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ABSTRACT

Certain intermetallic hydrides are safe, convenient and inexpensive hydrogen storage compounds. A particular advantage of such compounds is the ease with which their properties can be modified by small changes in alloy composition or preparation. This quality can be exploited to optimize their storage properties for particular applications, e.g. as intermetallic hydride electrodes in batteries. The purpose of this paper is to review the chemistry of such hydrides with particular reference to those materials which are of interest for energy storage applications.

INTRODUCTION

The unique properties of hydrogen make it attractive for use as a non-polluting, almost universal fuel. On earth there is almost no free molecular hydrogen but it can be made from readily available raw materials such as coal and natural gas or, alternatively, by the electrolysis of water using power produced by some primary energy source. However, one of the major barriers which has prevented its wide use as a fuel is the difficulty involved in its storage and portability. Currently, hydrogen is stored as a compressed gas or as cryogenic liquid. Neither method is suitable for common, everyday use. A convenient and economical alternative to conventional storage methods for many applications is storage as a metal hydride. Their advantage is derived from the high volumetric density of hydrogen in the hydride phase which usually exceeds that of liquid hydrogen and the relative ease and safety with which they can be used. Further, recent work has shown that the performance of batteries incorporating metal hydride electrodes may constitute an important advance in battery technology. However, although many elemental metals will react directly and reversibly with hydrogen to form such hydrides, few, if any, can satisfy the criteria required for wide use as a hydrogen storage compound. Thus, most research in this area has been centered on alloy hydrides particularly those involving intermetallic compounds. We will be concerned herein with the more important aspects of the thermodynamic and structural principles which regulate the behavior of intermetallic hydrogen systems and then illustrate their application using the archetype hydrides of $LaNi_5$, FeTi and Mg alloys. The practical utility of these classes of materials will be briefly noted. Apropos of the nature of these proceedings this review is not meant to be an exhaustive treatment of intermetallic hydrides; rather its purpose is to survey the field and to provide a point of departure for those who wish to pursue the subject matter more thoroughly; in this connection a comprehensive review volume has recently been published (1); an earlier review of the properties of binary hydrides is also recommended (2).

FUNDAMENTAL ASPECTS

A hydrogen-metal system may be defined as consisting of an amorphous or crystalline metal phase, perhaps containing dissolved hydrogen, in interfacial contact with molecular, atomic, or ionized hydrogen. In many cases, depending on the temperature and pressure, a crystalline metal hydride phase will form of which there are three general categories; ionic, covalent and metallic. Intermetallic hydrides are, of course, a sub-group of the latter class, in which hydrogen occupies interstitial sites in the metal lattice and the hydride phase is crystalline. There are a large number of intermetallic compounds many of which a will form a hydride via the direct and reversible reaction with hydrogen. Consequently, even though most may not be of interest for practical applications, the sheer number of possible systems constitute the great advantage of the class over that consisting of binary hydrides (hydrogen + elemental metal).

Thermodynamics

Recently Flanagan and Oates extensively reviewed this subject (3); also recommended is the work of Libowitz (4) who treated the thermodynamics of binary systems with exceptional clarity. The pressure - temperature - composition relationships of any metal/hydrogen system can be conveniently summarized by a P-T-C diagram of which an idealized version is shown in figure 1. It is essentially a special type of phase diagram which consists of a family of isotherms that relate the equilibrium pressure of hydrogen with the concentration of hydrogen in the solid. Initially the isotherm ascends steeply as hydrogen dissolves in the metal to form a solid solution which by convention is designated as the α phase. At low concentrations the behavior is ideal and the isotherm obeys Sievert's Law, i.e.,

