U-Ti alloy as a promising storage material for hydrogen isotopes

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Abstract
Conventionally, uranium metal is used for the storage of heavier isotopes of hydrogen (D and T). However, it has several disadvantages with respect to handling due to the formation of very fine powder which leads to high pyrophoricity. It has also very low retention power for $^3$He at ambient temperature. Uranium alloys are better choice with respect to above properties. This paper summarizes some aspects of storage behavior of hydrogen isotopes in uranium-titanium alloy.

Introduction
Storage of hydrogen isotopes (H, D and T) in the solid state is the safest and most advantageous method over other conventional methods like gaseous storage in high pressure gas cylinders and liquid storage in cryogenic tanks. Hydrogen and its isotopes can be stored in the solid state by combining it with a solid state material through physisorption, chemisorption or by chemical reactions. At elevated temperatures, hydrogen reacts with many transition metals, f-block elements and their alloys to form hydrides. The nature of the chemical bond determines the thermodynamic stability of the hydride, the hydrogen stoichiometry of the material, and the mechanisms for hydrogen absorption and release. For the metal hydride to be used as a storage medium, it should satisfy certain requirements such as high hydrogen storage capacity, facile reversibility of hydride formation and decomposition reactions, compatible absorption-desorption kinetics, resistance to deactivation etc. In recent years, some selected metal hydrides are chosen as potential medium for hydrogen storage.

Storage of $^3$H isotope as metal hydrides
The heaviest isotope of hydrogen ($^3$H or T) is one of the critically important elements in the field of fusion reactor technology. It is radioactive in nature and does not exist in significant amount. Therefore any equipment used for the storage of this isotope should be designed in such a way that it does not release it easily into the environment under ambient conditions. In this sense, T-storage equipment using metallic beds is rated to be more suitable than that using either the gaseous or liquid form of storage. Some of the metallic systems used for T-storage are alloys of titanium, zirconium, lanthanum and uranium. However, for the appropriate absorption-desorption of T, at intermediate temperature range of 300-400°C, only ZrCo and some of the uranium...
alloys are suitable candidate materials. In particular, ZrCo alloy absorbs reversibly an appreciable amount of hydrogen isotopes (maximum $H/ZrCO = 3$), exhibits low hydrogen release pressure under ambient conditions and resistant to pyrophorocity and hence considered as a suitable material for storage and transport of hydrogen isotopes in the international thermonuclear experimental reactors (ITER). Research on storage and release behavior of ZrCo alloy with respect to $H_2$, $D_2$, and $T_2$ has been carried out in our laboratory [1] and it was demonstrated that this alloy has favorable dissociation pressures and reaction kinetics for this ITER application. However, under high hydrogen pressure at high temperatures or during repeated absorption-desorption, this alloy loose its hydriding ability. Under thermal cycling, ZrCo undergoes hydrogen induced disproportionation into more stable hydride $ZrH_2$ and hydrogen non-absorptive intermetallic compound $ZrCo$, thus reducing its storage and recovery ability.

On the other hand, uranium bed, in particular, is predominantly used to pump, store and purify $T_2$ in gaseous form because: (i) large quantities of $T_2$ can be stored in the smallest volume ($T/U$ atomic ratio upto 3); (ii) it exhibits a dissociation pressure less than $10^{-3}$ Pa at 298 K, thus preventing the release of $T_2$ to the atmosphere under ambient conditions; (iii) the pressure of $T_2$ can be controlled by adjusting the uranium bed temperature. Typically at 700 K, it exhibits a dissociation pressure sufficiently high to release $T_2$; (iv) the PC isotherms show a wide plateau, assuring a constant release pressure over a wide hydrogen concentration range; (v) fast uptake of $T_2$ even at low pressures is possible; (vi) surplus $T_2$ can easily be recovered at room temperature from the vacuum system and be reabsorbed back onto the getter for later use thereby reducing the discharge to the environment by orders of magnitude; (vii) the decay product $^3\text{He}$ which has accumulated during storage can simply be pumped off.

