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A panoramic overview of hydrogen storage alloys from a gas reaction point of view

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Abstract

This is a broad historical and property-related review of the extraordinary variety of hydriding alloys that have been developed. The principal focus is on reactions of alloys with gaseous H_2 and their important H-capacity and PCT (pressure–composition–temperature) properties. However, there are a number of important secondary properties that must also be considered: activation, decrepitation, H_2 absorption/desorption kinetics, impurity effects, cyclic stability, safety, raw materials cost and ease of manufacture, among others. The main part of this survey will cover the families of alloys that will reversibly store H_2 at temperatures of 0–100°C and pressures of 1–10 atm absolute, ranges useful to many applications. Alloys include solid solutions and intermetallic compounds of the generic families AB_5, AB_2, AB, A_2B, among others. Conventional alloys are reaching thermodynamic limits in PCT and H-capacity. Near-term R&D is likely to focus new directions toward the areas of catalyzed complex hydrides and carbon.

Keywords: Review; Hydride; Applications; Alloy; Intermetallic Compound; Complex hydride; Carbon

1. Introduction

The science and technology of reversible metal hydrides, principal topics of this symposium, have a long and rich history. The hydriding and dehydriding of metals M by both direct dissociative chemisorption of H_2 gas and electrochemical splitting of H_2O are deceptively simple:

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x \tag{1}$$

$$M + \frac{x}{2} H_2O + \frac{x}{2} e^- \leftrightarrow MH_x + \frac{x}{2} OH^- \tag{2}$$

It is the main objective of this review to give a broad overview of the the metals and alloys M which have been developed and studied relative to the direct gas reactions (Eq. (1)). Others will review those alloys that have been studied for electrochemical purposes [1,2]. In some ways, there are commonalities with the two processes; in some ways, not.

We must begin by carefully defining the various pressure–composition–temperature (PCT) and other numerous engineering properties associated with Eq. (1). This must be followed closely with a brief listing of practical applications, because each application tends to require slightly different properties. These topics will be followed by a comparative review of the several families of hydriding alloys. The overall task is not easy because there are thousands of papers on the above subjects and the limited space available in this Proceedings. In order to minimize details and the length of the reference list, the reader should consult other lengthy reviews by the author in the areas of hydride properties [3–5] and applications [6,7]. Of particular interest to the hydride scientist or engineer are the numerous IEA hydride databases and extensive reference list freely available on the Internet [5].

2. Hydride properties

2.1. Pressure–composition–temperature properties

The most common expression of PCT properties is the familiar isothermal P–C hysteresis loop, shown in generalized form in Fig. 1. Most practical hydriding metals do not show perfectly flat plateaux or zero hysteresis. Fig. 1 is included to clearly show the mathematical and numerical definitions of hysteresis, plateau slope and H-capacity that will be used in this review. In particular, there are several ways to show H-capacity. The reversible capacity, $\Delta(H/M)_r$, is conservatively defined as the plateau width, which can be considerably less than the maximum capacity, $(H/M)_{max}$. In practice, depending on available pressure and temperature ranges, engineering capacity is usually somewhere between $\Delta(H/M)_r$ and $(H/M)_{max}$. Capacity

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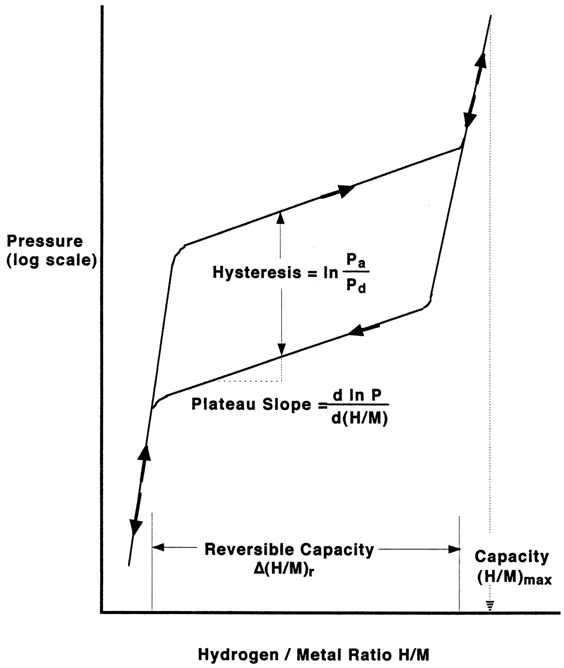

Fig. 1. Schematic isothermal pressure–composition hysteresis loop.

can be listed in either atomic H/M ratio or weight percent, both of which are used in the tables below. In calculating wt.%, both H and M (i.e., not only M) are included in the denominator. In addition, it is sometimes useful to express capacity in volumetric terms, e.g., number of H atoms per unit volume (such as crystal cm^3). This measure is listed in some of the tables below as $\Delta N_H/V$, where ΔN_H represents the reversible capacity as defined in Fig. 1. Note this measure represents the volumetric density in crystal terms and does not include the void volumes inherent in engineering containers.

In general, the mid-desorption plateau pressure, P_d, will be used in the graphs and tables below. Of course thermodynamics dictate the plateau pressures P must increase with temperature, usually close enough to the van't Hoff equation for engineering and comparison purposes,

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R}, \qquad (3)$$

where ΔH and ΔS are the enthalpy and entropy changes of the hydriding reaction, T is absolute temperature and R is the gas constant. For all of the hydrides to be discussed, ΔH and ΔS are negative, i.e., the hydriding reaction is exothermic and the dehydriding reaction is endothermic. The knowledge of ΔH especially is important to the heat management required for practical engineering devices and is a fundamental measure of the M–H bond strength. The van't Hoff plot ($\ln P$ vs. $1/T$) is a convenient graphical way to compare hydrides of varying thermal stability and will be used extensively below. In general, this review will concentrate on alloys that will release H_2 at or near ambient conditions, specifically 1–10 atm (absolute) and 0–100°C.

2.2. Other important properties

There are a number of important hydride properties that must be considered in addition to the primary PCT properties. Some of the more important ones are listed below.

Activation is the procedure needed to hydride a metal the first time and bring it up to maximum H-capacity and hydriding/dehydriding kinetics. The ease of initial H_2-penetration depends on surface structures and barriers, such as dissociation catalytic species and oxide films. A second stage of activation involves internal cracking of metal particles to increase reaction surface area.

Decrepitation means the self-pulverization of large metal particles into powder, a common phenomenon that results from a combination of hydriding volume change and the brittle nature of hydriding alloys (especially when they contain some H in solution). The morphology of the decrepitated powder affects *heat transfer* and also the tendency of powder migration into undesirable places like valve seats. Unfortunately, most hydride powders have poor heat transfer coefficients and require engineering means for thermal enhancement (e.g., Al foam, internal fins, etc.). The morphology of the power can affect packing, which in turn can lead to internal gas impedance and container deformation.

