KINDS AND CHARACTERISTICS OF HYDROGEN STORAGE ALLOY

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Summary

Metals belonging to groups IIA to VA in the Periodic Table readily combine with hydrogen to form metal hydrides. Except for Vanadium, all of these metals form very stable hydrides, which are difficult to absorb and desorb hydrogen reversibly around the normal temperature and pressure.

While many alloys which compound between these metals (metal A) and one of third transition metals not forming hydride (metal B) can form hydrides, too. Some of these alloys readily absorb and desorb hydrogen, which may be utilized for storing hydrogen, and are named “hydrogen storage alloy”.

A number of alloys, which can absorb and desorb hydrogen with relative ease, have been reported.
The first group is the combination of alkali earth metal A and transition metal B in the form of A₂B, as represented by Mg₂Ni. The alloy has a relatively higher capacity of hydrogen storage, but the stability of the hydride is so high that hydrogen cannot be desorbed at normal temperature.

The second group consists of alloys of combination type AB. A typical example is TiFe. These alloys form 𝛽-hydride (H/M = 0.5), and 𝝌-hydride (H/M = 1). For this reason, their hydrogen storage characteristics have two-stepped plateau and relatively extensive hysteresis. The third group includes alloys of type AB₂, of which metal A is Ti or Zr, and metal B is a third transition one.

Their crystal structures have Laves phase of type C₁₄ or C₁₅. A number of binary alloy hydrides have been recognized based on different combination of these metals. The fourth group is composed of alloys given by AB₅. Typical examples are LaNi₅, of which the hydrogen storage capacity is around H/M = 1.

Owing to the superior hydrogenation properties of LaNi₅, a lot of studies have been made on its properties and basic characteristics. Finally, alloys in the fifth group are of a solid solution type with BCC structure, which are characterized by large hydrogen storage capacities, H/M > 1.5.

1. Classification of Hydrogen Storage Alloys

Hydrogen is readily incorporated in hydrogen storage alloys, and when the concentration of hydrogen in the alloy comes to a certain limit, metal hydrides are formed. As a result, hydrogen occupies certain sites among the metal lattices.

The properties of hydrogen storage in an alloy are determined by the interaction of hydrogen with metal atoms at the interstitial site, and hence, the hydrogen storage characteristics depend largely upon the crystal structure of the alloy. Up to now, a number of hydrogen-storing alloys have been developed, and they may be classified into five groups shown in Table 1, based on the crystal structure of alloy and the similarity of hydriding characteristics.

The first group is the combination of alkali earth metal A and transition metal B in the form of A₂B, as represented by Mg₂Ni. All of alloys classified in this group have not always identical crystal structures, and hydrides formed may have different structures.

However, all of alloys contain magnesium, and their hydrogenation characteristics are similar very closely. These alloys have relatively higher capacity of hydrogen storage, but the stability of hydride is so high that hydrogen can be desorbed only when heated to higher temperatures.

The second group consists of alloys of combination typed AB. A typical example is TiFe. These alloys form 𝛽-hydride phase at around H/M = 0.5, and 𝝌-hydride phase at H/M = 1.
For this reason, their hydrogen storage characteristics have two-stepped plateau and relatively extensive hysteresis.

The third group includes alloys of type AB$_2$, of which metal A is Ti or Zr, and metal B is third transition one. Their crystal have Laves phase of type C14 or C15.

A number of binary alloy hydrides have been recognized based on different combinations of these metals.

The fourth group is composed of alloys given by AB$_5$. Typical examples are LaNi$_5$ and CaNi$_5$. The capacity of hydrogen storage of these alloys is around $H/M = 1$.

Owing to the superior hydrogenation properties of LaNi$_5$, a lot of studies have been made on its properties and basic characteristics.

Finally, alloys in the fifth group are of solid solution type with BCC structure, which are characterized by large hydrogen storage capacity, $H/M > 1.5$. 

