established [71–74] and under ambient conditions, any freshly polished or cleaned uranium surface would be expected to have an immediately formed and initially thin coating of uranium oxide, formed by reaction of the metal with the ambient (or sometimes controlled) atmosphere. The oxide phases of uranium between UO2-UO3 are the principal products of uranium metal
heat treatments prior to hydriding reaction greatly enhance UH3 in-
species or re-hydrogenation. oxide limiting parameters only after the oxide over-layer becomes
initiation by reducing the preceding induction period and increasing
length; though only up to a thickness of [70] suggesting a control exerted by the increasing transport path-
However, it is also found to increase with increasing oxide thickness
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The induction time to UH3 formation (after initial exposure to H2) is
recognised to depend on the reaction temperature and H2 pressure [55].
However, it is also found to increase with increasing oxide thickness [70] suggesting a control exerted by the increasing transport path-
length; though only up to a thickness of ∼ 50 nm [56] after which the effect is lost, attributed to a loss of coherence of the oxide, i.e. cracking and spallation. For controlled dry oxidation the passing properties of the oxide layer were found to be effective up to a thickness of ∼ 200 nm [56]. Interestingly, it has been found that vacuum annealing heat treatments prior to hydriding reaction greatly enhance UH3 ini-
tiation by reducing the preceding induction period and increasing nucleation rates [52,82,83]. This effect is not unique to the uranium-hydrogen system [84,85] and has been attributed to modifications of the oxide layer induced by heating from:

i. Desorption of physisorbed and chemisorbed water (part of the SPL),
which leaves the outermost surface of the passive oxide layer more active to H2 uptake ∼ increasing the surface sticking property [24,86].

ii. Slight changes in the stoichiometry of the oxide induced by heating (i.e. the oxygen to metal ratio) resulting in an increased diffusivity [87]. Recent studies by Knowles [88] also showed that partial oxide transformation into an UOxCyc sub-layer may be observed at the metal-oxide interface as part of high temperature (∼ 200 °C) thermal annealing. These phase modifications could result in en-
hanced mobility of H2 through the oxide lattice [88].

Correspondingly, this thermal treatment is found to significantly reduce or even remove the reaction induction time [70]. It is notable that for hydrogen storage applications, hydride that has undergone decomposition in an oxygen-free environment has little or no SPL, and so it is highly reactive (sometimes termed “activated”) with oxidising species or re-hydrogenation.

The hydride’s subsequent growth becomes independent of these oxide limiting parameters only after the oxide over-layer becomes
ruptured [43]. Evidence suggests that the induction period prior to the hydriding reaction is controlled by variations in the above diffusion and surface related properties of the oxide.

3.2. Location of nucleation sites

The initial development of hydrides on massive metallic surfaces is observed to occur in isolated zones or ‘spots’ [1,2,41–45], indicating that certain surface areas are more favourable for the onset of hydride-forming reactions [56,59,89]. These nucleation sites lie at the metal-oxide interface and not in the metal subsurface [90].

As previously stated, the precipitation of a hydride phase resulting from a gas-solid reaction only occurs when the local concentration of H2 in the metal exceeds the solubility limit. During a hydriding experi-
ment, it follows that the first hydride spots to form do so in areas where the SPL is weakest or the metal most susceptible, leading to hydrogen build up and initial nucleation of the hydride phase. For example, in a ‘natural’ uranium-hydrogen system the composition and thickness of the oxide layer may differ at locations across the surface due to defects, cracks and topographic variations. Owing to the inhomogeneity of this surface oxide layer, the physisorption of hydrogen onto the oxide and its subsequent permeation through this layer to the oxide-metal inter-
face varies across the surface, providing ‘active’ zones where H2 reaches the critical concentration faster to nucleate first [91]. These regions could potentially be identified prior to hydriding experiments.

3.2.1. Hydride growth types

The picture is further complicated by observations that the character of the hydride may differ depending on its rate of growth or due to the characteristics of its nucleation site on the metal surface [2,66]. Four types of hydride nucleation families have been identified [2], tending to be characterised by either a high nucleation rate with a low growth velocity or vice versa [46]:

i. Sub-micron sized blisters with a high surface distribution density tend to be located on scratches.

ii. 1–10 μm blisters formed below the oxide layer at point defect sites on the metal surface. The oxide acts to confine and slow the UH3 growth [92,93].

iii. Hydride nucleation around carbide inclusions at the metal surface.

iv. Rapid growth at oxide discontinuities or features of the metal sur-
face such as twins or grain boundaries.

It has been observed that prior to the development of hydride growth spots, nucleation and growth of sub-micron size hydride spots occurs. The growth of these nuclei proceeds below the oxidation layer,
and occasionally their volume expansion is insufficient to rupture the overlying oxide layer. Hence, a substantial compression field can be generated, which increases with the size of the grown nucleus, resulting in slow and decelerating growth rates of the nuclei. In fact, if no rupture of the oxidation layer occurs, the growth of the hydride nuclei finally halt, attaining a certain critical size range (< 3–4 μm) typical of a 'small' family precipitate [94].