Kinetics of hydriding and dehydriding can vary markedly from alloy to alloy. Fortunately, many room temperature hydrides have excellent intrinsic kinetics, so that the cycling of storage containers tends to be limited by heat transfer designs or accidental surface contamination (see next paragraph). However, there are some materials that are kinetics limited, especially at low temperature.

Gaseous impurity resistance is a very important property, especially when the application is 'open-ended' and uses new H_2 for each H/D cycle, that H_2 often being impure. Depending on the alloy–impurity combination, there can be several types of damage [8]: (1) *poisoning*, where capacity is quickly lost without a concurrent decrease of initial kinetics; (2) *retardation*, where kinetics are quickly lost without loss of ultimate capacity; (3) *reaction*, where the alloy is slowly corroded; (4) *innocuous*, where there is no surface damage but there can be pseudo-kinetic decreases due to inert gas blanketing, an interparticle gas diffusion problem. Damages from poisoning and retardation are usually recoverable, but reaction damage is usually not.

Cyclic stability is important and widely variable from alloy to alloy. Alloys and intermetallic compounds are usually metastable relative to *disproportionation*, the tendency to break up metallurgically to form stable, not easily reversed hydrides. Even if very pure H_2 is used, disproportionation can occur with a resultant loss of reversible capacity.

Safety usually centers around pyrophoricity, the tendency for a hydride powder to burn when suddenly exposed to air, e.g., an accidental tank rupture. But the term can also include toxicity resulting from accidental ingestion or inhalation.

Alloy cost is influenced by several factors, including *raw materials cost*, *melting and annealing costs*, *metallurgical complexities*, *profit* and the degree of *PCT precision* needed for the particular application. It is difficult to cover all of these factors in this short review. For simplification, I will cover only raw materials cost in tables below, i.e., the weighted averages of the prices of metals used in the alloy (mid-1996 prices [3]). This will be normalized to US$ per gram of reversible H-storage capacity as defined in Fig. 1. Bear in mind that the above factors in addition to raw materials cost can easily raise true alloy cost by more than 100%.

3. Hydride applications

It may be useful to briefly list the main hydride applications, proposed and commercial, in terms of the properties required. More detail can be found elsewhere [6,7].

3.1. H-Storage

Stationary storage usually implies bulk storage and large amounts of alloy, so low alloy cost tends to be an important property. On the other hand *vehicular storage* tends to require high hydrogen weight percent; in fact most existing hydrides fall far short of what is desired in this property, as we shall see. Both kinds of storage desire easy activation to minimize container pressure and temperature requirements for the one-time activation. In both cases, good resistance to gaseous impurities is desirable in case impure H_2 is used or the inevitable accidental introduction of air occurs. In both cases, PCT properties should be roughly in the ambient temperature and pressure area so that waste heat from the environment or vehicle engine (or fuel cell) can be used for endothermic H_2 desorption. Kinetics are somewhat less important because of the relatively slow cycling of storage tanks.

3.2. Compression

The compression of gaseous H_2 using thermal swings of hydride beds is an open-ended process and generally requires the alloy to have good impurity resistance (impure H_2 pumped) and cyclic stability (high temperatures involved). H/D cycling is relatively fast, so good kinetics and heat transfer are desired. If rapid cycling can be achieved, then relatively small inventories of alloy are needed and alloy cost becomes secondary to other properties. Good H-capacity is desired so that parasitic heat losses associated with thermal swings are minimized. PCT properties must be tunable to the input and output pressures desired and the input and heat sink temperatures available.

3.3. Closed thermodynamic systems

This class of hydride applications includes the following: (1) *heat engines*, where heat is converted to mechanical energy in an expansion engine; (2) *heat storage*, for example solar heat; (3) *heat pumps*, where low-temperature heat is ‘upgraded’ to higher temperature; and (4) *refrigerators*, where heat is converted to refrigeration. Included in heat engines are *actuators* and *temperature sensors*. All of these devices are closed systems, where H_2 is a contained ‘working fluid inventory’, so generally impurity resistance is relatively unimportant (assuming the systems are built very cleanly to start). Most (except (2)) are expected to cycle rapidly and involve relatively high temperatures, so good kinetics and cyclic stability are important. Like compressors, good capacity is desirable and PCT must be carefully tuned to the application. In the special case of heat pumps and refrigerators, where two or more different hydrides must be carefully matched to each other, achieving the exact desired PCT properties can be difficult or expensive. To work properly, or at least to maximize overall efficiency, most closed thermodynamic systems demand low hysteresis and low plateau slope.

3.4. Separation

Separation can be divided into two classes: (1) *H_2 separation* from other gases; and (2) *H-isotope separation*. The first class can be further divided into gross *separation*, *purification* and *gettering*. All three subclasses require impurity tolerance, tailored PCT properties and other properties that are application specific. In the case of getters, to remove trace amounts of H_2 from vacuum systems or other gases, very low room-temperature plateau pressures are required (e.g., 10^{-6} to 10^{-10} atm).

H-isotope separation requires special properties involved with kinetic and PCT property differences among protium (H), deuterium (D) and tritium (T).

3.5. Other applications

There are a number of lesser-known hydride applications: *liquid H_2 control* and *boiloff capture, cryocooling, chemical catalysis, ammonia synthesis, methane synthesis, diamond synthesis* [9], *permanent magnet production* and others too numerous to detail here. Some are covered in these Proceedings. The biggest commercial application is the *nickel metal hydride (NiMH) battery* discussed extensively by others in this Proceedings.

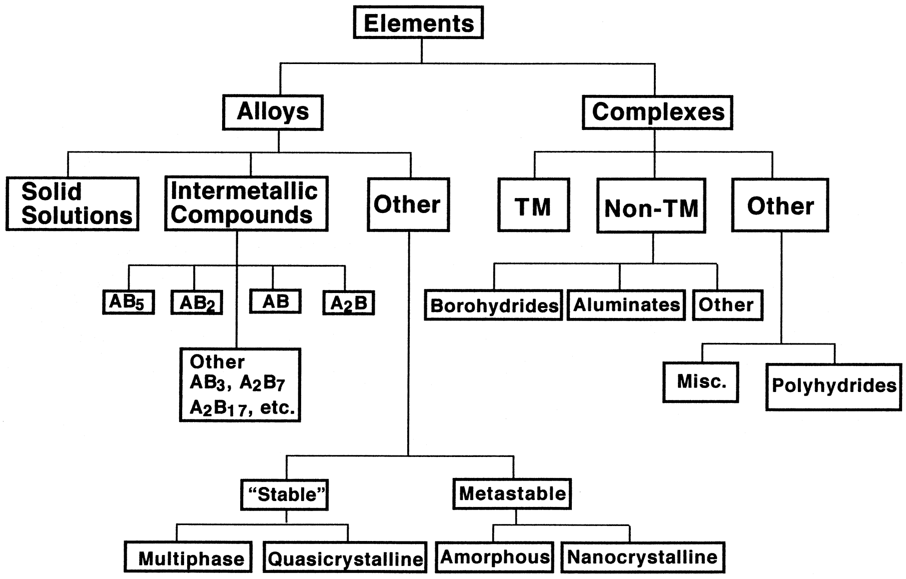

Fig. 2. Family tree of hydriding alloys and complexes. TM = transition metal.