However, U easily disintegrates into fine powder on hydrogenation. Such powdering reduces its heat conductivity and hence temperature control of specimens becomes difficult. Further, in an accidental situation, the powder may ignite on coming in contact with leaking air. Therefore, U is desired to be improved as to its hydrogen storage property by alloying. The hydrogen storage behavior of uranium alloys has been studied to a limited extent and hence opens up a new area of research. In particular, U-Zr and U-Ti alloys are thought to be promising materials for $T_2$-storage [2, 3]. The U-Ti system comprises of an intermetallic compound $U_2\text{Ti}$. As titanium exhibits high durability to powdering on hydrogenation, the $U_2\text{Ti}$ intermetallic compound may possess an excellent durability to powdering. The $^3\text{He}$ retention capacity of uranium bed is very low even at ambient conditions whereas that for titanium is very high. Hence, $U_2\text{Ti}$ alloy is expected to have intermediate capacity for retention of $^3\text{He}$.

We have studied the hydrogen absorption-desorption behavior of $U_2\text{Ti}$, and its application as a storage material. In order to get an insight into the $T_2$ storage behavior of $U_2\text{Ti}$, we first carried out a detailed study of its hydrogen storage behavior, and subsequently extrapolated our results to draw conclusions regarding its $T_2$ storage property.

**Thermodynamics of hydrogen absorption-desorption**

In general, the metal-hydrogen reaction can be expressed by the following reaction:

$$M(s) + \frac{x}{2}H_2(g) \rightarrow MH_x(s) + Q$$  \hspace{1cm} (1)

where, $M$ is a metal, a solid solution or an intermetallic compound, $MH_x$ is the metal hydride, ‘$x$’ is the ratio of hydrogen to metal denoted as $H/M$ and $Q$ is the heat released during reaction.
The hydrogen absorption reaction is generally exothermic. Metal hydride formation comprises of the following five essential processes: (1) physisorption of hydrogen molecules; (2) dissociation of hydrogen molecules and chemisorption; (3) surface penetration of hydrogen atoms; (4) diffusion of hydrogen atoms through the hydride layer; either by an interstitial or a vacancy mechanism and (5) hydride formation at the metal/hydride interface. For dehydrogenation, the process is the reverse.

The behavior of metal-hydride systems can be best represented by pressure-composition isotherms (PCIs). The host metal initially dissolves some hydrogen as a solid solution (α-phase). As the hydrogen pressure together with the concentration of H in the metal is increased, interactions between hydrogen atoms become locally important, and we start to see nucleation and growth of the hydride (β) phase. While the two phases coexist, the isotherms show a flat plateau, the length of which determines how much H\(_2\) can be stored reversibly with small pressure variations. In the pure β-phase, the H\(_2\) pressure rises steeply with the concentration. At higher H\(_2\) pressure, further plateaus and further hydride phases may be formed. The two-phase region ends in a critical point \(T_c\), above which the transition from α to β phases is continuous. The plateau or equilibrium pressure depends strongly on temperature and is related to the changes in enthalpy and entropy of the metal-hydrogen reaction. Stable hydrides require higher temperatures than less stable hydrides to reach a certain plateau pressure.

Thermodynamic parameters like changes in standard free energy (\(\Delta_r G^\circ\)), enthalpy (\(\Delta_r H^\circ\)) and entropy (\(\Delta_r S^\circ\)) of metal-hydrogen reaction are calculated from PC isotherms, using the following equations:

\[
\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ
\]  
\[
\ln P_{H_2} = \frac{2 \Delta_r H^\circ}{x \cdot RT} - \frac{2 \Delta_r S^\circ}{x \cdot R}
\]

From a number of measurements of plateau pressures \(P(H_2)\) at different temperatures, a van’t Hoff plot is constructed by plotting \(\ln P(H_2)\) as function of \((1/T)\). The \(\Delta_r H^\circ\) and \(\Delta_r S^\circ\) are evaluated from the slope and intercept using equation (4). As the entropy change corresponds mostly to the change from molecular hydrogen to dissolved hydrogen, the entropy for all metal hydrogen systems under consideration is approximately same.