If the oxide over-layer becomes ruptured by the growing hydride nucleus, the compression field is relieved, and the initiation of more rapid hydride growth occurs, as it becomes independent of the confining oxide. In this case, a hydride growth typical of a 'large' family precipitate develops. Thus, it is assumed that the formation of a 'large' family hydride growth site is related to a special location where the rupture of the oxidation layer is easier, e.g. a micro-crack, along with an oxide-carbide interface, or an area where the oxide is thinned. However, weaknesses in the metal lattice which provide nucleation sites for hydride formation cannot be separated from the structural effect these defects have on the oxide layer that has formed overlying these sites [58,95]. Metal surface defects can propagate through the oxide, i.e. susceptible areas tend to enhance their own weakness to hydrogen attack. The main features which have been identified are now described.

3.2.2. Surface damage

Scratches or any other extrinsic damaging to the oxide or SPL provide a direct route for H2 to reach the metal surface and are well-established loci for hydride nucleation [2,96,97], as highlighted in Fig. 9. The sample shown in Fig. 9 was polished (~ 20 nm surface roughness) and annealed at 550 °C for 16 h under UHV before being exposed to air for five minutes to thicken the surface oxide. The sample was then scratched with a pair of stainless steel tweezers in an Ar-filled glove box before being reacted at 250 °C with a D2 gas pressure of 500 mbar. The reaction was halted after a 5-mbar pressure drop was observed and the sample transferred to the FIB then secondary ion mass spectrometry (SIMS) instrument for analysis. FIB imaging (Fig. 10) revealed a significant incidence of corrosion along the length of the surface scratch, which SIMS positive ion mapping (Fig. 10) revealed to be Ud2+. Ion clusters associated with deuteride growths (UD+, UD2+, UOD+, UO2D+ and UO2D2+) could be clearly resolved relative to the U+ ion and UD2+ ion clusters more typically associated with the surface uranium oxide.

3.2.3. Surface inclusions

Inclusions are not coherently covered by the surface oxide, and so can provide gaps or physical disruptions in the metal oxide, providing a passage for hydrogen along the inclusion-oxide interface (Figs. 11 and 12). Such pathways are considered to enhance transit through the bulk oxide [1,58,98]. Therefore inclusions in uranium have been found to act as preferable nucleation sites for hydrogen attack [1,2,58,95] though this has not been observed by all studies [99,100] as these sites can be passivated by electropolishing [98,101]. Hydrides around these regions exhibit a high growth velocity breaching the oxide surface and moving deep into the metal while joining up to form large pits [1,96].

Nucleation at these sites may be influenced further by the geometry of the inclusion with respect to the metal surface and by residual stresses in the surrounding metal allowing a localised concentration of H2 in the metal. The low activation energy at the margins of these sites allows easy access of hydrogen to these regions. Exploratory work has been carried out using electron back-scattered diffraction (EBSD) to look for crystallographic distortion as an indication of residual strain in the metal lattice [13] (Fig. 13). Whilst this work has yet to be built upon it provides tantalizing evidence to show that elevated levels of crystallographic distortion can be identified surrounding inclusion sites which can be related to the differing thermal expansion coefficients of the uranium metal and uranium carbide.

3.2.4. Grain boundaries

Grain boundaries are well-established as preferential sites for hydride nucleation [42,59,65,90,96,99,101,102], especially in higher purity metals where inclusion particle number density is low. Recent work in our lab [101], employed EBSD to statistically analyse hydride growth location on natural Magnox uranium. The analysis has shown that more than 90% of the hydride growth sites were directly related to grain and twin boundaries (Fig. 14a & b). Grain boundaries (including sub-grains and twins) are believed to have a greater diffusion coefficient than the bulk grain and, so, provide a route into the metal sub-surface, allowing concentration of hydrogen within the metal [59]. The angle of incidence of the grain boundary with respect to the metal surface is also believed to alter its favourability as a site for hydride formation [65]. Boundaries which intersect the metal surface at an acute angle are thought to be more susceptible to reaction as a larger area of the grain boundary region is exposed and the wedge tip of the grain is geometrically favoured for most rapid hydrogen accumulation, as shown in the schematic in Fig. 15 [65]. In addition, it has been observed that the rate of metal oxidation varies with crystal orientation in the early stages of oxidation [95]. This results in a structural discontinuity in the oxide over grain boundaries that may enhance the ingress of hydrogen to these locations [95,101]. Fig. 16 provides a schematic to explain this process with yA, yB and yC representing the thickness of the oxide for grains A, B and C, as a function of oxidation time. At t1, oxidation rates between the grains sharing a low misorientation angle boundary (LMA) are comparable (yA ≈ yB) while for B and C (high misorientation angle boundary) are very different (yB < < yC). As oxidation progresses (t2), the areas of initially thinner oxide catch up those which grew at a faster rate, hence stress at the oxide–oxide interface is generated. Through this mechanism, the grain boundary discontinuity is reflected as a mirroring oxide discontinuity on the surface [101].