4. Review of hydriding metals and alloys

Hydrogen is a highly reactive element and has been shown to form hydrides and solid solutions with thousands of metals and alloys. A hydride 'family tree' of the elements, alloys and complexes is shown in Fig. 2. This review will concentrate on the alloy side of the tree, where H is usually bound in interstitial sites in a metallic state with usually minor distortions of the generally stable H-free alloy structures. However, the review will also briefly discuss the complexes which have the most significant potential for future development, in the author's opinion.

4.1. Elements

Most of the 91 natural elements above H will hydride under appropriate conditions. Unfortunately, as shown by the van't Hoff lines of Fig. 3, the PCT properties are not very convenient relative to the 1–10 atm, 0–100°C range of utility chosen for practical applications (small box on the right of the diagram). Only vanadium is in the range and there is past and present interest in solid solutions of V and other metals (to be discussed later). Nb is similar to V. Pd has been used for more than 100 years for H-storage, but it is very expensive, doesn't hold much H and requires heating well above 100°C to liberate that H.

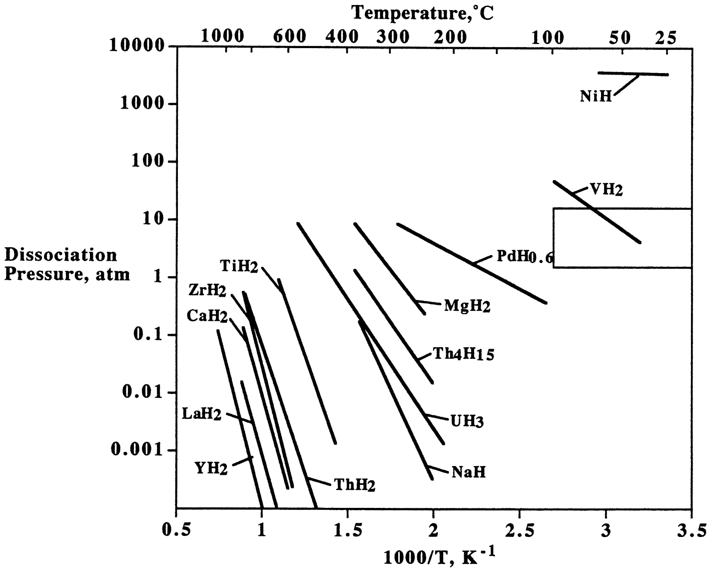

Fig. 3. Van't Hoff lines (desorption) for elemental hydrides. Box indicates 1–10 atm, 0–100°C ranges.

4.2. Alloys

In order to capitalize on practical applications of reversible hydrides, we have been required to combine strong hydride forming elements A with weak hydriding elements B to form alloys (especially intermetallic compounds) that have the desired intermediate thermodynamic affinities for hydrogen. A classic and well-known example is the combination of La (forming LaH_2 with 25°C $P_d \approx 3 \times 10^{-29}$ atm and $\Delta H_f = -208$ kJ mol^{-1} H_2) with Ni (NiH, 25°C $P_d = 3400$ atm, $\Delta H_f = -8.8$ kJ mol^{-1} H_2) to form the intermetallic compound $LaNi_5$ ($LaNi_5H_{6+}$, 25°C $P_d = 1.6$ atm, $\Delta H_f = -30.9$ kJ mol^{-1} H_2). This extraordinary ability to 'interpolate' between the extremes of elemental hydriding behavior has led to the modern world of reversible hydrides.

4.2.1. AB_5 intermetallic compounds

The AB_5 hydriding intermetallics generally have a hexagonal crystal structure (Hauke phase, prototype $CaCu_5$, Strukturbericht $D2_d$, Pearson hP6, space group *P*6/*mmm*). The near-ambient PCT properties of the hydrides were discovered accidentally at Philips Eindhoven about 1969 while studying the magnet alloy $SmCo_5$. The family has an extraordinary versatility because many different elemental species can be substituted (at least partially) into the A and B lattice sites. A-elements tend to be one or more of the lanthanides (at. no. 57–71), Ca or other elements such as Y, Zr, etc. The B-elements are based on Ni with many other possible substitutional elements such as Co, Al, Mn, Fe, Cu, Sn, Si, Ti, etc. Modern commercial AB_5 hydriding alloys are mostly based on the use of the lanthanide mixture mischmetal (Mm = Ce + La + Nd + Pr) for the A side and Ni + Al + Mn + Co + ··· on the B-side. The highly substituted Mm-based alloys were initially developed in the 1970s by this author in the USA and Osumi et al. in Japan and later optimized by Sakai et al. for NiMH battery applications [2]. Various versions of Mm(Ni, Co, Mn, Al)$_5$ form the basis of most of today's commercial NiMH battery anodes.

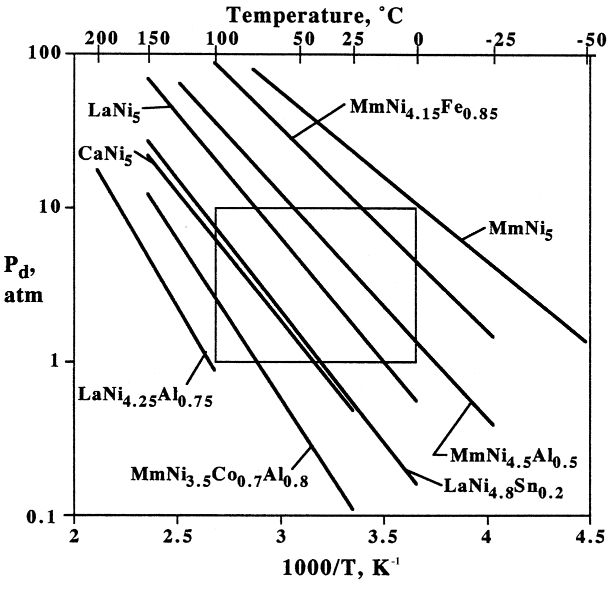

Fig. 4. Van't Hoff lines for various AB_5 hydrides.