$$H_{solid} = K_s P^{1/2} \qquad [1]$$

where H is the concentration of hydrogen in the metal, K_s is Sievert's constant and P is the equilibrium hydrogen pressure. As the H content of the solid increases the system departs from ideal behavior due to H-H attractive interactions primarily caused by elastic strain in the metal; this is reflected by a decreasing slope in the isotherm. Point A marks the terminal solubility of hydrogen in the α phase as well as the appearance of the hydride phase which is designated, again by convention, the β phase. The solubility of hydrogen in many metals can be appreciable and thus the phases formed in such systems usually have a relatively wide homogeneity range. Upon the appearance of the β phase the hydrogen pressure will remain constant and forms a "plateau" as more hydrogen is added. The plateau is a consequence of the phase rule and will persist as long as the two solid phases coexist. In practical terms the length of the plateau corresponds to the hydrogen storage capacity of the system. Upon the disappearance of the α phase at B the system regains a degree of freedom and pressure will rise again as a function of the hydrogen content. In this region of the diagram electronic factors become dominant as the limiting hydrogen concentration is approached. It is also possible that more than one hydride phase exists in which case a second plateau will appear. If so the same considerations apply. In most metal/hydrogen systems there is a significant hysteresis effect in the phase conversion process which is reflected by a higher isotherm plateau pressure for formation of the hydride phase than its corresponding decomposition. The effect of increasing temperature is shown by the higher temperature isotherms T2 and T3. Usually as the temperature increases the miscibility gap narrows and eventually disappears as the consolute temperature is reached.

The reaction of a metal with hydrogen may be written as

$$M + (x/2)H_2 \rightleftharpoons MH_x \qquad [2]$$

Thermodynamic quantities for a system may be determined from the van't Hoff equation which defines the equilibrium constant, K, in terms of the reaction enthalpy, ΔH and the temperature, T.

$$d\ln K/dT = \Delta H/(RT^2) \qquad [3]$$

$$K = a_{MHX}/(a_M f_{H2})^{x/2} \qquad [4]$$

Under ideal conditions the activity of a solid may be taken as unity and the fugacity as the pressure, then [3] may be rewritten as

$$d(\ln(P_{H2})^{-x/2})/dT = (\Delta H/RT^2)dT \qquad [5]$$

which upon integration yields,

$$\ln P_{H2} = 2/x(\Delta H/RT) + C. \qquad [6]$$

The enthalpy of the β/α phase conversion can be determined via equation [6] by plotting the log of the decomposition plateau pressure, P_{plat}, vs. the reciprocal temperature. When hysteresis is present the plateau pressure of the decomposition isotherms are used because they are more reproducible. When the solubility of hydrogen in the metal (α) phase is small then $\Delta H_{plat} = \Delta H_f$, the enthalpy of formation of the hydride from the metal (5); the intercept, C, is equal to $2/x(\Delta S_f/R)$. Equation [6] is commonly presented in the form

$$\ln P_{H2} = (A/T) + B \qquad [7]$$

where the constants A and B are specified. Thermodynamic data for some representative compounds are given in Table 1.

Electronic Properties

Switendick was the first to apply modern electronic band theory to metal hydrides (6). He compared the measured density of electronic states with theoretical results derived from energy band calculations in binary and pseudo binary systems. More recently attention has been given to the changes in the band structure of intermetallic hydrides including $LaNi_5H_x$ and $FeTiH_x$; the results for these more complicated systems have been summarized in a review article by Schlapbach and Gupta (7). All exhibit certain common features upon the absorption of hydrogen and the formation of distinct hydride phase. These are 1: the density of states versus energy function is changed, 2; new low lying states having an s-like character appear and are associated with hydrogen, 3; to the extent that the hydrogen electrons cannot be accommodated in the new low lying states they are inserted into empty states near the Fermi level which in turn shift.

Reaction Rules and Predictive Theories

There have been numerous studies with the object of gaining an understanding of the factors that influence the stability, stoichiometry and H site occupation in hydride phases. These factors have been correlated with cell volume or the size of the interstitial hole in the metal lattice and certain thermodynamic parameters. None have been universally successful although they have been widely applied.

Westlake (8) developed a geometric model which successfully predicts the stoichiometries and site occupation of the H atom in AB_2 and AB_5 hydrides. It is based on the finding that the partial molar volume of the H atom, V_H, in a metal hydride crystal is relatively constant at 1.7 $cm^3(g\ atom\ H)^{-1}$ (9) and therefore addition of hydrogen causes lattice expansion and increases the radii of the interstitial hole which the hydrogen atom occupies. It involves two structural constraints; that the minimum hole size necessary to accommodate a H atom has a radius of 0.40 Å and that the minimum distance between two H occupied sites is 2.10 Å. The former criterion was empirically derived from a survey of known hydride structures while the latter was suggested by Switendick and based on electron band structure calculations (10).