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### Kinds and Characteristics of Hydrogen Storage Alloy

<table>
<thead>
<tr>
<th>Type</th>
<th>Alloy</th>
<th>Crystal structure</th>
<th>Lattice Constant nm</th>
<th>Hydride*2</th>
<th>Plateau width Δ(H/M)</th>
<th>Desorption Pressure (Temp) MPa (K)</th>
<th>Multiple alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;B</td>
<td>Mg&lt;sub&gt;2&lt;/sub&gt;Ni</td>
<td>(P6222)</td>
<td>a=0.522 c=1.320</td>
<td>Mg&lt;sub&gt;2&lt;/sub&gt;NiH&lt;sub&gt;4&lt;/sub&gt;*3</td>
<td>1.3</td>
<td>0.54 (595) Mg&lt;sub&gt;2&lt;/sub&gt;Ni&lt;sub&gt;0.75&lt;/sub&gt;Cu&lt;sub&gt;0.25&lt;/sub&gt; Mg&lt;sub&gt;2&lt;/sub&gt;-xAl&lt;sub&gt;x&lt;/sub&gt;Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg&lt;sub&gt;2&lt;/sub&gt;Cu</td>
<td>(Fdd)</td>
<td>a=0.5284 b=0.907 c=1.825</td>
<td>MgH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>~ 1.0</td>
<td>0.6 (568)</td>
<td>MgCuAl</td>
</tr>
<tr>
<td>AB</td>
<td>TiFe</td>
<td>B2(CsCl)</td>
<td>a=0.297</td>
<td>TiFeH&lt;sub&gt;1.1&lt;/sub&gt; TiFeH&lt;sub&gt;1.2&lt;/sub&gt;</td>
<td>1</td>
<td>0.72 (313) 1.08 (313) Fe-Ti-O TiFeMnMm TiCo&lt;sub&gt;0.8&lt;/sub&gt;Mn&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiCo</td>
<td>B2 (CsCl)</td>
<td>a=0.2994</td>
<td>TiCoH&lt;sub&gt;1.4&lt;/sub&gt;</td>
<td>~ 0.7</td>
<td>0.21 (423)</td>
<td>TiCo&lt;sub&gt;0.8&lt;/sub&gt;Mn&lt;sub&gt;0.2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>ZrCo</td>
<td>B2 (CsCl)</td>
<td>a=0.3272 b=0.9965 c=0.415</td>
<td>ZrNiH&lt;sub&gt;1&lt;/sub&gt; ZrNiH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~ 1.8</td>
<td>0.18 (423)*4 ZrCo&lt;sub&gt;0.84&lt;/sub&gt;Ni&lt;sub&gt;0.16&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZrNi</td>
<td>(CrB)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiCr&lt;sub&gt;1.8&lt;/sub&gt;</td>
<td>C15</td>
<td>a=0.6939</td>
<td>TiCr&lt;sub&gt;1.3&lt;/sub&gt;H&lt;sub&gt;2.6&lt;/sub&gt;</td>
<td>0.52</td>
<td>0.71 (213) Ti&lt;sub&gt;0.8&lt;/sub&gt;Zr&lt;sub&gt;0.2&lt;/sub&gt;Cr&lt;sub&gt;1.4&lt;/sub&gt;Fe&lt;sub&gt;0.4&lt;/sub&gt; Ti&lt;sub&gt;1.2&lt;/sub&gt;Cr&lt;sub&gt;1.2&lt;/sub&gt;Mn&lt;sub&gt;0.8&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C14</td>
<td>a=0.4927</td>
<td>TiCr&lt;sub&gt;1.3&lt;/sub&gt;H&lt;sub&gt;2.6&lt;/sub&gt;</td>
<td>0.36</td>
<td>0.09 (213)</td>
<td></td>
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<tr>
<td></td>
<td>TiMn&lt;sub&gt;1.5&lt;/sub&gt;</td>
<td>C14</td>
<td>a=0.4862</td>
<td>TiMn&lt;sub&gt;1.3&lt;/sub&gt;H&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>0.64</td>
<td>0.7 (293) Ti&lt;sub&gt;0.77&lt;/sub&gt;Zr&lt;sub&gt;0.23&lt;/sub&gt;Mn&lt;sub&gt;0.8&lt;/sub&gt;Cr&lt;sub&gt;1.0&lt;/sub&gt;Cu&lt;sub&gt;0.2&lt;/sub&gt; Ti&lt;sub&gt;0.9&lt;/sub&gt;Zr&lt;sub&gt;0.1&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;Cr&lt;sub&gt;0.4&lt;/sub&gt;V&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZrCr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C15</td>
<td>a=0.722</td>
<td>ZrCr&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3.8&lt;/sub&gt;</td>
<td></td>
<td></td>