The PCT and other properties of various representative AB_5 alloys are shown in Fig. 4 and Table 1. The broad range of PCT versatility and tunability is evident, with the 25°C plateau pressure variable over at least three orders of magnitude depending on the composition. With the exception of $MmNi_5$ itself, hysteresis is generally quite low for the AB_5s. By annealing out the as-cast metallurgical composition fluctuations, rather flat plateaux are possible, even with multicomponent alloys. H-capacity is on the uncomfortably low side, not exceeding 1.3 wt.% on the plateau basis we are using for definition of the reversible component. Alloy raw material cost is a little high, at least in comparison to other systems (AB_2 and AB) to be shown later. $CaNi_5$ has a good potential for both lower cost and higher H-content than the Mm- or La-based alloys, but unfortunately it has three plateaux and only the main (middle) plateaux is counted in Table 1. Even though that plateau has low $\Delta(H/M)_r$, the low density of $CaNi_5$ results in competitive wt.% and cost to the other AB_5s.

The AB_5 alloys are easy to activate, seldom requiring any heating. They decrepitate on the first H/D cycle to fine powder which is mildly pyrophoric if suddenly exposed to air, a well-known factor that must be included in safety considerations. Both easy activation and pyrophoricity means the AB_5 alloys do not form protective oxide layers. This property is a distinct advantage that gives AB_5s unusually good tolerance to small amounts of O_2 and H_2O in the H_2 [8]. These impurities do not poison the AB_5s but act as reactants that only slowly reduce capacity. CO is a strong poison, but regeneration can be accomplished by mild heating (e.g., 100°C) and flushing with clean H_2. Intrinsic kinetics of the AB_5 alloys are very good, almost always better than practical engineering heat transfer (at least in good purity, CO-free H_2). AB_5 metallurgy is rather well understood and virtually single phase alloy can be relatively easily melted in large commercial quantities by vacuum induction melting. $CaNi_5$, and to lesser extents $LaNi_5$ and $MmNi_5$, are subject to disproportionation. The partial substitution of Al or Sn on the B-side greatly reduces the disproportionation problem in $LaNi_5$ and $MmNi_5$-based alloys.

4.2.2. AB_2 intermetallic compounds

Like the AB_5s, the AB_2 intermetallics represent a large and versatile group of hydriding materials with PCT properties of value for the ambient temperature realm. The Internet database presently includes nearly 500 AB_2 entries, including multiple data on certain binary and multicomponent compounds by various investigators [5]. The

Table 1
PCT and cost properties of selected AB_5 hydrides[a]

Composition	ΔH kJ mol^{-1}	ΔS kJ mol^{-1} K^{-1}	25°C P_d atm	T for 1 atm P_d	Plateau	
					Hysteresis	Slope
$MmNi_5$	21.1	0.097	23	−56	1.65	0.54
$MmNi_{4.15}Fe_{0.85}$	25.3	0.105	11.2	−32	0.17	0.36
$MmNi_{4.5}Al_{0.5}$	28.0	0.105	3.8	−6	0.11	0.36
$LaNi_5$	30.8	0.108	1.8	12	0.13	0.13
$LaNi_{4.8}Sn_{0.2}$	32.8	0.105	0.5	39	0.19	0.22
$CaNi_5$ (M)	31.9	0.101	0.5	43	0.16	0.19
$MmNi_{3.5}Co_{0.7}Al_{0.8}$	39.8	0.115	0.11	73	0.2 est.	1.2
$LaNi_{4.25}Al_{0.75}$	44.1	0.117	0.024	104	0.23	2.7

Composition	Density g cm^{-3}	$(H\text{-Capacity})_{max}$		$(H\text{-Capacity})_r$			Alloy RMC[c]	
		H/M	wt.%	ΔH/M	Δwt.%	$\Delta N_H/V$[b]	\$ kg^{-1}	\$ g^{-1} H
$MmNi_5$	8.6	1.06	1.46	0.90	1.24	5.2	7.94	0.64
$MmNi_{4.15}Fe_{0.85}$	8.1	0.82	1.14	0.65	0.90	3.8	7.12	0.79
$MmNi_{4.5}Al_{0.5}$	8.1	0.85	1.2	0.58	0.83	3.5	7.17	0.86
$LaNi_5$	8.3	1.08	1.49	0.93	1.28	5.2	9.87	0.77
$LaNi_{4.8}Sn_{0.2}$	8.4	1.06	1.4	0.92	1.24	5.1	9.69	0.78
$CaNi_5$ (M)	6.6	1.05	1.87	0.55	0.99	3.4	7.56	0.76
$MmNi_{3.5}Co_{0.7}Al_{0.8}$	7.6	0.85	1.24	0.36	0.53	2.2	13.25	2.50
$LaNi_{4.25}Al_{0.75}$	7.6	0.77	1.13	0.53	0.78	3.1	9.68	1.24

[a] (M) = middle plateau for $CaNi_5$.
[c] RMC = Raw Materials Cost; \$ g^{-1} H based on $(H\text{-Capacity})_r$.
[b] Reversible volumetric capacities are approximate and in units of 10^{22} H-atoms/crystal cm^3.

A-elements are often from the IVA group (Ti, Zr, Hf) and/or rare earth series (at. no. 57–71) or Th. The B-elements can be a variety of transition or non-transition metals with something of a preference for atomic numbers 23–26 (V, Cr, Mn, Fe). A very wide variety of substitutions are possible for both A- and B-elements, thus providing a high degree of fine tuning of PCT properties.

The AB_2s are largely based on two related Laves phase crystal structures: hexagonal (prototype $MgZn_2$, Strukturbericht C14, Pearson hP12, space group *P*63/*mmc*) and cubic (prototype $MgCu_2$, Strukturbericht C15, Pearson cF24, space group *Fd*-3*m*). The first reported Laves phase hydrides were reported in the 1950s and 1960s by principal USA authors Trzeciak, Pebler and Beck. Practical AB_2 hydrides were identified in the 1970s by groups led by Shaltiel (Israel), Gamo (Japan), Buschow (Netherlands), Wallace (USA), Reilly (USA), Burnasheva (USSR) and others. These groups continued into the 1980s and were joined by efforts led by Kierstead (USA), Bernauer (Germany) and Ivey (Canada), among others. AB_2 R&D has continued to this day in many laboratories around the world. Many others in addition to those listed above deserve credit. A much more complete list of references can be found in the AB_2 on-line database [5].

