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 A_2B, as represented by Mg_2Ni. 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 b-hydride (H/M = 0.5), and g-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 AB_2, 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 AB_5. Typical examples are $LaNi_5$, of which the hydrogen storage capacity 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 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 A_2B, as represented by Mg_2Ni. 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 b-hydride phase at around H/M = 0.5, and g-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.

Type	Alloy	Crystal structure	Lattice Constant nm	Hydride*[2]	Plateau width Δ(H/M)	Desorption Pressure (Temp) MPa (K)	Multiple alloys
A_2B	Mg_2Ni	(P6222)	a=0.522 c=1.320	Mg_2NiH_4*[3]	1.3	0.54 (595)	$Mg_2Ni_{0.75}Cu_{0.25}$ $Mg_{2-x}Al_xNi$
	Mg_2Cu	(Fddd)	a=0.5284 b=0.907 c=1.825	MgH_2	~ 1.0	0.6 (568)	MgCuAl
AB	TiFe	B2(CsCl)	a=0.297	$TiFeH_{\sim 1}$ $TiFeH_{\sim 2}$	1 1	0.72 (313) 1.08 (313)	Fe-Ti-O TiFeMnMm
	TiCo	B2 (CsCl)	a=0.2994	$TiCoH_{1.4}$	~ 0.7	0.21 (423)	$TiCo_{0.8}Mn_{0.2}$
	ZrCo	B2 (CsCl)		$ZrCoH_2$	~ 1.8	0.18 (423)*[4]	$ZrCo_{0.84}Ni_{0.16}$
	ZrNi	(CrB)	a=0.3272 b=0.9965 c=0.415	$ZiNiH_1$ $ZrNiH_3$			
AB_2	$TiCr_{1.8}$	C15	a=0.6939	$TiCr_{1.8}H_{2.6}$	0.52	0.71 (213)	$Ti_{0.8}Zr_{0.2}Cr_{1.4}Fe_{0.4}$
		C14	a=0.4927 c=0.7961	$TiCr_{1.8}H_{2.6}$	0.36	0.09 (213	$Ti_{1.2}Cr_{1.2}Mn_{0.8}$
	$TiMn_{1.5}$	C14	a=0.4862 c=0.7969	$TiMn_{1.5}H_{2.5}$	0.64	0.7 (293)	$Ti_{0.77}Zr_{0.23}Mn_{0.8}Cr_{1.0}Cu_{0.2}$ $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$
	$ZrCr_2$	C15	a=0.722	$ZrCr_2H_{3.8}$			$Zr(Fe_{0.75}Cr_{0.25})_2$
		C14	a=0.5097 c=0.8322	$ZrCr_2H_3$	0.65	0.15 (423)	$Zr_{0.8}Ti_{0.2}Cr_{0.6}Fe_{1.4}$ $Zr(Cr_{0.8}V_{0.2})_2$
	$ZrMn_2$	C14	a=0.5035 c=0.8276	$ZrMn_2H_3$	~ 0.8	~ 0.05 (483)	$Zr(Mn_{0.5}Fe_{0.5})_2$ $ZrMn_{1.45}Co_{0.55}Al_{0.07}$
	ZrV_2	C15	a=0.744	$ZrV_2H_{2.8}$ $ZrV_2H_{4.9}$	~ 0.3	~ 20 Pa (791)	$ZrV_{0.8}Cr_{1.2}$
AB_5	$CaNi_5$	($CaCu_5$)	a=0.4943 c=0.3942	$CaNi_5H_6$	0.63	0.04 (298)	$Ca_{0.7}Mm_{0.3}Ni_{4.7}Al_{0.3}$ Ca1-xLaxNi5-yAly

	$LaNi_5$	($CaCu_5$)	a=0.5017 c=0.3987	$LaNi_5H_6$	1	0.32 (313)	$LaNi_{5-X}Al_X$
	$MmNi_5$	($CaCu_5$)	a=0.4912 c=0.3990	$MmNi_5H_6$	1	3 (298)	$MmNi_{5-X}Al_X$
Solid Solution	Ti-V	BCC	a=0.302 ~ 0.321	$Ti_{0.2}V_{0.8}H_{1.6}$	0.8	0.2 (353)	$Ti_{1-X}V_X$ Ti-V-Fe, Ti-Cr-V
	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_2Ni 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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Bibliography

Gamo T., Moriwaki Y., Yanagihara Y., and Iwaki T. (1983). Life properties of Ti-Mn alloy hydrides and their hydrogen purification effect. *J. Less-Common Metals* **89**, 495–504. [This is a first article present hydriding and P-C-T properties of $TiMn_{1.5}$ alloy.]

Johnson J. R. (1980). Reaction of hydrogen with the high temperature (C14) form of $TiCr_{2}$. *J. Less-Common Metals* **73**, 345–353. [This is a first article present hydriding and P-C-T properties of C14 type $TiCr_2$ alloy.]

Maeland A. J. (1964). Investigation of the vanadium-hydrogen system by X-ray diffraction techniques. *J. Physical Chemistry* **68**, 2197–2200. [This is a first article present hydriding and P-C-T properties of V.]

Reilly J. J. and Wiswall Jr. R. H. (1968). The reaction of hydrogen with alloys of magnesium and nickel and formation of Mg_2NiH_4. *Inorganic Chemistry* **7**, 2254–2256. [This is a first report on hydriding and P-C-T properties of Mg_2Ni alloy.]

Reilly J. J. and Wiswall Jr. R. H. (1974). Formation and properties of iron titanium hydride. *Inorganic Chemistry* **13**, 218–222. [This is a first article present hydriding and P-C-T properties of TiFe alloy.]

Sandrock G. D., Murray J. J., Post M. L., and Taylor J. B. (1982). Hydride and deuteide of $CaNi_5$. *Materials Research Bulletin* **17**, 887–894. [This is a first article present hydriding and P-C-T properties of $CaNi_5$ alloy.]

Schlapbach L., (1988). *Hydrogen in Intermetallic Compounds I, II*. Berlin: Springer-Verlag. [This is one of the most reliable and popular books that describes hydrogen in intermetallic compounds in many aspects.]

Van Vucht J. H. N., Kuijpers F. A., and Bruning H. C. A. M. (1970). Reversible room-temperature absorption of large quantities of hydrogen by intermetallic compounds. *Philips Research Reports* **25**, 133–140. [This is a first report on hydriding and P-C-T properties of $LaNi_5$ alloy.]

Biographical Sketches

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