Miedema and co-workers (11,12) have developed a semi-empirical model to predict the enthalpy of formation of an intermetallic hydride. Briefly the model states that the enthalpy (ΔH_{ft}) of formation of a ternary hydride from an intermetallic compound (not from the elements) is composed of three terms, i.e.,

$$\Delta H_{ft}(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - \Delta H(AB_n) \qquad [8]$$

where A and B are metals and A is a stable hydride former, e.g. Ti. The rule has been quite successful when applied to systems involving the rare earth–transition metal intermetallic compounds, but has been less so with systems involving Ti alloy hydrides.

A relatively simple set of rules have been found to hold for all intermetallic hydrides useful for hydrogen storage (13). They may be stated as follows:

1. In order for an intermetallic compound to react directly and reversibly with hydrogen to form a distinct hydride phase it is necessary that at least one of the metal components be capable of reacting directly and reversibly with hydrogen to form a stable binary hydride.

2. If a reaction takes place at a temperature at which the metal atoms are mobile, the system will assume its most favored thermodynamic configuration.

3. If the metal atoms are not mobile (as is the case in low temperature reactions) only hydride phases can result in which the metal lattice is structurally very similar to the starting intermetallic compound because the metal atoms are essentially frozen in place. In effect the system may be considered to be pseudo binary as the metal atoms behave as a single component.

Rule 1 is purely empirical. It is based solely on experimental observations. The latter two rules are merely restatements of established thermodynamic and structural principles. They refer to two temperature dependent variables, the free energy and the metal atom diffusion rate, either one of which may be the dominant factor in system behavior. These simple rules have been found to be quite useful and they shall be invoked when appropriate in this review.

SPECIFIC INTERMETALLIC HYDRIDES

Alloy Preparation

The hydriding behavior of intermetallic compounds is strongly influenced by alloy microstructure, metal stoichiometry, the presence of additives and impurities. Thus an understanding of the physical metallurgy of a particular system as well as a knowledge of its phase diagram is required if one wishes to prepare alloys having properties which are reproducible and optimum for a particular application. Sandrock et al. (14) have studied the effects of such variables upon the hydrogen storage capacity, activation of the alloy towards hydrogen, particle attrition, and hydride stability of FeTi. More recently Percheron–Guegan and Welter have described both laboratory and industrial preparation techniques for many intermetallic hydride formers, particularly emphasizing $LaNi_5$ and its substituted analogues (15).

Activation, Hydride Formation and Deactivation

Usually the first hydriding reaction is relatively slow and may be considered an activation process. In some cases a prior outgassing and heating step is required to initiate the first reaction. After the initial formation the hydride phase is decomposed by outgassing and slight heating. After activation a very reactive alloy can be obtained by subjecting it to repetitive hydriding/dehydriding cycles; this treatment usually produces finely divided alloy powder with a surface area ranging from 0.2 – 0.5m^2/g. In some cases the alloy in this state may be pyrophoric. Detailed accounts of the laboratory scale preparation of iron titanium hydride ($FeTiH_{1.94}$) and aluminum lanthanum nickel hydride ($LaNi_4AlH_4$) are available (16,17).

All the intermetallic hydrides discussed here can be deactivated by various impurities in the gas phase. If the exposure is not overwhelming the alloy can be reactivated by heating and outgassing followed by repeated cycling in pure hydrogen. Sandrock and Goodell have discussed the results of an extensive experimental screening effort to define the interactions of a number gaseous impurities with AB_5 and FeTi alloys (18).

AB_5 Hydrides

Van Vucht et al. (19) found that a number of intermetallic compounds of the AB_5 type (where A is a rare earth metal and B is Ni or Co) will react directly and reversibly with hydrogen to form a ternary metal hydride. The archetype and most thoroughly investigated of these alloys is $LaNi_5$; it reacts rapidly with hydrogen (even in ingot form after an induction period) at room temperature at a pressure of several atmospheres above the equilibrium plateau pressure. A P–T–C diagram for this system is shown in figure 2. It is notable that the hysteresis effect is relatively small, particularly when compared to other low temperature systems with a large and distinct miscibility gap. The nominal reaction may be written as follows:

$$LaNi_5 + 3H_2 \rightleftharpoons LaNi_5H_6 \qquad [9]$$

With reference to rule 3 we note that ΔG_{f298} for $LaNi_5$ and for LaH_2 are about −67 and −171 kJ respectively. Thus the following disproportionation reaction is highly favored (20),

$$LaNi_5 + H_22 \rightleftharpoons LaH_2 + Ni \ \Delta G_{298} = -100 \text{ kJ/mol } H_2 \qquad [10]$$