### Hydrogen Isotope Effect on dissociation pressure of metal-hydrogen systems

It is well known that the pressure-composition isotherms (PCIs) of metal or intermetallic compound-hydrogen systems are affected to some extent by the type of hydrogen isotopes. The isotope effect arises from the interplay of two thermodynamic factors namely, entropy and enthalpy that control the relative stabilities of the corresponding isotope hydrides. Since the absolute entropies of hydrogen isotopes in the gas phase follow the order \(S(H_2) > S(D_2) > S(T_2)\), therefore the \(\Delta S^\circ\) of the heavier isotope hydride is more negative than the lighter ones leading to a ‘positive or normal’ isotope effect. The enthalpy of hydrogenation reaction also decides the nature of isotope effect. When the \(\Delta_r H^\circ\) of the lighter isotope hydride is more negative than the heavier isotope hydrides, a normal isotope effect is always observed. In this case the plateau pressure of the hydrogen isotopes will follow the trend:

\[
p(T_2) > p(D_2) > p(H_2)
\]  

On the other hand, when the \(\Delta_r H^\circ\) of the heavier isotope hydride is more negative than the lighter ones, a temperature dependent isotope effect is expected. Below a certain temperature, inverse isotope effect will be observed whereas above this temperature the isotope effect is normal.
The U-H system shows positive isotope effect. Literature data on this system shows that the enthalpy of hydrogenation of uranium metal is nearly same (within 1 kJ/mole) for H₂, D₂ and T₂. Hence, the difference in equilibrium plateau pressure for these three isotopes arises due to the difference in entropy of reaction. Hence, by knowing the van’t Hoff relation for only one hydrogen isotope in the uranium system and the isotopic effect on the entropy of hydrogenation reaction, one can predict the equilibrium plateau pressures of higher isotopes D₂ and T₂.

Studies on hydrogen storage behavior of U-Ti system

In the present investigation, the hydrogen absorption-desorption behavior and the Pressure-Composition Isotherms (PCIs) of the intermetallic compound U₂Ti was investigated using a Sievert-type volumetric apparatus (Fig.1). The apparatus essentially comprises of: (1) a cylindrical sample holder of known volume; (2) a kanthal wire wound resistance furnace; (3) a hydrogen reservoir of known volume; (4) Piezoresistive-type pressure transducer of range 0 - 0.15 MPa to monitor system pressure; (5) a rotary vacuum pump backed by a diffusion pump; (6) a pirani gauge with gauge head to measure vacuum pressure; (7) K-type thermocouples to measure the temperature. The reaction vessels are made of quartz while the other parts are made mostly of stainless steel. The maximum attainable vacuum is of the order of 10⁻⁵ Pa.

Hydrogen absorption-desorption properties of U₂Ti

Typical hydrogen absorption-desorption curves for three successive hydrogen absorption-desorption cycles are shown in Fig.2 which indicate two-stage absorption-desorption for this alloy. From the hydrogen concentration measurement, it is inferred that the high-temperature absorption is primarily due to the reaction:

\[ \text{U}_2\text{Ti} + \frac{3}{2} \text{H}_2 \rightarrow \text{U}_2\text{TiH}_2\text{H}_4 \]  

(5)
whereas the low temperature absorption is due to the reaction:

$$U_2\text{TiH}_{2.4} + \frac{5.2}{2}H_2 \rightarrow U_2\text{TiH}_{7.6}$$  \hspace{1cm} (6)

A misfit was observed between the absorption and desorption curves indicating the presence of hysteresis. From this figure, it can also be seen that after each cycle there was a decrease in the final pressure of the system due to partial decomposition of $U_2\text{Ti}$ matrix to $\beta(\text{Ti})$ and $\gamma(\text{U})$ phases. The extent of decomposition increased with number of thermal cycles. Also, the extent of hysteresis is observed to decrease with each successive cycle, indicating conversion of the macrocrystalline alloy to a microcrystalline form.