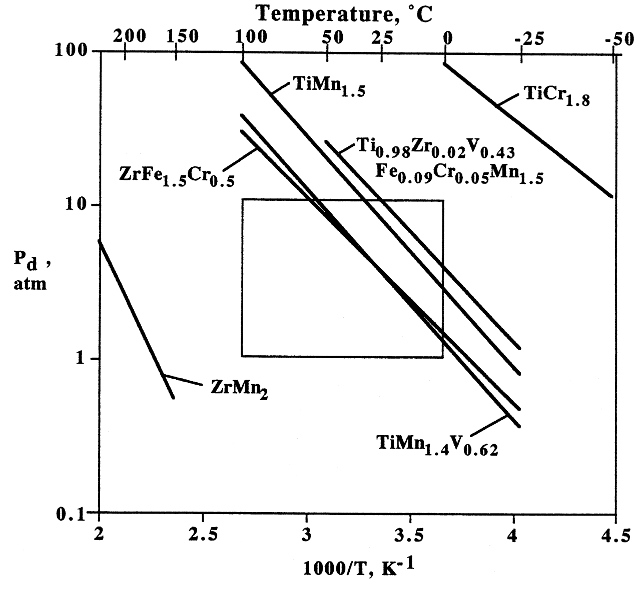

Fig. 5. Van't Hoff lines for various AB_2 hydrides.

The PCT and other properties of various representative AB_2 alloys are shown in Fig. 5 and Table 2. PCT properties can be adjusted over ranges of temperature and pressure that cover our 1–10 atm, 0–100°C preference. H-capacities of AB_2 alloys are comparable to AB_5s on a reversible (principal plateau) basis but generally higher on a $(H\text{-capacity})_{max}$ basis. The AB_2s often suffer from less distinct, narrower plateaux and a residual, essentially non-reversible 'heel' compared to AB_5s. When larger ranges of temperature and pressure are available from the application, AB_2s tend to show higher capacities than AB_5s.

The AB_2 alloys do offer significant advantages over the AB_5s in cost, at least if the A-element is mostly Ti and not Zr. As shown in Table 2, $TiMn_{1.5}$ and the widely used GfE commercial alloy $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$ have

Table 2
PCT and cost properties of selected AB_2 hydrides

Composition	ΔH kJ mol^{-1}	ΔS kJ mol^{-1} K^{-1}	25°C P_d atm	T for 1 atm P_d	Plateau	
					Hysteresis	Slope
$TiCr_{1.8}$	20.2	0.111	182	−91	0.11	0.12
$Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$	27.4	0.112	11	−28	–	1.1
$TiMn_{1.5}$	28.7	0.114	8.4	−21	0.93	0.57
$ZrFe_{1.5}Cr_{0.5}$	25.6	0.097	4.0	−10	0.34	1.26
$TiMn_{1.4}V_{0.62}$	28.6	0.107	3.6	−5	–	1.4
$ZrMn_2$	53.2	0.121	0.001	167	0.99	0.74

Composition	Density g cm^{-3}	(H-Capacity)$_{max}$		(H-Capacity)$_r$			Alloy RMC[b]	
		H/M	wt.%	ΔH/M	Δwt.%	$\Delta N_H/V$[a]	\$ kg^{-1}	\$ g^{-1} H
$TiCr_{1.8}$	6.0	1.25	2.43	0.45	0.85	2.7	8.64	1.02
$Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$	5.8	0.99	1.9	0.7	1.3	3.8	4.82	0.37
$TiMn_{1.5}$	6.4	0.99	1.86	0.65	1.15	3.8	4.99	0.44
$ZrFe_{1.5}Cr_{0.5}$	7.6	1.03	1.5	0.62	0.9	3.3	10.90	1.21
$TiMn_{1.4}V_{0.62}$	5.8	1.14	2.15	0.56	1.1	3.1	29.40	2.67
$ZrMn_2$	7.4	1.2	1.77	0.6	0.9	2.9	11.29	1.25

[b] RMC = Raw Materials Cost; \$ g^{-1} H based on (H-Capacity)$_r$.

[a] Reversible volumetric capacities are approximate and in units of 10^{22} H-atoms/crystal cm^3.

(H-capacity)$_r$-normalized raw materials costs about half those of the best AB_5s (Table 1). To make an important point on the use of V in AB_2 compositions, $TiMn_{1.4}V_{0.62}$ should be compared to $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$. Both alloys are similar in composition (including V-content) and have similar capacities, but $TiMn_{1.4}V_{0.62}$ has six to seven times the raw materials cost. That is because pure V is very expensive compared to ferrovanadium, a low-cost product used by the steel industry. Therefore, V-containing alloys should also have some Fe present to allow the use of low-cost ferrovanadium.

AB_2 alloys are generally somewhat more difficult to activate than AB_5s, although some will activate without heating, especially those higher in Zr or Mn (as opposed to Ti and Cr). Once activated, H/D kinetics are usually high. Although little good quantitative data exist, AB_2s seem to be relatively sensitive to impurities in the H_2 used; alloys high in Ti seem to passivate easily. When lanthanide elements are used in the A-side, AB_2s are very prone to disproportionation (even on the first cycle). The Ti or Zr-based alloys seem to have only minor disproportionation tendencies. Like the AB_5s, AB_2s decrepitate into fine powder. Alloys high in Zr and Mn are highly pyrophoric in the activated state, whereas those high in Ti and Cr seem not to be. The commercial production of AB_2 compounds is more difficult than AB_5 compounds and requires great metallurgical care. Because of the high melting points of the principal elements (Ti = 1670°C; Zr = 1855°C; Cr = 1863°C), along with their high reactivities, it is often very difficult to use standard vacuum induction melting (VIM) in a conventional oxide crucible. More expensive cold-crucible vacuum arc melting is usually required. The author has successfully induction-melted $ZrMn_2$ (melting temperature 1450°C) under argon in Al_2O_3 crucibles but Mn has a high vapor pressure and corrections must be made for its evaporation during melting.

4.2.3. AB intermetallic compounds

The first demonstration of a reversible intermetallic hydride was demonstrated with the AB compound ZrNi by Libowitz in 1958. Unfortunately, $ZrNiH_3$ has a 1 atm desorption temperature of about 300°C, too high for practical applications. The first practical AB hydrides were demonstrated with TiFe around 1970 by Reilly and Wiswall at Brookhaven National Laboratory, USA. TiFe and its substitutional modifications remain the best of the AB alloys today.