whereas for reaction [9] $\Delta G_{298} = 0$. Cohen et al. (21) noted a substantial loss in H storage capacity after repetitive cycling between 300 and 570 K which they suggested was to the formation of LaH_2 via reaction [10]. However, Benham et al. (22), using a neutron scattering technique, found no evidence of the presence of LaH_2 after cycling between 323 and 523 K under 10 atm. of H_2 although other unidentified species were produced. This is not surprising since there are 7 other intermetallic compounds in the La/Ni system all of which are richer in La than $LaNi_5$ and form more stable hydride phases. Of course LaH_2 is very stable (Table 1) and its formation becomes increasingly likely at high temperatures where the metal atoms become mobile.

However, disproportionation on the surface of polycrystalline $LaNi_5$ occurs readily at room temperature as determined from x-ray photoemission spectroscopy, Auger electron spectroscopy and magnetic susceptibility studies (23). They determined that there is a surface enrichment of La to give a ratio of $La/Ni \approx 1$; the La is associated with oxygen but Ni remains metallic and is present as clusters on the surface containing about 6000 atoms. Thus, the surface of highly cycled $LaNi_5$ appears to consist of islands of La associated with oxygen, (La_2O_3 or $La(OH)_3$) and Ni. The oxygen species, which may be designated as La_2O_3, was produced by the presence of small amounts of oxygen present initially in the alloy and/or in the H_2 gas. It was proposed (23,24) that such surface disproportion into a stable oxide and an easily reduced transition metal is the mechanism by which an aggressive catalytic surface is formed, readily capable of dissociating the H_2 molecule which is prerequisite for hydride formation. Indeed the mechanism seems generally applicable to other intermetallic hydrides in which the metal components consist of a metal from group 2-4 of the periodic table and a transition metal, e.g., Mg_2Ni, $MgCu_2$ and TiFe (25,26).

The kinetics of the formation and decomposition of $LaNi_5$ hydride have been widely studied with just as widely varying results (27). In almost all cases the investigations were done using static beds of metal/metal hydride particles in contact with gaseous hydrogen. Such systems have inherently poor heat transport and exchange characteristics and, since reaction rates are extremely high and exothermic, isothermal conditions are difficult if not impossible to maintain. Consequently the data are difficult to interpret and the likely cause of the disparity in reported results. The problem can be ameliorated by the addition of an inert thermal ballast, such as nickel powder, which is intimately mixed with the active material (27,28). However, even in this case there is significant departure from isothermal conditions over the course of the experiment. Recently it was noted that β $LaNi_5H_x$ would form and decompose in liquid suspensions, in which heat exchange is extremely facile, thereby providing a means to carry out isothermal experiments. The initial effort was concerned with the kinetics of hydrogen absorption by $LaNi_5$ and $LaNi_{4.7}Al_{.3}$ suspended in n-undecane and n-octane. The rate limiting process was the dissolution of the H_2 molecule in the liquid phase in both cases (29,30). This finding, while interesting in itself, revealed little about the kinetics of hydride formation. However, kinetic behavior for the corresponding decomposition reaction, again using a suspension of β $LaNi_5H_x$, is completely different (31). Here the kinetics are well described by a shrinking core model where the rate limiting process is the solid state transformation taking place at the interface between the unreacted core hydride and the metal product layer. The rate equation is as follows,

$$kt = (1 - (1 - X)^{1/3})\mathrm{Ln}(P_e/P) \qquad [11]$$

where k is a rate constant, t is time, X is the fraction converted, P_e is the equilibrium plateau pressure of the hydride and P is H_2 pressure in the gas phase. The expression $\mathrm{Ln}(P_e/P)$ is a thermodynamic factor which was held constant. It has been reported that the formation of $\beta LaNi_5H_x$ can also be described by a shrinking core model (32). Indeed it is quite possible that such phase-boundary controlled reactions may be quite common in metal hydrogen systems since the decomposition of ($Pd_{.85}Ni_{.15}$ hydride (33) and β $LaNi_{4.7}Al_{.3}H_x$ (34) obey similar phase boundary controlled kinetic models.

