

METAL HYDRIDES

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Summary

It was known around the end of the 19th century that metals belonging to Groups IA to VA in the periodic table react directly with hydrogen to form metal hydride. These metals form, however, stable hydride following in the reaction with hydrogen, so that hydrogen cannot be desorbed readily. Around the end of 1960s, it was found that alloys formed by combining hydride-forming metals with those not absorbing hydrogen could readily absorb and desorb hydrogen in the hydrogen atmosphere of normal pressure and temperature. They were named hydrogen storage alloys.

The hydrogenation reaction to form metal hydride is governed by external hydrogen pressure or temperature of alloys, and it is possible to control the reaction by use of

these parameters. Hydrogen itself has mechanical energy in the form of gas pressure. The formation and dissociation of hydride are exothermic and endothermic reactions, respectively, allowing us to take out thermal energy. On the basis of these relations, it is possible to take out heat energy by using mechanical energy of hydrogen gas, and conversely, to desorb hydrogen gas through the consumption of heat energy for using the gas for mechanical work. If alloys absorb hydrogen ion generated electrochemically in place of hydrogen gas, electrical charge of hydrogen ion can be taken out to keep metal hydride in electrical neutrality, thus allowing us to store electrical energy. In this way, by utilizing various forms of energy in hydrogen and chemical reactions between metal and hydrogen, it is possible to convert energy forms one from another: mechanical, thermal and electrical, via chemical energy of the reaction.

1. Hydrogen Storage Metal

It was known around the end of the 19th century that metals belonging to Groups IA to VA in the periodic table react directly with hydrogen to form metal hydride. These metals form, however, stable hydrides following the reaction with hydrogen, so that hydrogen can not be desorbed readily. On the other hand, some metals such as Fe, Mn, Ni, and so on, hardly react with hydrogen under normal temperature and pressure, failing to form metal hydride. Around the end of 1960s, it was found that alloys formed by combining hydride-forming metals with those not absorbing hydrogen could readily absorb and desorb hydrogen in the hydrogen atmosphere of normal pressure and temperature. They were named hydrogen storage alloys.

A group of Philips Laboratories, the Netherlands, found toward the end of 1960s that one of ferromagnetic materials, SmCo_5 could readily store a large amount of hydrogen. This study was further extended in 1969 leading to the discovery of an alloy more suited for the practical purpose, LaNi_5 . At about the same time, another group at the Brookhaven National Laboratory, U.S. discovered Mg_2Ni and less expensive hydrogen storage alloy, TiFe . Most of basic compositions for alloys currently available for the practical applications were established around this time.

The hydrogen storage metals are attracting broad attentions not only as a safe means for storing a great amount of hydrogen but also for the potential of providing a number of functions based on hydrogen absorbing and desorbing reactions, which are of chemical nature involving large reaction heat, such as heat-to-heat conversion between different temperatures, heat-to-power or power-to-heat conversion, catalytic reaction utilizing active hydrogen desorbed from the alloy, storage of electric energy based on electrochemical reaction, separation of hydrogen isotopes, purification and recovery of hydrogen, and other functions which may be used widely in industries. The utilization of these functions has been exploited in various industries since the discovery of hydrogen storage alloys.

Recently, the global environmental issues have been requesting to revise the conventional way of energy utilization based on the consumption of fossil fuels. In order to reduce the dependence on fossil fuels, the development of clean energy is urgently needed. In the automobile industries, on the other hand, the research and development of electric-and fuel cell-powered vehicles have been intensively pursued

for the purpose of reducing the fuel consumption and the emission in exhaust gas of CO₂ causing the global warming and NO_x causing air pollution. For the electric car, it is expected that the metal-hydride (MH) battery will be employed using hydrogen storage alloy as a cathode for the sake of safety and car performance. The manufacturers of car and battery are focusing their efforts in the development of this type of battery.

2. Properties of Hydrogen Storage Alloys

2.1 Function and Features of Hydrogen Storage Alloys

The most important fundamental properties of hydrogen storage alloys are capability of storing a great amount of hydrogen. Table 1 compares hydrogen density and hydrogen content for various state of hydrogen, many kinds of metal hydride and hydrogen storage alloy.

The atom density of hydrogen is 4 to 5 x 10²² atoms/cm³, in either liquid or solid phase. In case of hydride of vanadium (V) or titanium (Ti), the hydrogen atom density is twice as high as that of solid hydrogen.