TiFe-based AB alloys are based on an ordered body-centered-cubic structure (prototype CsCl, Strukturbericht B2, Pearson cP2, space group *Pm*-3*m*). They tend to have two plateaus (two distinct hydrides), both with reasonable pressures at room temperature. PCT properties can be modified by partial substitution for Ti and Fe, e.g., Mn or Ni for Fe as shown in Fig. 6. Tabulation of PCT properties and costs of typical alloys are shown in Table 3. TiFe and $TiFe_{0.85}Mn_{0.15}$ show good volumetric and gravimetric reversible H-capacities, competitive with the best of the AB_5s and AB_2s. However, $TiFe_{0.8}Ni_{0.2}$ is not so useful because of its low capacity and low plateau pressure. The low capacity of $TiFe_{0.8}Ni_{0.2}$ is due to the fact the upper plateau is absent in this alloy, i.e., is at too high a pressure range to be useful. TiFe and $TiFe_{0.85}Mn_{0.15}$ offer low price, lower on a per unit H_2 storage capacity than anything heretofore presented. Hysteresis tends to be on the high side.

Activation is relatively slow and difficult for the TiFe-

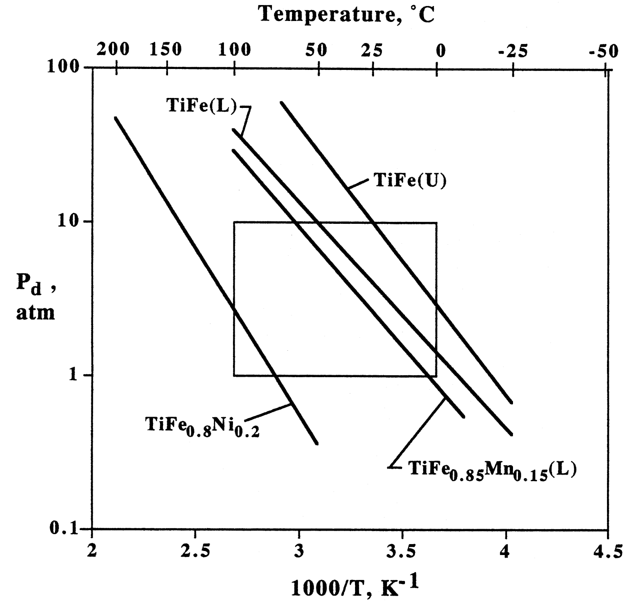

Fig. 6. Desorption van’t Hoff lines for TiFe-type hydrides. (L) indicates lower plateau; (U) indicates upper plateau.

based ABs. Binary TiFe needs to be heated to disrupt the natural oxide surface layer. Mn-modified TiFe will usually slowly activate at room temperature. In any event, it may take a day or more and high pressures (50+ atm) for complete activation. As might be expected, the passive oxide films that can easily form on TiFe (and its derivatives) result in a high degree of sensitivity to gaseous impurities in the H_2 used. On the positive side, and because of the tendency to form passive Ti-oxides, these materials seem to have little or no tendency for pyrophoricity. Cyclic stability of the lower plateau is excellent, but the upper plateau tends to drift higher and higher with H/D cycling, ultimately rendering it unusable.

The melting of TiFe-based ABs requires care. The metallurgy is made complex by the tendency of the alloys to pick up oxygen, which in turn tends to lower reversible capacity. Conventional oxide melting crucibles are not stable enough. Expensive arc melting will work. The author has successfully made tonnage quantities of good TiFe and Ti(Fe, Mn) by air melting in clay graphite crucibles, but only when mischmetal deoxidation is used.

In summary, TiFe-based AB alloys have good PCT properties, good H-capacities and low raw materials costs, but the problems associated with activation, gaseous impurities and upper plateau instabilities have largely prevented their large scale commercial use in gas applications. They will apparently not work at all in NiMH batteries.

4.2.4. A_2B intermetallic compounds

The A_2B family of compounds represent an area of historical activity. Various crystal structures are possible. In one subfamily, A is typically of the Group IVA elements Ti, Zr or Hf and B is a transition metal, typically Ni. Another family is based on Mg_2Ni, discovered in the late 1960s by Reilly and Wiswall (USA). Unfortunately, the A_2Bs offer little in the 0–100°C, 1–10 atm range, at least with the present state of the art. They are invariably more stable.

There has been extensive work on Mg_2Ni for nearly three decades, both from fundamental and applications points of view. Actually, Mg_2NiH_4 is a transition metal complex, not a metallic hydride (see Section 4.3.1). As shown in Table 4, H-capacity and cost properties of Mg_2Ni are attractive, but desorption temperatures are too high for most applications. Mg_2Ni is not very amenable to modification of PCT properties by ternary and higher-order substitutions. Numerous attempts to significantly decrease desorption temperatures have not been particularly successful. There have been several successful attempts to increase absorption and desorption kinetics by surface treated or nanocrystalline and amorphous versions of Mg_2Ni-related alloys (sometimes including catalysts), but the basic hydride thermodynamics have not been improved much.

Table 3
PCT and cost properties of selected TiFe-type hydrides, (L) = lower plateau

Composition	ΔH kJ mol^{-1}	ΔS kJ mol^{-1} K^{-1}	25°C P_d atm	T for 1 atm P_d	Plateau	
					Hysteresis	Slope
TiFe (L)	28.1	0.106	4.1	−8	0.64	0.0
$TiFe_{0.85}Mn_{0.15}$ (L)	29.5	0.107	2.6	3	0.62	0.92
$TiFe_{0.8}Ni_{0.2}$ (L)	41.2	0.119	0.1	73	0.05	0.36

Composition	Density g cm^{-3}	(H-Capacity)$_{max}$		(H-Capacity)$_r$			Alloy RMC[b]	
		H/M	wt.%	ΔH/M	Δwt.%	$\Delta N_H/V$[a]	\$ kg^{-1}	\$ g^{-1} H
TiFe	6.5	0.975	1.86	0.79	1.5	5.0	4.68	0.31
$TiFe_{0.85}Mn_{0.15}$	6.5	1.0	1.9	0.80	1.5	5.0	4.83	0.32
$TiFe_{0.8}Ni_{0.2}$	6.5	0.7	1.3	0.42	0.8	2.9	5.5	0.68

[b] RMC = Raw Materials Cost; \$ g^{-1} H based on (H-Capacity)$_r$.

[a] Reversible volumetric capacities are approximate and in units of 10^{22} H-atoms/crystal cm^3.