The consequences of this type of kinetic behavior are important in several respects. In hydride formation a growing product layer of β $LaNi_5H_x$ proceeds inward from the surface while in hydride decomposition the reaction also proceeds inward from the surface but now the growing product layer is α $LaNi_5H_x$. The various reaction pathways are illustrated in figure 4. Such behavior significantly affects the catalytic activity of the solid surface even though the surface of highly cycled $LaNi_5$ consists primarily of La_2O_3 and Ni. The mechanism is probably related to expansion or contraction of the surface layers caused by the presence or absence of sub-surface hydride phases (35).

A particular advantage of the AB_5 hydride family is that the properties of the alloy-hydrogen system can be varied almost at will by substituting, in whole or in part, other metals for lanthanum and Ni. For example, mischmetal, which is a mixture of rare earth metals, when substituted for La forms a hydride having about the same hydrogen content but is much more unstable. Lundin et al. (36) have carried out a systematic study of such substitutional alloys and have correlated the free energy of formation (plateau region) with the change of the interstitial hole size caused by the substituted metal component. Gruen et al. (37) have taken a similar approach, but rather correlate the cell volume with ΔG as shown in figure 5.

The crystal structure of $LaNi_5D_7$ has been determined (38,39). The hexagonal unit cell is doubled along the c axis due to deuterium ordering. The deuterium occupies three different sites, two tetrahedrally coordinated with Ni_4 and La_2Ni_2 neighbors and one octahedral site with La_2Ni_4 neighbors. It is of interest to note that the geometric model of Westlake holds for this structure (39). The Ni_4 tetrahedron has the smallest interstitial volume in $LaNi_5$ lattice with a spherical hole radius of 0.27 Å, much to small to accommodate the H atom. However, if the La_2Ni_2 and La_2Ni_4 sites are occupied first then it was calculated that radius of the Ni_4 site is increased to 0.38 A due to expansion of the unit cell. This is large enough for insertion of the D atom after which the radius is increased to a final measured value of

0.46 Å. This may be compared to Ni itself in which the hole radius of the tetrahedral site is 0.28 Å while that of the octahedral site is 0.52 Å. It is the latter site which is occupied in $NiH_{0.6}$ (40) which increases the radius to 0.55 Å. The tetrahedral hole radius also increases slightly to 0.30 Å but it is still to small for hydrogen insertion and remains unoccupied.

Applications of AB_5 Hydrides

This class of hydrides is particularly suited for many applications because the AB_5 phase can accommodate a large number of substitutional alloys. Thus it is possible to design a hydride to optimally fit a given application. Even small changes in alloy composition can affect PCT properties. This is illustrated in figure 3 where the properties of the archetype hydride of LaNi5 can be modulated merely by varying the Ni content (41). The capability of varying A or B, either by ratio or by substitution, makes it possible to enhance desirable properties and eliminate undesirable ones. Thus, these materials have been of particular interest for applications where efficient operation requires that the hydride properties be modified to closely match the operating parameters of the system. Heat pumps employing metal hydrides is one such application where the hydride properties are modulated via alloy composition so that efficient operation can be obtained with a given heat source and sink temperature (42,43).

A major problem in heat pumps and all other applications involving the reaction of gaseous H_2 with an metal hydride former is that the effective rate limiting process for both hydride formation and decomposition is the removal from or addition of heat to the solids. This is due to the poor thermal characteristics of a static bed of fine particles in a gas. It arises primarily from the very low effective thermal conductivity of the bed because of the interfacial resistance to heat flow between the particles. This may be improved by the use of compacts where the active alloy is compacted with another metal such as aluminum to form a porous compact (44), but heat exchange requirements still remain the dominant factor in engineering design; this problem has been the primary obstacle to the design of competitive heat pumps employing metal hydrides. A possible solution involves the replacement of a dry bed systems with metal hydride slurries which have excellent thermal properties and have been suggested for several applications (45,46).

The virtues of these materials have not been lost on those interested in electrochemical applications. Particularly attractive are the use of metal hydrides as hydrogen storage electrodes since a number of problems associated with gas/solid systems are bypassed. The constraints involved in P-T-C relationships are much more relaxed than in gas solid systems since only a small efficiency penalty, expressed in millivolts, is suffered if ΔG_f is slightly positive or varies over the course of the phase conversion process due to non-ideal behavior. In gas/solid systems such behavior may very well eliminate an otherwise attractive material from consideration. Heat removal or addition is no longer a major difficulty. An early study of the $LaNi_5H_x$ electrode by Ewe et al. found that its electrochemical storage capacity was about half that of the limiting composition of $LaNi_5H_6$ (47). Subsequent studies by Percheron - Guegan et al. (48) of $LaNi_{5-x}M_x$, where M is Cu,Cr, Al and Mn, increased electrode stability. Willems and Buschow (49) extended this approach and correlated the electrode corrosion in a KOH electrolyte with the volume expansion of the alloy as a result of hydriding. By judicious partial substitution of Nd, Co and Si to give $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}$, they reduced the volume increase substantially thereby effecting a large increase in electrode lifetime. This work is a prime example of designing an AB_5 alloy for a specific application.