3.2.5. Intergranular sites

Intergranular sites, such as twins and sub-boundaries, provide regions of metal lattice distortion and therefore low energy nucleation sites [58,59,65,95], and regions of unequal oxide growth resulting in an inhomogeneous oxide layer. These features are considered to arise in

Fig. 9. A series of stitched secondary electron (SE) images of the middle of the scratched area on the sample. Areas of deuteride growth on the scratched material are highlighted in red. Growth areas on the undisturbed uranium surface not positively identified as deuteride growths are highlighted in blue. Areas positively identified as deuteride growths are marked in purple. Stitching lines between secondary electron images are marked by horizontal grey lines. Graph reproduced from reference [102].
3.3. Growth of hydride sites

The UH$_3$ nucleation rate tends to follow a Gaussian dependence, peaking at 7–10% surface coverage, then decaying to zero, due to further reaction resulting almost exclusively at already established hydride sites [44,46]. This localised attack acts increase the proportion of metal susceptible to reaction as an irregular surface topography is produced. Due to the considerable density difference between UH$_3$ and uranium metal [104], Table 1, resulting in a $\sim 1.75 \times$ volume expansion upon reaction, strain fields accompany the reaction [105] and may contribute to perpetuating the growth of already existing hydride.

Due to the ductility of uranium and the brittle nature of the reaction product, the hydride fractures and spalls as a fine black powder [4,106]. This has led to the suggestion that the rate-limiting step for the reaction occurs at the metal-hydride interface [46]. Any overlying
surface oxide is split and forced apart by the UH$_3$ forming beneath, providing a direct pathway for further ingress of hydrogen. This direct route is then more preferable for hydrogen ingress due to the ionic character of UH$_3$ bonding (higher than the U–H bond) [107]. As a consequence, it has been reported that the reaction follows a step like procedure, attributed to the accumulation and subsequent release of stress [42].

3.4. The bulk reaction

The individual hydride sites experience linear lateral growth and eventually overlap [42] engulfing the metal surface. Once the surface sites coalesce, the bulk reaction begins, following a decreased, linear kinetic regime [51], propagating into the metal, following a ‘contracting envelope’ or ‘shrinking core’ function [47]. Under steady state conditions the UH$_3$ layer moves into the bulk metal at a fixed velocity and with a constant adherent thickness [108] and numerous models have been produced to describe the reaction [24,28,37,51,68,109–112].

Due to the volume expansion and lack of coherence of the corrosion product, stress cracking occurs, causing the hydride to spall along planes parallel to the metal surface. At the nanoscale, the volume expansion associated with the reaction causes cracking in the parent metal which accelerates the rate of H$_2$ ingress to the metal in these areas [108].

For a reacting surface area of constant size, the reaction rate generally varies linearly with time at low temperatures; this behaviour may be related to the formation of a constant-thickness adherent hydride layer beneath the continually spalling hydride. The value of the apparent activation energy deduced from rate versus 1/T curves appears to reduce with increasing temperatures due to the increasing dissociation pressure of the hydride as the temperature increases. So, for a constant applied hydrogen pressure, the H$^-$ ion concentration gradient across the adherent hydride layer continually decreases with increasing temperature. This effect partially negates the increasing H$^-$ ion diffusion coefficient in the hydride with increasing temperatures, so giving a reduced value for activation energy. For typical uranium samples exposed to hydrogen, the reacting area generally varies with time during the early stages of the reaction. This variation is reflected in a changing reaction rate until complete coverage of the sample is attained. Rate curves tend to follow a decelerating parabolic curve for high temperatures that becomes ‘S’ shaped at lower temperatures [51,69], indicating an initial reaction period followed by a bulk reaction stage.

This is highlighted in Fig. 18 which shows a schematic graph of the U + H$_2$ reaction for a range of temperatures following pressure (gas consumption) over time. Bulk reaction rate and velocity of the hydride reaction front can also be enhanced by annealing at temperatures > 450 °C. This phenomenon is assumed to relate to grain size increase due to heat-induced microstructural changes in the metal [83,113].