Table 4
PCT and cost properties of Mg_2NiH_4

$\Delta H = -64.5$ kJ mol^{-1} H_2
$\Delta S = -0.122$ kJ mol^{-1} K^{-1}
25°C $P_d = 10^{-5}$ atm (extrapolated)
T for 1 atm $P_d = 255$°C
$(H/M)_{max} = 1.33$
$(wt.\%)_{max} = 3.6$
$(\Delta H/M)_r = 1.23$
$(\Delta wt.\%)_r = 3.3$
$(\Delta H/V)_r = 5.2 \times 10^{22}$ H-atoms/cm^3
Alloy Raw Materials Cost = \$6.26 kg^{-1}
Alloy Raw Materials Cost = \$0.19 g^{-1} H stored

4.2.5. Other intermetallic compounds

In addition to the AB_5, AB_2, AB and A_2B intermetallic compounds discussed above, several other families of intermetallics have been shown capable of reversible hydriding/dehydriding reactions [3,5]. Examples include AB_3, A_2B_7, A_6B_{23}, A_2B_{17}, A_3B and others. Most structures involve long-period AB_5 and AB_2 stacking sequences and are thus crystallographically related to these two classic families. Although none of these have attained commercial levels of interest, at least the AB_3 and A_2B_7 phases do have PCT properties are in the range of our interest. Most either have narrow plateaux with long sloping upper legs (e.g., $GdFe_3$) or multiple plateaux (e.g., $NdCo_3$ or Pr_2Ni_7). La_2Mg_{17} was once reported to have 6 wt.% H-capacity, recoverable at room temperature [10], but that claim has never been independently confirmed.

4.2.6. Solid solution alloys

Metallurgically speaking, the term ‘solid solution alloy’ designates a primary element (solvent) into which one or more minor elements (solutes) are dissolved. Unlike the intermetallic compound, the solute need not be present at an integer or near-integer stoichiometric relationship to the solvent and is present in a random (disordered) substitutional or interstitial distribution within the basic crystal structure. Several solid solution alloys form reversible hydrides, in particular those based on the solvents Pd, Ti, Zr, Nb and V.

Perhaps the largest family of solid solution hydrides consists of the face-centered-cubic (A1) Pd-based alloys [5]. Although the PCT properties of many of the Pd solid solution hydrides are useful, they are of generally low gravimetric and volumetric H-capacity, e.g., seldom exceeding 1.0 wt.% H. In addition they are prohibitively expensive. Ti- and Zr-based solid solution alloys form hydrides that are too stable, even when highly alloyed.

Vanadium has dihydride properties compatible with useful ambient temperature H-storage (Fig. 3), so it is logical that binary and higher component solid solution’s based on V offer further opportunities. These alloys are all based on the simple body-centered-cubic (A2) crystal structure and their dihydrides generally form a face-centered cubic structure (Strukturbericht C1, prototype CF_2, Pearson cF12 and space group *Fm*-3*m*). The first extensive hydride work on V solid solutions was done by the Reilly BNL (USA) group in the early 1970s, followed by the Libowitz Allied Chemical (USA) group in the 1980s. At present, there is strong activity by the Akiba group (Japan), which is reported in this volume [11].

There are many reported V solid solution hydriding alloys, but V–Ti–Fe seems to be one with good promise. For example, by varying x from 0 to 0.075 in $(V_{0.9}Ti_{0.1})_{1-x}Fe_x$, the dihydride plateau pressure can be varied over more than an order of magnitude without affecting capacity [12]. The PCT and cost properties of one alloy in this V–Ti–Fe family, $(V_{0.9}Ti_{0.1})_{0.95}Fe_{0.05}$, are shown in Table 5. PCT properties are attractive for room application with good $(\Delta wt.\%)_r$. Even using low-cost ferrotitanium for the source of the Fe, the alloy raw materials price is on the high side. As mentioned earlier (Section 4.2.2), pure V is very expensive and it this author’s opinion that any V-based solid solution alloy must contain Fe so that commercial ferrovanadium can be used in its manufacture. Fortunately, ferrovanadium has been used successfully in the production of V–Ti–Fe hydriding alloys, although the major impurities Al and Si do seem to change the PTC properties significantly [13].

A new family of ‘Laves phase related BCC solid solution alloys’ based on V–Ti–Mn has recently been reported [11]. Alloys contain a nanoscale lamellar structure, possibly resulting from partial spinodal decomposition, and offer good room temperature capacity and reversibility.

There is relatively little literature on the non-PCT properties of V solid solution hydrides, e.g., gaseous impurity effects. The high melting temperatures and high reactivities of V alloys probably restrict the available melting techniques to ‘cold crucible’ methods such as vacuum arc or electron beam melting. No large-scale commercial batches of such alloys have been produced and hydrided. There has been no long-term cycling of V alloy hydrides, so it is uncertain if disproportionation or other metallurgical instabilities occur.

Table 5
PCT and cost properties of $(V_{0.9}Ti_{0.1})_{0.95}Fe_{0.05}$ hydride

$\Delta H = -43.2$ kJ mol^{-1} H_2
$\Delta S = -0.140$ kJ mol^{-1} K^{-1}
25°C $P_d = 0.5$ atm
T for 1 atm $P_d = 36$°C
Hysteresis = 0.80
Plateau Slope = 0.45
$(H/M)_{max} = 1.95$
$(wt.\%)_{max} = 3.7$
$(\Delta H/M)_r = 0.95$
$(\Delta wt.\%)_r = 1.8$
$(\Delta H/V)_r = 4.9 \times 10^{22}$ H-atoms/cm^3
Alloy Raw Materials Cost = \$10.63 kg^{-1}
Alloy Raw Materials Cost = \$0.59 g^{-1} H stored

Table 6
Qualitative overview of hydride types as to attributes[a]

Attribute	AB_5	AB_2	AB	A_2B	V–SS
Versatility	+	+	+	−/0	0
H-Capacity	0	0/+	0/+	+	+
PCT	+	+	+	−	+
Activation	+	0	−/0	0	0
Impurity effects	+	0	−	0	−/?
Cyclic stability	−/0/+	−/0/?	−/0	0/?	?
Ease of manufacture	+	0	+	0	?
Pyrophoricity	0	−	+	+	+/0
Cost	0	+	+	+	−/0

[a] Attribute key: − = problem; 0 = neutral; + = good; ? = uncertain.

4.2.7. Summary of hydriding alloys

A qualitative summary of PCT and non-PCT properties of the alloy families discussed above is given in Table 6. Such a summary is mainly based on the experience and opinions of the present author. Another reviewer might have slightly different opinions in general, or strong specific differences in a few cases. The AB_5, AB_2 and AB intermetallics offer the best collections of near room-temperature PCT properties, with the AB_2 and AB compounds offering the best combinations of good H-capacity and lowest raw materials cost. V solid solutions offer good capacity, but cost is questionable, secondary properties are not known well. The important point to be made is that there are no ideal hydriding alloys. There are many gaps to be filled and particular areas of R&D to follow within the framework of AB_5, AB_2, AB, A_2B and V solid solution alloys, to be sure [3]. However, it must be argued that we are reaching a point of diminishing returns involving limits to the inherent thermodynamics and metallurgy of these conventional families of hydriding alloys. We need to explore new and different approaches.