	Density D _v ($\Xi 10^{22}$ H atoms/cm ³)	Content D _w (mass%)
H ₂ , gas at 0.1MPa	5.4 $\Xi 10^{-3}$	100.0
H ₂ , liquid at 20 K	4.2	100.0
H ₂ , solid at 4 K	5.3	100.0
H ₂ O, 288 K	6.7	11.19
MgH ₂	6.6	7.66
TiH ₂	9.1	4.04
VH ₂	10.5	3.81
ZrH ₂	7.3	2.16
LaH ₃	6.9	2.13
LaNi ₅ H ₆	6.2	1.38
TiFeH _{1.95}	5.7	1.86
Mg ₂ NiH ₄	5.6	3.62
H ₂ in 47 l Cartridge at 15MPa	0.81	1.17*

* Include cartridge weight.

Table 1. Hydrogen density and content of various media.

The hydrogen atom density in LaNi₅ or other hydrogen storage alloys is higher than that of liquid or solid hydrogen. Some of inorganic compounds have high hydrogen density, but the highest density is 7.5 x 10²² atoms/cm² of ammonia.

Some organic compounds have higher density, but high temperatures are required for reversible storage and release of hydrogen. In case of metal hydride, hydrogen can be readily absorbed and desorbed at normal temperatures, and some metals have capacity of storing hydrogen at higher density. In fact, these metals constitute compounds capable of storing hydrogen at the highest possible density.

2.2. Thermodynamics of Metal Hydride

Other major features of metal hydride involve, in addition to storage of a large amount of hydrogen, reversible absorption and desorption of hydrogen through the control of hydrogen pressure over a few atmospheres at temperature close to the room temperature at a very high reaction rate. The major part of the hydrogen absorption and desorption consists of chemical reaction as in case of other chemical substances.

The equilibrium state of this reaction is given by Eq. (1).



where M represents a metal. The equation indicates that 1 mol of metal reacts with n mols of hydrogen atom to form metal hydride MH_n . In case of hydrogen storage alloy, this reaction is usually exothermic. The reaction is reversible, and the equilibrium state is determined by the temperature (T) and the pressure (P). The pressure of hydrogen at the time of equilibrium is called equilibrium dissociation pressure (P_d).

The parameter values P_d and T in the equilibrium state are defined by enthalpy changes (ΔH) and entropy changes (ΔS) of the system in this reaction, as expressed by (2).

$$\ln = \left(\frac{P_d}{P_0} \right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2)$$

where P_0 represents pressure in the normal state, which is usually set to 1 atm, R is the gas constant, and (ΔH) and (ΔS) represent enthalpy changes and entropy changes, respectively, per 1 kg/cm² (0.1 MPa) of hydrogen molecule. As the reaction is exothermic, both (ΔH) and (ΔS) are negative. Equation (2) means that natural logarithm of equilibrium dissociation pressure ($\ln P_d$) changes linearly in respect to $1/T$, with a slope (ΔH) and y-intercept (ΔS). It has been demonstrated that in many metal hydrides the equilibrium dissociation pressure Pe is in fact linearly related to reciprocal of temperature $1/T$.

2.3. Reaction and Equilibrium in Metal-Hydrogen System

2.3.1. Pressure-Composition-Isotherms (P-C-T)

Figure 1 shows a typical pressure-composition-isotherm (P-C-T diagram) for the metal-hydrogen reaction. Since the equilibrium state is defined by three parameters: equilibrium hydrogen pressure (P_d), temperatures (T) and hydrogen concentration in metal, the equilibrium diagram is to be represented three-dimensionally with these three parameters set as axes of the coordinates. Figure 1 may be regarded as two cross-sections vertical to the temperature axis of a three-dimensional curve. The horizontal axis of Figure 1 represent hydrogen concentration, which is expressed by a ratio of the number of hydrogen atoms to that of metal atoms within the metal.

