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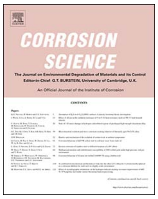

Review

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

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ABSTRACT

Uranium hydride (UH_3) 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 (UH_3)

Under the correct conditions, uranium and hydrogen readily combine to form a metal hydride (UH_3) 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.

$$2U + 3H_2 \leftrightarrow 2UH_3 \tag{1}$$

1.1. *Corrosion*

When uranium is corroded by hydrogen, the formation of UH_3 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. *UH_3 potential uses and applications*

The hydriding reaction (Eq. (1)) is reversible as the UH_3 decomposes upon heating to uranium metal and H_2 (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 $U + H_2$ system. More recently, the reactor research community has added to the list of interested parties for UH_3 research, investigating it as a candidate fuel material for future small modular nuclear reactors (SMRs) [11]. Such SMR concepts harness the effectiveness of H_2 as a neutron moderator with the fact it is evolved from UH_3 at high temperatures. This relationship between temperature and H_2 release creates a feedback loop (charge-discharge

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Table 1
The different phases and structural properties of uranium and uranium hydride. U [18,19], UH_3,UD_3 [20–22] and UT_3 [23].

Metal/ compound	Symmetry	Lattice cell parameter (Å)			Density (g/cm^3)
α-UH_3	Cubic	4.160 ± 0.001			11.12
α-UD_3	Cubic	4.150			11.33
α-UT_3	Cubic	4.142 ± 0.002			11.55
β-UH_3	Cubic	6.645			10.92
β-UD_3	Cubic	6.620 ± 0.002			11.11
β-UT_3	Cubic	6.625 ± 0.003			11.29
		a	**b**	**c**	
α-uranium	Orthorhombic	2.85	5.87	4.96	$19.07_{(25\,^{\circ}\mathrm{C})}$
β-uranium	Tetragonal	10.76	/	5.66	$18.17_{(662\,^{\circ}\mathrm{C})}$
γ-uranium	Body centred Cubic	3.52	/	/	$17.94_{(772\,^{\circ}\mathrm{C})}$

cycles) that can allow the reactor to self-regulate its temperature and criticality. Recent work has also shown that due to the kinetic isotope effect between hydrogen and deuterium (D_2), UH_3 shows promise as a material for industrial gas chromatographic separation of hydrogen isotopes [12].

The following sections of this review examine the published literature which describes the physical and chemical properties of UH_3, first focusing on the properties of the material, then the formation reaction, and finally the interaction between UH_3 with its surrounding environment. This understanding is applicable across the spectrum of uses, with greatest importance for safe uranium storage.

2. Fundamental properties

A large density difference exists between the hydride and the precursor metal (Table 1), meaning that UH_3 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 UH_3 are known; α-UH_3 and β-UH_3 (Table 1) [20]. In both phases, each uranium atom is surrounded by 12 equidistant hydrogen atoms at a distance of 2.32 Å [22], as shown in Fig. 1a & b. The lattice parameter for both phases is observed to decrease as a function of molecular weight.

The phase exhibited (or proportion of phases present) is observed to depend on the temperature of formation [24]. The more common phase is β-UH_3 which is formed rapidly, especially at high temperature [25–27]. A small number of studies have investigated the relationship between hydride phase and formation temperature (See Table 2). The proportion of α-UH_3 phase forming is reported to increase with decreasing reaction temperature, and given a sufficiently low reaction temperature, a pure α-UH_3 phase may be formed; however, at very low temperatures and ordinary pressures, the rate of hydride formation would be small and a pure sample of bulk α-UH_3 has yet to be formed. Therefore β-UH_3 is regarded as the ‘default’ hydride reaction product, and the expected phase for most reaction conditions explored in the literature.

2.1.1. α-UH_3

The more compact of the two hydride phases, α-UH_3 has been observed to possess a cubic lattice (Pm3n) with 2 uranium atoms per unit cell, of dimension 6.160 ± 0.001 Å (Fig. 1a) [20]. Results from atomistic modelling have suggested that α-UH_3 is isomorphous with α-U but not β-UH_3, allowing α-UH_3 to form via spinodal decomposition in a hydrogen saturated metal to then act as nucleation sites for subsequent β-UH_3 formation [28].

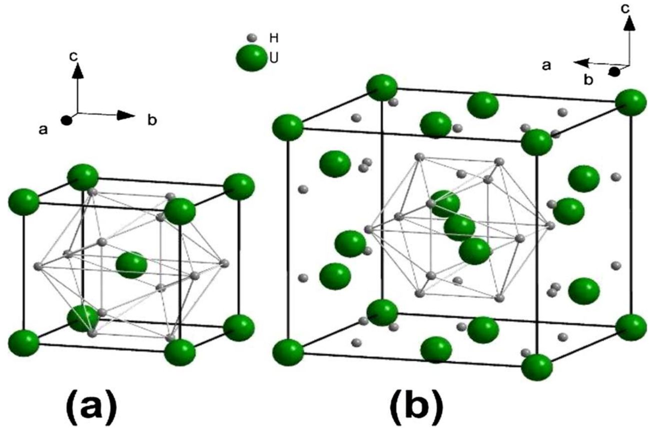

Fig. 1. Crystal structure of (a) α-UH_3 and (b) β-UH_3 drown using Diamond (version 2.1c) software. The small and large spheres stand for hydrogen and uranium atoms, respectively. For α-UH_3 the 12 nearest hydrogen atoms are shown around the U (½,½,½) atom, occupying the H: ± (1/4,0,1/2) (1/2,1/4,0), ± (0,1/2,1/4). For β-UH_3 the 2 UI ions sit on the bcc lattice, whilst the 6 UII atoms make up the rest of the structure. The hydrogen atoms around the UII lie on: ± (0,u, ± 2u), ± (1/2, ± 2u,1/2 + u) where u = 0:155. All UI and UII distances are the same. Figure reproduced from reference [102].

Table 2
The proportion of α:β-UH_3 formed over a range of temperatures.

Temperature (°C)	a:β-UH_3	Reference
− 80	1:0	[20,25]
Room temperature	1:1.5	[20,25]
125	1:5.7	[20]
200	0:1	[25–27]

2.1.2. β-UH_3

Like with the α-phase, β-UH_3 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 UH_3 and 6.627 ± 0.001 Å for UD_3, 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-UH_3 holds ≈ 1.105 times as much H_2 as β-UH_3 per unit volume. Also, according to theoretical data, α-UH_3 contracts with applied pressure by 0.25 A^3/GPa for low-pressure regimes [29] while for β-UH_3 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-UH_3 and β-UH_3 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 surface adsorbed H_2 and the UH_3 [31]. The rate of exchange between gas and solid, for environments of 70–700 kPa H_2 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-UH_3 has been recorded as co-existing in a stable state with the β-phase but is totally converted to β-UH_3 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 UH_3 and UD_3 measured at 25 °C (i.e. a