The importance of microstructure and metallurgical techniques to prepare an alloy having improved electrocatalytic activity was recently demonstrated by Notten and Hokkeling (50) using a relatively simple metallurgical technique. They prepared an AB_5 electrode with a small Ni excess as indicated by the Ni/La phase diagram. Rather than producing a single phase, as in reference (49), they adopted a procedure that precipitated the excess nickel as small particles uniformly distributed on the AB_5 granules, resulting in an alloy with greatly improved catalytic properties.

Iron-Titanium Alloys

The iron-titanium alloys are possibly the most promising candidates for simple, straightforward storage of hydrogen. Their advantage is derived from the low cost and high abundance of the raw material from which the starting alloys can be produced. The archetype compound FeTi will react directly with hydrogen to form a mono-hydride and a dihydride (51). The reactions which take place stepwise may be written (starting with the hydrogen saturated metal) as follows:

$$2.13\ FeTiH_{0.1} + H_2 \quad 2.13\ FeTiH_{1.04} \qquad [12]$$

$$2.20\ FeTiH_{1.04} + H_2 \quad 2.20\ FeTiH_{1.95} \qquad [13]$$

The products of the reactions are gray metal-like solids with essentially the same appearance as the initial alloy. Exposure of $FeTiH_x$ compounds to air will deactivate them and, even though they may have dissociation pressures appreciably above 1 atm at 298 K, they will decompose (i.e., evolve hydrogen) only very slowly, if at all. They may be reactivated by repeating the initial activation procedure. Such deactivation of $FeTiH_x$ has been used to advantage as it permits one to handle samples in open air without decomposition; both X-ray and neutron diffraction measurements and density determinations have been made using such deactivated samples. A family of dissociation pressure-composition isotherms for the FeTi/H system is shown in figure 6; also shown is an absorption isotherm which illustrates the rather large hysteresis effect. The rate of decomposition of iron titanium hydride near room temperature has been reported (13); the reaction is very rapid and a thermal ballast was used in an attempt to approach isothermal conditions. The decomposition of the monohydride phase obeyed first order kinetics.

As with many other alloy hydrides, the P-C-T properties of the system can be modified by the addition or substitution of another transition metal component. However the possibilities are much more limited than the AB_5 class of compounds. One particular ternary alloy is of interest, $TiFe_xMn_y$ since it can be activated at or near room temperature whereas pure FeTi requires outgassing at 473 K before activation (52).

Titanium forms a rather stable binary hydride ($\Delta G_{f298} = -83$ kJ) and the disproportionation of FeTi upon reaction with hydrogen is thermodynamically favored as noted below:

$$2\ FeTi + H_2 \rightleftharpoons TiH_2 + Fe_2Ti \quad \Delta G = -84\ kJ/mol\ H_2 \qquad [14]$$

However, the reaction does not occur at low temperatures to any measurable degree despite the large thermodynamic driving force (13). This was demonstrated in several long-term experiments in which FeTiH was subjected to up to 30,000 hydriding-dehydriding cycles with the temperature ranging from 273 to 373 K. While no significant disproportion of bulk FeTi has been noted, even at elevated temperatures (773 K) other Ti intermetallic compounds which form ternary hydrides at room temperature have been observed to do so. Yamanaka et al. (53) report the following alloys disproportionate, at the indicated temperature, in the presence of hydrogen; TiNi (773 K), Ti_2Ni (525 K), $TiCu_3$ (773 K), TiCu(473 K) and Ti_2Cu (473 K).