The reaction rate is observed to have a decreasing pressure dependence with increasing hydrogen pressure [51]. For moderate pressure conditions, a half-order dependence has been recorded [37,114]. This observation designates dissociation and diffusion of atomic hydrogen to the metal bulk as being the driving influence. This experimental observation was mirrored by modelling results from Taylor and Lillard [115] who confirmed the thermodynamic preference of dissociated H diffusion on an α-U (001) surface using density functional theory (DFT) [115]. At constant hydrogen pressure, increasing reaction temperature causes a decrease in the hydriding rate [114] giving an apparent negative activation energy of $-6.65$ kJ mol$^{-1}$. As the applied hydrogen pressure reaches the adsorption equilibrium pressure (i.e. high temperatures or low pressures) kinetics also slow as the decomposition reaction begins [46]. This approach to equilibrium and the decrease in reaction rate has been observed by numerous investigators [24,51,83,110]. At pressures much greater than equilibrium, pressure independence is exhibited [24,51,111]. Recent experimental work by Stitt et al. [116] working on hydriding of uranium in grouted systems has shown that the temperature of the reacting metal may play a more influential role in early UH$_3$ formation than the temperature of the gas as previously believed (Fig. 19).

The body of evidence, from both modelling and experiments, indicates that the physical characteristics of both the surface oxide and underlying metal are important for dictating the hydride formation behaviour. For storage applications it is therefore valuable to understand both the elemental make-up and microstructure of the metallic uranium (which is informed by its fabrication and in-reactor history) as well as its current state of corrosion, including the thickness and stoichiometry of the enveloping oxide and the relative abundance of hydride as a proportion of the total mass of corrosion product.

4. Additional effects on the rate of the U + H$_2$ reaction

4.1. U-Alloying

Much of the emphasis of UH$_3$ research has been directed at better understanding its formation on exposed α-U metal surfaces. However, one of the intrinsic properties of all metals is the level of impurities and the hydrogen content they acquire during the fabrication process [117].

4.1.1. Hydrogen content versus embrittlement in pure uranium

At low concentrations, hydrogen may be accommodated in uranium by impurities like carbides [118,119], as absorption and trapping at these sites is thermodynamically more preferable [120]. At higher contents, hydrogen is diluted in uranium up to the point where UH$_3$ precipitates start to form [119,121]. It has been postulated that for any uranium metal there may be small, micron-sized (or smaller) hydride
precipitates, finely disseminated throughout the microstructure [118] formed during initial crystallisation of the metal from a molten state. Grain boundaries have been addressed as initial locations for hydrogen trapping [121], however, this assumption is disputable [122]. It is notable that the ductility of uranium decreases significantly when the hydrogen content exceeds 0.5 ppm [120] with maximum embrittlement observed at 2.5 ppm hydrogen [123], implying an influence of grain boundary UH₃ precipitates. The loss of ductility as an effect of UH₃ precipitation and other impurities can also be directly correlated with enhanced hydriding kinetics [120].

4.1.2. Other alloys

Across the literature, there are a respectable number of investigations of the hydriding reaction for various uranium alloy compositions. Low alloying can be either unavoidable as part of the manufacturing process (Al, C, Cr, H₂, Si, V, etc.) or deliberate to enhance the performance of the material (Nb, Ti). Uranium-chromium and –vanadium alloys were found to react faster than pure uranium during hydrogen exposure [42,64]. Carbon and silicon contents along with the various thermal treatments are regarded as controlling mediums of the grain size with the higher content resulting in finer grains [117]. However,
silicon at elevated content (> 100 ppm) increases the hydriding kinetics by promoting spalling across the metal lattice [113]. Niobium is a well-known additive used to increase the oxidative corrosion resistance of the material. Contrary to their oxidising behaviour with O₂/H₂O, U-Nb alloys respond with more complexity to hydrogen corrosion with U-2.5 wt% Nb reported to react faster than pure uranium, but U-5.7 wt% Nb to appear significantly more resistant to corrosion [53]. This may be partly influenced by the phase composition of the alloy which transitions from an orthorhombic α-phase to a γ-phase at ∼6 wt % Nb. Similar influences have been observed in the U-Cr system where β-quenched alloy have been observed to show enhanced hydriding kinetics[103]. Finally, titanium was recognised as an additive that increases the life-performance of the uranium-fuel to both oxidising and hydriding environments due to its stainless properties [58]. This alloy has since found widespread use in artillery and other military ordinance.

4.2. Surface passivation

For the nuclear industry, the prospect of hydride formation in bulk quantities is undesirable. Accordingly, several studies between 1983 and 2006 have examined the possibility of coating or altering the uranium surface to prevent corrosion. In an effort to delay if not prevent...
this reaction, ion-surface implantation has been employed [124–131]. Oxygen [125,131], carbon [126,128–130], nitrogen [127–129] and sulphur [128] ions have all been investigated as passivating agents. All studies have shown that the induction period was extended, and the reactive surface was minimized to site-specific regions leaving a large fraction of the implanted surface unaffected. However, except for sulphur, stress build-up was recorded in the uranium lattice as result of implantation which persisted even after the surface implanted layer was nominally removed [128].