4.3. Other Approaches

New directions for hydriding materials include amorphous and nanocrystalline alloys, quasicrystalline alloys, transition and non-transition metal complexes and carbon. In the area of amorphous nanocrystalline alloys, usually made by sputtering or ball milling, there has been good progress made in increasing the A/D kinetics, but this reviewer is pessimistic that the desorption thermodynamics can be permanently changed, i.e., there seems to be little or no evidence the desorption temperatures of Mg alloys can be permanently decreased or the H-capacities significantly increased. Amorphous alloys do not have a plateau, which can limit practical applications. They are inherently metastable in nature and will tend toward the equilibrium crystalline forms or larger grain sizes. In the relatively new area of quasicrystalline alloys, there are only a limited number of available alloys. Those that have been hydrided are high in Ti, resulting in impracticably high desorption temperatures.

4.3.1. Hydride complexes

Complex hydrides are well known. One category comprise the transition metal complexes. When certain transition metals are combined with a Group IA or IIA element in the presence of hydrogen, a low valence complex of the transition metal and multiple H atoms will form. Such complexes are stabilized by the donation of electrons from the more electropositive IA or IIA elements. A well used example of this is Mg_2NiH_4, where Mg donates electrons to stabilize the $[NiH_4]^{-4}$ complex. In effect, four hydrogen atoms bond with a single Ni atom and the two Mg atoms donate two electrons each to stabilize that high-H transition metal complex. There are a number of such transition metal complex hydrides that have been discovered around the world and are at least four groups that have contributed much of the historical activity in this area: (1) the Yvon group at the University of Geneva, (2) the Noréus group at Stockholm University, (3) the Bronger group at the Technische Hochschule Aachen and (4) the Moyer group at Trinity College (USA).

Mg_2NiH_4 is an exception to the general situation of TM complex hydrides in that it has a corresponding Mg_2Ni intermetallic. It is very significant that transition metal complex hydrides can be synthesized from combinations of electropositive elements and transition metals that do not form intermetallic compounds. For example, it is well known that Mg and Fe do not alloy at all in the H-free solid metallic state. Yet when Mg and Fe powder are sintered in H_2, the high-H complex hydride Mg_2FeH_6 forms. Because the formation and decomposition of transition metal complex hydrides usually require some metal atom diffusion, the kinetics tend to be rather slow compared to the traditional interstitial hydrides and high temperatures are needed for H_2 desorption. However the high hydrogen contents possible (e.g. $Mg_2FeH_6 = 5.5$ wt.% H) give potential to these materials as storage hydrides. We need to learn how to make the TM complex hydrides more reversible, especially in the low temperature H_2 desorption mode. This area is reviewed in this volume by Yvon [14].

Another major area of complex hydrides comprises the non-transition metal complexes. Examples include aluminates and borohydrides such as $LiAlH_4$ and $NaBH_4$ ($[AlH_4]^-$ and $[BH_4]^-$ complexes), among many others. Although long used to generate H_2 gas by reaction with H_2O, these hydrides have never been known to be very reversible from the gas phase point of view. Recently, Bogdanovic has importantly discovered that the two-step gas reaction for $NaAlH_4$ can be made reversible (absorption and desorption) by the addition of Ti-catalysts [15]:

$$NaAlH_4 \leftrightarrow 1/3\,Na_3AlH_6 + 2/3\,Al + H_2 \leftrightarrow NaH + Al + 3/2\,H_2 \tag{4}$$

The H-capacity for Eq. (4) is about 5.6 wt.%; under cyclic conditions about 4 wt.% reversible capacity can achieved below 150°C. Catalyzed complex hydrides offer a whole new area for low temperature, high capacity reversible hydrides. Recent developments with Ti- and Zr-catalyzed $NaAlH_4$ are reported by Zidan et al. [16].

4.3.2. Carbon

Study of storing H_2 on or in various forms of carbon has been very active lately. It has long been known that high surface area activated carbon will physisorb molecular H_2 and serve as a storage medium for the gas. However, because adsorption is by relatively weak Van der Walls interactions, significant storage of H_2 on C occurs only when the C is cold ($<$150 K) and high pressures are applied. On the other extreme, H can be chemically bonded to the C60 and C70 fullerenes. H-contents as high as $C_{60}H_{48}$ (6.3 wt.% H) have been achieved. Unlike the purely physisorption process with activated carbon, C_{60} carbon atoms form relatively strong covalent bonds with H atoms, with ΔH on the order of 285 $\mathrm{kJ\,mol^{-1}}$ H_2. This means that temperatures on the order of 400°C are needed for the breaking of that bond and the desired desorption of H_2 gas. The question is can the chemistry of the fullerene hydrides be controlled to lower stability, much like what has been successfully achieved with the metallic hydrides reviewed above?

A clear potential has been demonstrated for room storage of H_2 molecules in single wall carbon nanotubes (a tubular form of the normally spherical fullerenes) by a group led by Heben (USA) [17]. SWNTs have internal dimensions on the order of 1–2 nm, about what is needed for the capillary ‘condensation’ of H_2 near room temperature. Predictions of room temperature reversible 5–10 wt.% H have been made. If confirmed, such H-contents would surpass what is known for any reversible metal hydride and open a new technology for ‘solid’ hydrogen storage.

One final form of carbon proposed for near ambient temperature H-storage applications are ‘graphite nanofibers’, developed by Rodriguez and Baker of Northeastern University (USA). The new form of graphite is made by reacting hydrocarbons and CO on Ni- and Fe-based catalysts. By a mechanism not fully understood by the developers, this form of carbon is said to be capable of ‘condensing’ extraordinary amounts of molecular H_2 within the graphite layers, up to 67 wt.% [18]. Because H-contents of strongly bonded C–H chemical compounds do not exceed methane CH_4 (25 wt.% H), as well as no obvious a priori physical process that could account for such high levels of H-intercalation, the reported measurements have been met with considerable scepticism. At this writing, the measurements of Rodriguez and Baker have apparently not been independently substantiated to date. If even partially confirmed, this new form of graphite would obviously be of great interest for H-storage. As always in science, time will be the great resolver of this interesting controversy.

5. Conclusions

The development of reversible metal hydrides has had a long, interesting and successful history. There are numerous alloys and intermetallic compounds that have properties of real commercial interest and value for applications. However, those hydrides that will readily release their H_2 at room temperature have reversible gravimetric H-densities no more that about 2 wt.%. This is not sufficient for fuel cell vehicles, perhaps the most active new area of hydrogen application. From a gas reaction point of view, the conventional alloys and intermetallic compounds seem to be reaching their thermodynamic limits relative to PCT and H-capacity. Greater promise for the future lies in catalyzed hydride complexes. In the non-metal area, carbon has offered some renewed potential.

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