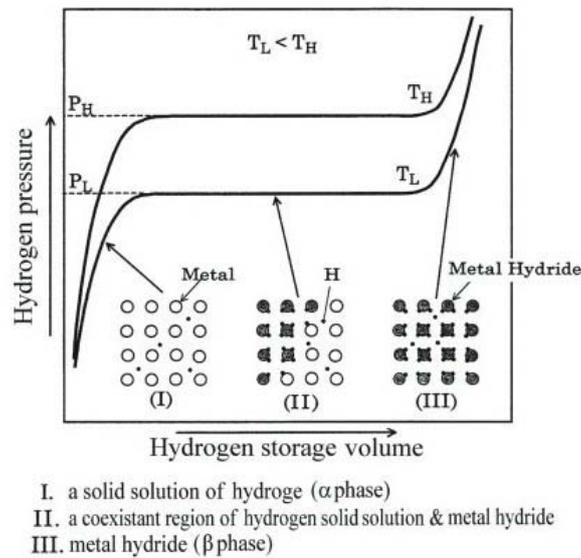


Figure 1. A typical pressure-composition-isotherm (P-C-T diagram) for the metal-hydrogen reaction.

If the surface of metal is clean, hydrogen is readily absorbed in metal to form a solid solution of hydrogen (α -phase). It is known that the amount of hydrogen contained in solid solution increases in proportion to a square root of hydrogen pressure, and in the P-C-T diagram, the area of solid solution corresponds to steep rise of equilibrium pressure.

When the hydrogen content in metal solid solution rises to a certain level, a part of solid solution turns into metal hydride (β -phase) according to the Eq. (1). If hydrogen is further fed in, the proportion of metal hydride in solid solution increases. As the reaction proceeds under a fixed hydrogen pressure, the area of hydride formation is represented as an area of constant pressure in P-C-T diagram.

This area is called “plateau” where hydrogen solid solution and metal hydride coexist. The hydrogen pressure at this plateau is equilibrium dissociation pressure (P_d). When all the metal is turned into hydride, hydrogen starts to dissolve into metal hydride, and the hydrogen pressure begins to rise again.

2.3.2. Pressure-Temperature (P-T) Diagrams

As mentioned above, the equilibrium pressure (P_d) is governed by the Eq. (2). The relation between P_d and reciprocal of temperature ($1/T$) is called P-T diagram. In Figure 2, P-T diagrams of various metals and alloys are compared.

Each of P-T diagrams is nearly rectilinear, and the reaction heat, that is, enthalpy change, (ΔH), can be determined from the slope of this line. As shown in Figure 2, the P-T characteristics vary extensively depending upon the nature of metal or alloy.

Ti-V (a solid solution)	A2 structure	TiVH ₄	Smaller pulverization Very stable Highest storage capacity	TiCrV TiVMn
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* Mm; mischmetal

Table 2. Comparison hydriding characteristics for the binary hydrogen storage alloys.

One of typical hydrogen storage alloys, LaNi₅ with the crystalline structure just like CaCu₅ can store 1.4 wt% hydrogen by forming hydride LaNi₅H₆. With equilibrium dissociation pressure of 0.2 MPa at 293 K or so, the LaNi₅ has been used most frequently for basic research and developmental studies because it can absorb and desorb hydrogen with relative ease and its hydriding future is very stable.

In view of cost, alloys based on MmNi₅, where Mm is “mischmetal” (Mm, mixture of rare earth metals), have been given priority for the development, and used as negative electrode material for the Ni-MH battery, commercialized lately.

TiFe alloys, which had been regarded to be closest to the practical application owing to the lowest price, were used for the hydrogen storage tank. However, difficulties in initial activation and control of hydrogen absorption pressure have made them applicable only to storage.

Since the discovery of such alloys as TiMn_{1.5} and TiCr₂ around 1975, a number of alloys of Laves structure have been developed. They have basic composition of AB₂, Where A = Ti or Zr, and B = Cr, Mn, Fe or Ni.

The hydrogen storing properties of these alloys can be controlled by changing alloy combination and composition ratio. Besides, as their capacity of hydrogen storage is larger than that of LaNi₅ and the durability is better than the latter, a number of Laves alloys have been developed for the practical applications.

Recently, in response to the requirement for alloys of larger hydrogen storage capacity, Ti-V based alloys of BCC structure have been developed, to be partly applied to the storage tank. While Ti-V alloys have hydrogen storage capacity as larger as 3.5 wt%, desorption of hydrogen requires heating up to five to six hundreds of Kelvin.

If another metal such as Mn or Cr is added to the alloy to make a ternary alloy, it becomes possible to absorb and desorb hydrogen under the hydrogen atmosphere of normal temperatures and pressure.

However, the ternary alloys have some improvement, such as capable desorbing hydrogen is only 2.3 wt% or so, which is about 60% of stored hydrogen, extensive hysteresis and poor durability, and energetic efforts are being paid to improve these demerits.

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Biographical Sketches

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