Hydriding properties of uranium alloys for purposes of searching for new hydrogen storage materials (Postprint)

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Abstract

Hydriding properties of uranium alloys have been studied to search for new hydrogen storage materials to be applied to hydrogen energy systems. Application of uranium-base hydrogen storage materials can be expected to alleviate the risk, as well as to reduce the cost incurred by globally-stored large amounts of depleted uranium left after uranium enrichment. Various uranium alloys have been examined in terms of hydrogen absorption-desorption properties, among which UNiAl intermetallic compound showed promising characteristics, such as lower absorption-desorption temperatures and better anti-powdering strength. First principle calculation has been carried out on UNiAl hydride to predict the change of crystal structure and the lattice constant with increasing hydrogen content, which showed this calculation to be promising in predicting candidates for good hydrogen absorbers.

Full Text

Preamble

Hydriding properties of uranium alloys for purposes of searching for new hydrogen storage materials

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Hydriding properties of uranium alloys have been studied to search for new hydrogen storage materials for hydrogen energy systems. Application of uranium-based hydrogen storage materials can be expected to alleviate the risk and reduce the cost incurred by globally-stored large amounts of depleted uranium left after uranium enrichment. Various uranium alloys have been examined in terms of hydrogen absorption-desorption properties, among which the UNiAl intermetallic compound showed promising characteristics, such as lower absorption-desorption temperatures and better anti-powdering strength. First-principle calculations have been carried out on UNiAl hydride to predict the change of crystal structure and the lattice constant with increasing hydrogen content, demonstrating that this calculation approach is promising for identifying candidates for good hydrogen absorbers.

Keywords: Depleted uranium, Hydrogen storage material, Uranium alloys, UNiAl intermetallic compound, First principles calculation
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Introduction

The hydrogen energy system requires a large-scale stationary storage facility at hydrogen generation plants. Common forms for hydrogen storage include compressed gas, cryogenic liquid, and metal hydrides [1]. Each storage method has advantages and disadvantages, as well as requiring some degree of energy consumption that mainly arises from gas compression, maintaining cryogenic temperature, or heating metal hydrides for desorption. One advantage of using metal hydrides is inherent safety, as they only require moderate pressure for storage and passively contain hydrogen in case of power loss. One disadvantage of metal hydrides for mobile storage is limited mass energy density, though this is not a practical concern for stationary systems; rather, they may achieve volume energy density as high as other methods. The cost of metal hydride storage systems depends largely on the material and operational temperature range. Yamawaki et al. have previously proposed a surplus electricity storage system utilizing depleted uranium as a base storage material [2, 3].

Depleted uranium has been produced abundantly as waste from uranium enrichment but has never been used effectively, usually stored idly as uranium fluoride gas or in solid form. Conversely, uranium is one of the highest-capacity hydrogen storage materials, readily absorbing hydrogen to form uranium hydride (UH_3) at room temperature and discharging hydrogen reversibly at elevated temperature. Uranium has commonly been used to store tritium, the radioactive isotope of hydrogen, since the room-temperature desorption pressure is low enough to securely contain it. However, discharging hydrogen at a dissociation pressure of

10^5 Pa requires heating the hydride to about 700 K, which is rather high for hydrogen storage applications and incurs significantly large operational energy loss. Further, uranium undergoes large volumetric expansion upon hydrogenation due to substantial crystal structure changes, causing severe powdering that leads to low thermal conductivity and increased pyrophoricity. To address these issues, Yamawaki and co-workers have studied hydrogen absorption-desorption properties of various uranium alloys to find materials with improved anti-powdering capacity and higher desorption pressure [3–10].

The objective of this paper is to summarize the status and development approach of uranium alloys as hydrogen storage materials.