<td>Zr(Cr&lt;sub&gt;0.75&lt;/sub&gt;V&lt;sub&gt;0.25&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C14</td>
<td>a=0.5097 c=0.8322</td>
<td>ZrCr&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.65</td>
<td>0.15 (423) Zr&lt;sub&gt;0.8&lt;/sub&gt;Ti&lt;sub&gt;0.2&lt;/sub&gt;Cr&lt;sub&gt;0.6&lt;/sub&gt;Fe&lt;sub&gt;1.4&lt;/sub&gt; Zr(Cr&lt;sub&gt;0.8&lt;/sub&gt;V&lt;sub&gt;0.2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZrMn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C14</td>
<td>a=0.5035 c=0.8276</td>
<td>ZrMn&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~ 0.8</td>
<td>~ 0.05 (483) Zr(Mn&lt;sub&gt;0.5&lt;/sub&gt;Fe&lt;sub&gt;0.5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; ZrMn&lt;sub&gt;1.45&lt;/sub&gt;Co&lt;sub&gt;0.55&lt;/sub&gt;Al&lt;sub&gt;0.07&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZrV&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C15</td>
<td>a=0.744</td>
<td>ZrV&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2.8&lt;/sub&gt; ZrV&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4.9&lt;/sub&gt;</td>
<td>~ 0.3</td>
<td>~ 20 Pa (791) ZrV&lt;sub&gt;0.8&lt;/sub&gt;Cr&lt;sub&gt;1.2&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>AB&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CaNi&lt;sub&gt;5&lt;/sub&gt;</td>
<td>(CaCu&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>a=0.4943 c=0.3942</td>
<td>CaNi&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.63</td>
<td>0.04 (298) Ca&lt;sub&gt;0.8&lt;/sub&gt;Mn&lt;sub&gt;0.2&lt;/sub&gt;Ni&lt;sub&gt;4.7&lt;/sub&gt;Al&lt;sub&gt;0.3&lt;/sub&gt; Ca1-xLaxNi&lt;sub&gt;5&lt;/sub&gt;-yAly</td>
<td></td>
</tr>
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| Solid Solution | Ti-V   | BCC     | Ti$_{0.2}$V$_{0.8}$H$_{1.6}$ | 0.8   | 0.2 (353) | Ti$_{1-X}$V$_X$  
|                | V-Nb   | BCC     | V$_{0.1}$V$_{0.9}$H$_{1.9}$ | ~ 1   | 0.15 (313) | V$_{1-X}$Nb$_X$ |

*1 Classification following to "Strukturbereicht". A representative alloy or space group is denoted in parenthesis.
*2 A typical composition of the metal hydride, which have relatively wide plateau region in the P-C-T diagram.
*3 Two types of metal hydrides are found out in Mg$_2$Ni alloy; namely high temperature form and low temperature form.
*4 Equilibrium pressure at hydrogen absorption

Table 1. Kinds and characteristics of hydrogen storage alloys
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Biographical Sketches

**Toshiki Kabutomori** was born 23 April 1954, in Japan; he received his education from the Department of Applied Physics, Hokkaido University with M.Sc. degree in solid state; he has been engaged in research and development in Muroran Research Laboratory of the Japan Steel Works, Ltd.; received a doctor’s degree from Hokkaido University in material engineering; is the Committee Staff of The Japan Institute of Metals (1998); has published over 30 papers and expositions on the metal hydride and their application systems and is manager of Hydrogen Energy Center headquarters of JSW.

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