4.3. Strain

In a variety of other metallic systems, corrosion is recognized to be influenced by tensile or compressive loading (stress), commonly

Fig. 16. Schematics showing how the oxidation kinetics progresses on grains with different rotational mismatch. As the oxide of the initially slower oxidising grains thickens to catch up the other ($t_1 \rightarrow t_2$), stress is generated on the oxide–oxide interface. LMA and HMA refer to low misorientation angle and high misorientation angle boundaries, respectively. Schematics reproduced from [101].

Fig. 17. Showing hydride growth along an intergranular twin. The sample was reacted at 320 °C and 500 mbar D$_2$. The oxide layer was subsequently removed via ion etching to reveal the metal subsurface. Figure reproduced from [65].

Fig. 18. A schematic graph showing the effect of temperature on the U + H$_2$ reaction. The assumed reaction is occurring in a fixed volume of H$_2$ gas, hence the pressure decreases with time. Figure reproduced from reference [102].
referred to as stress corrosion. In uranium, this phenomenon has not been well explored.

Internal, external, surface and interface stresses are introduced to the material during the fabrication [132,133], preparation [96,102] and even during corrosion [134]. The generated strain, which is defined as the amount of deformation at distinct intervals of tensile or compressive loading, can be categorised into three distinct types:

i **Internal strain.** Stresses developed in the metal during the various thermal and mechanical preparations during manufacturing. These deformations are produced when the elastic flow is exceeded and plastic deformation occurs [132]. The latter may arise as a result of anisotropic thermal contraction between the grains and the surrounding aggregate during cooling after a thermal process (casting, β-quenching etc.) [133]. These stresses are commonly reflected as slip and twinning modes on the metal lattice. The (001)[100] slip mode is the primary system observed for uranium at room temperature [132]. There are 41 twinning modes identified for uranium and for simple shuffle mechanisms [135], with the most commonly detected to be the (130)〈310〉 and ‘(172)’〈312〉 systems [99]. It was shown in section 3.2.5 that these sites serve as preferred locations for hydride nucleation and growth.

ii **External strain.** These include the residual stresses on the surface after mechanical preparation, leaving a work-hardened layer e.g. cutting, grinding or polishing. Recent work has confirmed that polishing scratches facilitate hydride formation [96,102] and that a disrupted work-hardened layer transforms the reaction behaviour to be more rapid locally [94].

iii **Corrosion generated strain.** When oxidation occurs at the uranium surface the difference in density between the oxide and the underlying metal generates in-plane compressive stresses in the SPL and tensile stresses in the metal lattice. Stress is at the highest level at the metal-oxide interface and diminishes vertically away from it [136]. This strain can be relieved with cracking and flaking of the SPL which again modifies the reactivity of the metal towards hydrogen [56]. Differential volume expansion is also a driving stress generator when nucleation of hydride growths occurs [60,134,137]. The stress is partially relieved when hydrides breach the SPL [134] or by hydride ‘streamers’ moving into the bulk of the metal [90].

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**Fig. 19.** A set of consecutive radiographs exhibiting the grout encapsulated uranium rod (black) and resulting corrosion products (dark grey) through the temperature gradient. The warmest temperatures were exposed to the base of the sample and the temperature cooled with distance away from this region. The numbered lines correspond to the XRPD line scans. Figure reproduced from [116].

**Fig. 20.** SEM images of the pillars after reacting with 12 μmol of D₂. (a) Shows the entire array and (b)-(d) individual pillars that have commenced UD₃ nucleation on their apex. (e) Finite element modelling showing the distribution of tensile stresses induced by the loading of uniform oxide growth. The scale is represented in maximum principle stress (MPa); the red end of the colour spectrum indicated zones of high and blue low tensile stresses. Figures reproduced from [139]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Hydrogen embrittlement and alloying additions are inseparably linked with induced stresses; however, it is uncertain how strain affects the hydriding kinetics. Several DFT studies have mentioned that tensile/expansive forces in the metal could act to further enhance \( UH_3 \) formation while the reverse (compressive forces) could possibly result in reaction deceleration on the stage [115,138]. Stitt et al. [139] have worked on the early hydriding of uranium which was cut into a series of pillar shapes using ion beam milling (Fig. 20a). The study observed that \( UH_3 \) has first initiated at the apex of these features where tensile forces were considerably higher in value with regards to the rest of the bulk (Fig. 20b–c). Equally, these apex regions were geometrically predisposed to preferential hydride formation and hence it is not possible to extract which parameter exerted the greater control on early hydride formation.

Operationally the experimental data suggests that uranium metal that has been mechanically worked or strained as part of in-reactor burn-up is likely to exhibit a different corrosion behaviour, both for oxidation and hydriding, relative to an unstrained counterpart [94,96].