II. Hydrogen Absorption-Desorption Properties of Uranium Alloys

A. U-Zr and U-Ti Alloys

Hydrogen absorption-desorption properties and air reactivity of U-Zr and U-Ti alloys were investigated for use in depleted uranium-based energy storage systems and tritium storage systems [3-8]. Some U-Zr and U-Ti alloys exhibit hydrogen absorption-desorption properties comparable to pure uranium, while the pyrophoricity of Zr- or Ti-rich uranium alloys is more moderate than U-rich alloys due to higher resistance against powdering upon hydrogenation [3, 7]. Table 1 summarizes the hydrogen storage capacities of U-Zr and U-Ti alloys [3]. Upon hydrogenation, U-Zr and U-Ti alloys decompose into UH_3 and ZrH (x < 2) and UH_3 and UTi_2H (x < 5) phases, respectively, so that pressure-composition-temperature (P-c-T) diagrams consist of plateau regions of corresponding phases. Because of the low equilibrium hydrogen pressure of ZrH phases, the rechargeable hydrogen capacities of U-Zr alloys depend on the fraction of UH_3 phase (or U content in the alloy), except for UZr_2 where the UH_3 region becomes smaller after cycling.

In U-Ti alloys, ternary UTi_2H_5 phase formation consumes some uranium to narrow the UH_3 plateau region, while utilizing the lower-pressure UTi_2H_5 plateau can extend the rechargeable capacity. Alloying U with Zr or Ti basically maintains the equilibrium pressure of UH_3, while powdering is greatly reduced, especially with high Zr or Ti content. Table 1 also shows the degree of powdering after approximately 20 hydrogen absorption-desorption cycles [3]. UZr, UZr_2, and UTi_2 alloys demonstrated significant resistance against severe disintegration into fine powders even after more than 10 cycles. UZr especially possesses a good balance of large capacity and high resistance against powdering.

B. U-Mn, U-Fe and U-Ni Alloys

Uranium-rich intermetallic compounds, namely U_6M (M = Fe, Mn, Ni), commonly form in these binary systems. The cubic $MgCu_2$-type UM_2 phase is the only other intermetallic phase in the U-Mn and U-Fe systems, while four additional phases form in the U-Ni system, including UNi_5 and UNi_2 with known $AuBe_5$- and Cu_2Mg-type crystal structures, respectively, as well as U_5Ni_7 and U_7Ni_9. Hydrogen absorption properties of these compounds have been studied [6, 10], where none of the alloys except the U_6M-type compounds were found to be reactive with hydrogen. All U_6M-type compounds absorbed hydrogen to form UH_3 and the corresponding UM_2 phases. The P-c-T isotherms of these alloys basically consist of a wide single plateau of UH_3. As shown in Fig. 1 [Figure 1: see original paper], the plateau pressures in these U_6M alloys are all higher than pure uranium. Among the alloys, U_6Fe has the highest desorption pressure.

C. UCo

UCo, one of six known intermetallic compounds in the U-Co system, forms $UCoH_{2\cdot7}$ [9, 11]. Our study on hydrogen absorption-desorption behaviors revealed two-stage desorption reactions at temperatures above 473 K, while only a single stage was observed below 423 K. UCo readily absorbs hydrogen to form $UCoH_{2\cdot7}$ at temperatures below 423 K under hydrogen pressure of 10^5 Pa. It simply dehydrogenates reversibly at 423 K, while two phases, UH_3 and UCo_2, appear during desorption of $UCoH_{2\cdot7}$ above 473 K. This occurs due to two competing reactions:

$UCoH_{2\cdot7} = 0.5UCo_2 + 0.5UH_3 + 0.6H_2$,
$UCoH_{2\cdot7} = UCo + 1.35H_2$.