**Pressure-Composition Isotherms of $U_2\text{Ti}$**

In this study, Pressure-Composition-Isotherms for $U_2\text{Ti}$-H system were generated at three different temperatures 616, 647 and 678 K which are shown in Fig.3. In all the three cases, only one plateau was observed in this temperature region which can be attributed to the reaction:

$$\frac{2}{5.2} U_2\text{TiH}_{7.6} \rightarrow \frac{2}{5.2} U_2\text{TiH}_{2.4} + H_2$$  \hspace{1cm} (7)

However, the plateau corresponding to desorption from $U_2\text{TiH}_{2.4}$ to generate $U_2\text{Ti}$ was not observed at these temperatures but based on the absorption-desorption studies (Fig.2) it is expected to be observed at higher temperatures. Investigation of the second plateau is in progress and hence not reported here.

Using the plateau pressures of these three isotherms a van’t Hoff plot was constructed and is shown in Fig.3. From the van’t Hoff plot, temperature dependence of the plateau pressure was found to be expressed by the equation:

$$\ln \left( \frac{p_{24}}{p^0} \right) = (-10140/T) + 13.86$$  \hspace{1cm} (8)

From this relation, the enthalpy change and the entropy change of the reaction (7) for decomposition of $U_2\text{TiH}_{7.6}$ to $U_2\text{TiH}_{2.4}$ were deduced to be 83.7±6.4 kJ/mol $H_2$ and 116.6±9.9 J/(mol $H_2$ K), respectively. These values are in good agreement with the values reported in literature [2]. The values of dissociation pressures of reaction (7) and those of $U\text{H}_3$ from literature [4] are compared in Fig.4 which shows a higher dissociation pressure for $U\text{H}_3$.

From the experimental data, the increment in entropy of hydrogenation reaction of uranium metal
Table 1: Summary of isotope effect on the plateau pressures of U-H and U$_2$Ti-H systems.

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>van't Hoff equation: $\ln \left( \frac{P}{T^A} \right) = \frac{A}{T} + B$</th>
<th>$A$</th>
<th>$B$</th>
<th>This study</th>
<th>$A$</th>
<th>$B$</th>
<th>Ref. [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{2}{3} U_2TiH_{\frac{7.6}{2}} \rightarrow \frac{2}{3} U_2TiH_{\frac{2.4}{2}} + H_2$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\frac{2}{3} UH_\text{III} \rightarrow \frac{2}{3} U + H_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydride</td>
<td>10140</td>
<td>13.86</td>
<td>Experimental</td>
<td>10421</td>
<td>14.71</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>Deuteride</td>
<td>10140</td>
<td>14.16</td>
<td>Predicted</td>
<td>10363</td>
<td>15.81</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>Tritide</td>
<td>10140</td>
<td>14.30</td>
<td>Predicted</td>
<td>10297</td>
<td>15.15</td>
<td>Experimental</td>
<td></td>
</tr>
</tbody>
</table>

is 2.49 J/(mol H$_2$·K) from H$_2$ to D$_2$ and 1.16 J/(mol H$_2$·K) from D$_2$ to T$_2$. Using the same experimental entropy increment value and the experimental enthalpy of reaction obtained in this study, we have calculated the equilibrium plateau pressures of D$_2$ and T$_2$ for the reaction (7) and compared them in Fig.4. However, it is important to validate these predictions with experimental data and hence the PCT experiments with heavier isotopes of hydrogen are in progress.

Conclusions

The hydrogen absorption-desorption cycles of U$_2$Ti showed hysteresis with two-step absorption-desorption. With each cycle, a slight decrease in the final dissociation pressure was observed which was attributed to the partial decomposition of U$_2$Ti phase to β(Ti) and α(U) phase. The Pressure-Composition Isotherms were generated at 616, 647 and 678 K and from the van’t Hoff plot the enthalpy and entropy change of the reaction for decomposition of U$_2$TiH$_{\text{II}}$ to U$_2$TiH$_{\text{I}}$ were deduced to be 83.7 ± 6.4 kJ/mol H$_2$ and 116.6 ± 9.9 J/(mol H$_2$·K), respectively. Using positive isotope effect, the equilibrium plateau pressures of the heavier isotopes D$_2$ and T$_2$ were predicted.

References