5. Dehydriding

As previously set out in Eq. (1), the hydriding reaction may be reversed if H\(_2\) gas is removed and the temperature increased, usually done most effectively in vacuum. The point at which hydriding ceases and dehydriding begins is dependent on temperature and pressure, with the charge point highly dependent on the means of measurement [9]. Empirically, the decomposition pressures of \( UH_3 \), \( UD_3 \) and \( UT_3 \) have been given as:

\[
\log P = \frac{A}{T} + B
\]

For \( P \) in torr, \( T \) is in kelvin (K), \( A = 4500 \text{ K} \), \( B = 9.28 \) for \( UH_3 \), \( A = 4700 \text{ K} \), \( B = 9.46 \) for \( UD_3 \) and \( A = 4471 \text{ K} \) and \( B = 9.46 \) for \( UT_3 \) [9].

Reported values for the activation energy for \( UH_3 \) decomposition \( E_a \) ranges from 39.7 ± 2.5 kJ mol\(^{-1}\) [140] to 79.08 ± 7.5 kJ mol\(^{-3}\) [9,37,140] depending on the study, though all have found the rate to obey zero order kinetics. Recent theoretical studies by Lillard et al. [140] also deduced that the rate of dehydriding appears to be unaffected by the conditions under which the hydride was initially formed [140].

A study of the dehydriding of uranium following reaction with water vapour identified the following three regions of hydrogen release when heated from 0 up to 600 °C [141]:

- 250 °C: Release of hydrogen adsorbed on or inside the oxide surface, trapped on oxide grain boundaries or (to a lesser extent) inside the oxide lattice.

- ~250–400 °C: Release of hydrogen stored as \( UH_3 \).

- > 500 °C: Removal of hydrogen formerly dissolved (in solution) in the metal [142].

The material product of full dehydriding is a finely divided metallic powder consisting of micron-sized particles. This material is as equally pyrophoric as parent hydride. It is suggested that if dehydriding is only partially complete, particles may exhibit a \( UH_3 \) core that is encapsulated by uranium metal. As vacancy formation in the \( UH_3 \) core occurs, concomitant with structural changes in the metal, the rate controlling step for dehydriding, then, would be the diffusion of hydrogen through the metal to the uranium surface where it can then desorb into the gas phase.

Whilst there is relatively little published in the public domain regarding the dehydriding behaviour of uranium hydride, such research is potentially beneficial for both storage and SMR applications. For the former, it may be a consideration that for some uranium–containing wastes considered very likely to contain substantial \( UH_3 \), a thermal dehydriding treatment followed by controlled dry oxidation may be an appropriate but somewhat complex waste treatment strategy. For the latter, the dehydriding kinetics are important for predicting the breakdown rates over multiple charge-discharge cycles within a reactor core allowing more accurate modelling of reactor self-regulation for temperature and criticality.

6. The production of \( UH_3 \) with water

The reaction between uranium and water vapour has been well documented and the presence of \( UH_3 \) as a corrosion product is generally [38,39,74,79,143–147] but not universally accepted [33,148]. The role of hydrogen in the reaction remains uncertain. If the reaction occurs in a closed system (e.g. uranium containment in sealed drums), over time the environment becomes \( H_2 \)-rich (uranium oxidation by \( H_2O \) releases \( H_2 \) in the gas phase), increasing the likelihood of \( UH_3 \) formation via the usual gas metal reaction. It has been recently clarified experimentally that the hydride can form as part of the \( U + H_2O \) reaction mechanism (and not just as a separate \( U + H_2 \) reaction) [149]. Martin et al. [149] used atom probe tomography (APT) to examine the oxidation reaction of uranium by both normal and deuterated water vapour at an atomic/nanoscale. They observed a very thin (3–5 nm) interfacial hydride layer forming at the metal oxide interface just under the hyper-stoichiometric oxide layer. These findings were confirmed by both 3D atom probe maps (Fig. 21a–c) and proximity histograms (Fig. 21d) on the metal oxide interface.

This observed interfacial hydride layer may be considered as 1) a standard solid reaction product for all uranium and oxygen-free water reaction systems and 2) as operationally ‘harmless’ owing to its constant thickness and action to work as a reaction front, consuming the metal while simultaneously producing more \( UO_2 \). It may be assumed that this hydride is potentially amorphous, though its limited thickness (3–5 nm) would make it very difficult to verify.