The standard Gibbs energy changes, $\Delta G^0{}_1$ and $\Delta G^0{}_2$, for reactions (1) and (2), respectively, as functions of temperature T and hydrogen pressure p, were estimated as follows:

$\Delta G^0{}_1 = 8.4 \times 10^4 - 174T + 0.6RT \ln(p/p_0)$,
$\Delta G^0{}_2 = 7.4 \times 10^4 - 147T + 1.35RT \ln(p/p_0)$,

where p_0 is standard pressure (101,325 Pa), R is the gas constant (8.3 J/(mol · K)), and each Gibbs energy is calculated per mole of $UCoH_{2\cdot7}$. Fig. 2 [Figure 2: see original paper] plots $\Delta G^0{}_1$ and $\Delta G^0{}_2$ versus T with unfilled and filled symbols, respectively, for two pressure cases. Solid lines with circles represent $p = 10^4$ Pa, while broken lines with squares represent $p = 10^5$ Pa. For lower pressure ($p = 10^4$ Pa), $\Delta G^0{}_2$ is lower than $\Delta G^0{}_1$ over a wide temperature range below 650 K, while at $p = 10^5$ Pa, $\Delta G^0{}_1$ is lower at $T > 400$ K. This results in observation of a single-stage reaction (2) at lower temperature and pressure, while two-stage reactions including decomposition into UCo_2 and UH_3 occur at higher temperature and pressure.

While desorption operations may be limited in pressure range, UCo can reversibly absorb and desorb hydrogen at a relatively low temperature of 423 K with desorption pressure significantly higher than that of UH_3.

D. UNiAl and Other Fe_2P-Type Uranium Compounds

UNiAl intermetallic compounds have a hexagonal Fe_2P-type (also known as ZrNiAl-type) crystal structure. As illustrated in Fig. 3 Figure 3: see original paper, the unit cell consists of stacked planes, one with three U and one Ni atom and another with three Al and two Ni atoms. Table 2 shows atomic positions in terms of Wyckoff notation and representative partial coordinates. In the original crystal structure, two U atom triangles per unit cell, together with two Ni atoms on adjacent planes, create tetrahedral interstitial sites sharing the triangle, as also shown in Fig. 3(a). At hydrogen pressures below 10^5 Pa, UNiAl absorbs up to two hydrogen atoms per unit cell, or approximately 0.7 H per UNiAl formula unit (H/F.U.) [11-13]. Neutron diffraction study of deuteride $UNiAlD_{0\cdot7}$ showed D atoms occupy U_3Ni_1-type interstitial sites. At higher hydrogen pressure, absorption can reach approximately 2 H/F.U. [14]. Yamamoto et al. showed that the crystal structure of $UNiAlH_{2\cdot2}$ or $UNiAlD_{2\cdot2}$ has significantly different atomic positions while retaining the basic hexagonal structure. Table 2 also details the crystal structure of deuterides, including atomic positions. In $UNiAlD_{2\cdot2}$ formation, uranium positions shift to increase x in the representative coordinate (x, 0, 1/2) of the 3g position. Aluminum atoms also move within the plane in the same direction as U atoms, while Ni atoms in the 1b position move along the c-axis from $z = 1/2$ to $z = 0$. These changes are illustrated in Fig. 3(b), with Figs. 3(c) and 3(d) showing U and Ni atom positions on the $z = 1/2$ plane for UNiAl, $UNiAlD_{0\cdot7}$, and $UNiAlD_{2\cdot2}$, respectively. U atoms shift to increase x from 0.580 to 0.592 and 0.659, making the U triangle forming a U_3Ni_1-type interstitial site larger by 4% and 17%, respectively, presumably required to secure the U-D distance. Notably, these shifts also make other U triangles similarly equilateral. Deuterium-occupied sites are shown in Figs. 3(c) and 3(d) with three different triangle symbols for U_3Ni_1-type D(1), U_3Al_1-type D(2), and U_3Ni_{11}-type D(3) sites, respectively. The final D site structure suggests that atomic position shifts enable this compound to accept around six hydrogen atoms per unit cell.

Hydrogen desorption isotherms of UNiAl have been studied in detail by Yamanaka et al. [14]. Fig. 4 [Figure 4: see original paper] shows hydrogen desorption pressures at two plateau regions, between α and β and β and γ phases, corresponding to the following nominal reactions:

$$UNiAl + 1/3H_2 = UNiAlH_{0\cdot66},$$
$$UNiAlH_{0\cdot66} + 2/3H_2 = UNiAlH_2,$$

where H compositions are nominal values based on H atoms occupying the 4h site and the 4h, 3g, and 2e sites for β and γ phases, respectively. The figure indicates that desorption pressure for reaction (6) reaches approximately 10^5 Pa at 400 K, which is sufficiently high for hydrogen storage applications. The lower plateau reaches 10^5 Pa at approximately 550 K, which may be acceptable, while using only the higher plateau region allows recycling of around 2/3 of the total hydrogen capacity.

III. First Principles Calculations Based Approach to New Uranium Hydrides

Approximately 20 known ternary uranium compounds have ZrNiAl-type crystal structure. A few of them and their quaternary mixtures have been investigated for hydrogen absorption properties [16–19]. Among those examined, UNiAl has the largest hydrogen capacity at approximately 2 H/F.U., while all others hold no more than approximately 1 H/F.U. This suggests that metallic atom relocations described in the previous section are crucial for large hydrogen capacity. In searching for other ZrNiAl-type U intermetallic compounds that can hold large hydrogen amounts, knowing the possibility of such atomic relocations would provide valuable guidance. First-principle calculations of potential hydrides can examine this possibility. As a starting point, we carried out calculations of UNiAlH with n up to 2, which shows that the crystal unit in Fig. 3(a) holds up to six H atoms, to learn how theory can inform potential hydrogenation behavior.

First-principle calculations based on density-functional theory (DFT) were performed using the Vienna ab-initio simulation package (VASP) with generalized gradient approximation and projected augmented wave potentials [20, 21]. We employed a hexagonal unit cell containing three UNiAl formula units as shown in Fig. 3(a) with its Brillouin zone using 3$×3×$5 k-point sampling via the Monkhorst-Pack scheme [22]. The plane-wave energy cutoff was 350 eV. Atomic positions and cell size relaxations were iterated until the total energy between two ionic steps was smaller than 0.0005 eV.

Two metallic atom structures were considered. Structure A is based on the original UNiAl structure, while Structure B is based on the experimentally observed UNiAlD$_{2\cdot2}$ crystal structure. The key difference is that 1/3 of Ni atoms occupy 1(b) (0, 0, 1/2) positions in Structure A but 1(a) (0, 0, 0) in Structure B. Hydrogen atoms were initially placed in positions where D atoms were found to occupy in UNiAlD$_{0\cdot7}$ and UNiAlD$_{2\cdot2}$. Calculation details will be reported in the future, while preliminary DFT results support various experimental observations. For example, Fig. 5(a) shows the total enthalpy of the 3(UNiAlH) + 3(1−n/2)H$_2$ system from DFT calculations as a function of n for both metallic atom structures. Structure A has lower energy for n $\leq$ 2/3 (two H atoms in the crystal unit shown in Fig. 3(a)), while for n $\geq$ 1, Structure B becomes more energetically favored. The most stable crystal structure in DFT calculations also supports observed shifts in atomic positions of U and Al along the x-axis (listed in Table 2). Fig. 5(b) plots lattice constants a and c as functions of H concentration n (= H/UNiAl) for both DFT and experiments. The characteristic trends of increasing a while decreasing c with increasing n show qualitative agreement between calculations and experiments. Although these are preliminary results requiring more detailed quantitative comparison, they at least qualitatively support experimental trends, suggesting this approach can generate a list of candidates for good hydrogen absorbers.

IV. Conclusion

A hydrogen energy age is approaching where metal hydrides will be used as hydrogen storage materials. Alloys of uranium with Zr, Ti, Mn, Fe, Ni, and Co have each been examined for hydrogen storage potential. Each alloy has advantages and disadvantages, while the UNiAl intermetallic compound has been evaluated as considerably promising due to relatively low working temperatures and good anti-powdering strength. First-principles calculations have been carried out on UNiAlH to estimate changes in crystal structure and lattice constants with varying hydrogen content. The results support experimental trends, suggesting this approach is promising for generating a list of candidates for good hydrogen absorbers.

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