By comparison, the most problematic type of hydride is considered to be ‘bulk’ hydride which has formed in significant mass and with a large exposed surface area. That hydride type is mostly produced in enclosed systems where the generated hydrogen gas from U-oxidation cannot diffuse out to the environment but stays trapped in the near uranium metal surface. Water-formed \( UH_3 \) produced in an enclosed system has been encountered by investigators opening steel drums containing used fuel [150] and also determined experimentally [151]. The presence of water on such a system affects the duration of the induction period but not the subsequent rate of hydride formation after \( UH_3 \) initiation [152]. Environments such as cooling ponds and silos are considered as quasi-enclosed systems due to the complex way that the material is interim-disposed, causing hydrogen to build-up in pressure locally. These areas contain large amounts of intermediate level waste (ILW) such as U-contaminated fuel cladding, conditioned SNF parts along with other metals. The continuing oxidation of this material produces an excess of hydrogen gas that can only partly escape to the environment. If excess trapped hydrogen is generated near uranium, the reaction behaves as an enclosed system. \( UH_3 \) forms on such a system and is found to persist over time, even under a water-rich atmosphere [102,153].

In our laboratory, we tried to mimic these conditions by leaving a Magnox-uranium coupon to react with distilled/purified water under vacuum contained and immersed conditions for a long time period at different temperatures [102]. Fig. 22a provides a SIMS depth profile of the reacted surface of uranium in water at 70 °C for 330 h. From the graph, an almost bell-shaped line for the \( UH^+ \) intensity signal may be observed as the oxide surface is etched. The \( UH^+ \) signal which represents the hydride or hydrogen-rich phase attains its maximum value at \( t_1 \) very close to the point where the \( UO_2^+ \) and \( U \) lines intersect (metal-oxide interface, \( t_2 \) and then decreases in value. Based on the data from Fig. 22a, a simplified 2D illustration showing the cross-sectional face of the sample was produced (Fig. 22b). To provide more definitive proof and support these findings, the sample was subjected to a final three step desorption process while using RGA to analyse the
desorbed gases [102]. Hydrogen started emerging in the head-space at temperatures $\geq 220 \, ^\circ C$, comparable to the range responsible for desorption of $H_2$ stored as $UH_3$ ($\sim 250 \, ^\circ C$), as previously confirmed by Danon et al. [141].

Hydrides, hydroxides and hydrated oxides have been found along with oxide resulting from reaction between uranium and liquid or water vapour [102, 154]. The presence of hydrogen has not been found to impede the oxidation reaction [79] though trace levels of water vapour have been recorded as slowing the hydriding reaction [42].

7. $UH_3$ oxidation

Like uranium powder, a $UH_3$ powder also burns in oxygen [15, 16, 22, 155] making it a particularly unstable material to handle. Ignition and the ongoing combustion at room temperature have been confirmed experimentally by Le Guyadec et al. [15] working in an inert environment. Gaseous and solid and solid-only combustion was observed for $UH_3$ and uranium powders, respectively. Considerable temperature rise along with volume increase of the powder followed the phase transformation of $UH_3$ to $U_3O_8$ [15]. For uranium storage, this has the implication of unintended pyrophoric events where $UH_3$ has been unintentionally produced, by leaving metal in the presence of $H_2$ (i.e. storing with water vapour) which if re-exposed to air, can catch fire [14]. Therefore, the reaction has been modelled to investigate storage conditions [156, 157]. Due to the ferocity of the reaction between particulate uranium and oxygen, it is assumed that both materials oxidise in a similar fashion [155] with the reacting ion being $O_2^-$ [14, 16, 158]. Recent numerical models showed that the $UD_3 + O_2$ reaction is more rapid than the reported rate values of the $U + O_2$ system at room temperature [12, 157].

What also is apparent is the stability of spot hydrides in air. All of the images in this review acquired by SEM/FIB/SIMS involved a period of air exposure during transfer between reaction cell and instrument vacuum chamber ($\sim 2 \, \text{min}$). This stability is attributed to the formation

Fig. 21. (a) An atom probe map of a tip extracted from a uranium sample exposed to air for approximately 1 h, showing $U$ and $UO_x$ ions in green and yellow/orange, respectively. The original surface of the uranium is located at the top of the specimen. (b) A 24 at.% $UO/UO_2$ isosurface indicating two oxide regions on the specimen; (marked 1) at the original surface and (marked 2) generated on the side of the specimen during sample preparation. (c) The same atom map as in (a), but with an isoconcentration surface indicating 0.5 at.% $UH$ in blue to reveal the locations where hydride ions are detected. For (c), the front face of the dataset is cropped away to show a cross-section of the middle of the specimen. (d) Proximity histogram of the surface oxide feature marked as 1 in Fig. 21(b). All complex ions are decomposed into their constituent elements. Figures reproduced from [149]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 22. Showing on (a) Mass ion depth profiling for uranium oxidised in liquid water at 70 °C (Ga+ primary ion beam, 25 keV, 3 nA, positive ion mode, 45° angle of incidence) and (b) a 2D schematics of the cross-sectional view of the same sample by taking into account the data from (a). From the graph and 2D illustration, an almost linear increase in the $UH$ signal (red line) may be observed reaching its maximum value at the metal oxide interface (in the graph- where the blue and black curves intersect). $UOH$, $UOH_2$, $UO_2H$, $UO_2H_2$ and $UO_2H_3$ clusters were also traced at and/or near the gas-oxide interface indicating a $H_2$-rich oxide. Figure reproduced from [102]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
of a thin uranium oxide layer on the hydride, screening the bulk hydride from further rapid reaction. Due to the low surface area of hydride, the heat generated by oxidation was not sufficient to drive a pyrophoric response [159].

Fig. 23 shows SIMS depth profiles recorded at numerous positions across a hydride site, moving from hydride free metal surface to hydride spot. A primary observation revealed that both the metal surfaces and the deuteride growths were coated with a thin layer of uranium oxide < 50 nm thick (Fig. 21). The oxide layer on the deuterium growths must have developed during the transfer of samples between analysis systems. Ion beam etching and SIMS ion mapping also show that the oxide is more adherent to the hydride sites than to the metal.

To summarise, the nature of the UH3 + O2 reaction means the following points must be considered when studying or using UH3:

Fig. 24. Positive ion colour combination maps of a deuteride growth before and after etching for 30 min at a 3 nA beam current. Maps are RGB of U+ (dark blue), UO2⁺ (green), and UO⁺ (light blue), and UO₂⁺ (green) ion clusters with etch time using a 3 nA beam current from different 13 μm² areas across a 100 μm diameter hydride growth. The experiment was performed on an annealed DU coupon at 200 °C with 500 mbar D₂ pressure. The reaction was stopped by evacuation of the gas after a 4–5 mbar pressure drop was observed, equivalent to a 1–2% surface reaction. Figure reproduced from reference [102].
i. For safety UH₃ should be stored and handled in oxygen- and water-free environments to prevent ignition and/or pyrophoric reaction.

ii. If oxygen exposure is unavoidable, factors like exposed surface area [160] and mass of the reactive material [15,16] are proportional to the rate and amount of heat that may be released.

iii. Any UH₃ analysis performed outside of the reaction environment may have experienced some degree of atmospheric exposure. This would result in surface reaction and, due to the exothermic nature of the reaction, potentially provide sufficient heat to induce a phase transformation in the residual hydride, given a significant mass of UH₃.

iv. Likelihood of ignition at room temperature may be reduced by prior controlled exposure to a limited amount of oxygen or moisture [15,16].

v. During dehydriding, the arising metal powder readily reacts with any contaminant oxygen in the system to form an oxide (UO₂ ± x), acting to further purify the released gas. This, however, also has the effect of gradually reducing the hydrogen storage capacity of the metal over time due to the degree of oxide formation. This has significant relevance to uranium used in hydrogen storage beds where multiple loading and unloading cycles may degrade their operational performance.

8. Conclusion

It is now 60 years since the first fission reactor became operational, using uranium metal as fuel. Over this period a significant body of research has been accumulated on the corrosion of uranium metal and the formation and reactivity of UH₃ as one of its potential corrosion products. The current work has attempted to consolidate this significant body of knowledge into a more concise set of observations and descriptions, applicable for both nuclear waste storage and development of SMR concepts based on UH₃ as the fuel material. It is clear that gaps in understanding still exist, specifically in terms of mechanisms for behaviour and for research conducted on real spent fuel materials as opposed to non-irradiated counterparts.

Due to the reactive nature of UH₃, it is challenging to produce a sample and then characterise it ‘ex-situ’ without guaranteeing some degree of surface reaction. This, combined with the exothermic nature of the reaction which could easily convert α-UH₃ to β-UH₃ suggests there is much still to study in the α-UH₃ system to better understand its fundamental properties and corrosion behaviour. The literature contains a paucity of α-UH₃ data, and that which exists is very old. The majority of the hydride experiments reported in literature relate to the β-form and accordingly it would be academically and industrially interesting to better determine the physicochemical and mechanical properties of both phases.

Furthermore, an investigation is required largely to determine the nature of the hydride formed under different conditions, along with its subsequent reactivity when exposed to the atmosphere. A thorough understanding of these two related systems would permit operational risk to be more accurately quantified when working with this material.

Additionally, a thorough investigation and determination of the effect of localised stress in the metal on corrosion behaviour is recommended. The recent work on stress corrosion in uranium is tantalising but far from comprehensive. Certainly, it is the case that uranium components are frequently strained, via manufacturing, processing, irradiation etc. If the effect of strain is determined, then by knowing the level of stress, the long-term corrosion behaviour may be better predicted. This would be the case for spent uranium fuel materials, where there is little literature corrosion data available. A comprehensive study of hydride formation on spent/irradiated uranium metal fuel is therefore recommended to provide reaction rate data to better underpin safety predictions of material state in storage.

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