The crystallographic transformations in the FeTi/H system are very complicated. There are four distinct, non - stoichiometric hydrogen containing phases, a dilute hydrogen solid solution phase (α), two mono-hydride phases (β_1 and β_2) and a non - stoichiometric dihydride phase (τ) (Table 2). The structures of the β phases have been determined (54,55). These phases are unusual as they appear to be strain stabilized structures and precipitate only after the initial formation of the τ phase (56,57). The τ phase has also been the focus of several crystallographic studies. It was originally determined to be a monoclinic structure but it has recently been re-examined and was assigned an orthorhombic structure (58,59).

Application of FeTi hydrides

The first engineering scale use of a metal hydride for an energy storage application involved the use of FeTi alloys in a utility load leveling demonstration (60). This consisted of producing hydrogen electrolytically and storing it as a metal hydride. Subsequently, the hydride was decomposed to provide hydrogen to power a 12 kW Pratt & Whitney fuel cell. In practice hydrogen would be produced using off-peak power, stored then reconverted to electricity to satisfy on-peak loads. The hydrogen storage reservoir contained 400 kg of alloy and had an effective storage capacity of 6.4 kg of hydrogen. It was designed to operate through a complete sorption-desorption cycle once a day. The effective rate limiting process is the addition or removal of heat from the solids and this was the dominating factor in reservoir design. In the sorption mode, heat was removed by circulating cold water at 290 K through an internal heat exchanger; for the desorption reaction, heat was supplied by circulating warm water at 318 K. The system was subjected to about 60 full sorption-desorption cycles without difficulty.

FeTi based alloys have been widely used in experimental automotive applications. Even though the energy density by weight is much lower than that of gasoline it is still attractive when compared batteries as shown in Table 3. This advantage was readily recognized and the Billings Energy Corp. of Provo Utah converted a Winnebago Bus to run on hydrogen fuel using FeTi hydride as the storage compound (61). More recently the Daimler-Benz Corp tested, over a period of three years, a fleet of hydrogen powered cars which employed metal hydrides as the H storage media (62). Initially FeTi was used however it was replaced with an AB_2 alloy having the composition $Ti_{.98}Zr_{.02}V_{.43}Fe_{.09}Cr_{.05}Mn_{1.5}$. It was concluded that such vehicles could readily be produced that would have a performance and durability comparable to conventionally fueled vehicles.

Magnesium Alloy Hydrides

MgH_2 contains 7.7% hydrogen by weight. Unfortunately, it is relatively stable having a dissociation pressure of 1 atm at 569 K, a major disadvantage which has effectively prevented its use on any but a laboratory scale as a hydrogen storage compound. Thus, a great deal of effort has focused on the reaction of hydrogen with magnesium intermetallic compounds in an attempt to reduce stability yet maintain a high H storage capacity. While a large number of ternary hydrides were synthesized none are very attractive simply because none are significantly less stable than MgH_2 and all contain significantly less hydrogen by weight. Nevertheless two alloys are of interest, Mg_2Ni and Mg_2Cu, because they illustrate the general behavior of the class.

The phase diagram of the Mg-Ni system indicates the existence of two intermetallic compounds, M_g2Ni and $MgNi_2$. Only Mg_2Ni reacts with H_2 according to the following reaction (63)

$$1.08\ Mg_2NiH_{0.3} + 2H_2 \rightleftharpoons 1.08\ Mg_2NiH_{4.0} \qquad [15]$$

The product is a fine powder, has a rust colored, non-metallic appearance. It is, perhaps, debatable whether it should be classed as a metallic hydride.

A series of pressure-composition isotherms for this system is shown in figure 7. The hydride is stoichiometric as illustrated by the abrupt termination of the isotherms at a composition corresponding to $Mg_2NiH_{4.0}$. The maximum solubility of hydrogen in the α phase corresponds to a composition of $Mg_2NiH_{0.3}$ It is stable in air at room temperature for long periods, but may slowly darken over a period of years (in a glass container).

Mg_2NiH_4 is not very attractive as an energy storage compound. It contains less than one-half the amount, by weight, of hydrogen in MgH_2 with only a small decrease in stability. Its primary virtue lies in the fact that Mg_2Ni acts as a catalyst for the Mg/H_2 reaction (63); a P - C isotherm for a mixed phase alloy of Mg and Mg_2Ni is shown in figure 8.

It is rather interesting to note that the disproportionation of Mg_2Ni, as shown below, is less favored than the formation of the ternary hydride

$$2\ Mg_2Ni + 3\ H_2 \rightleftharpoons 3\ MgH_2 + MgNi_2 \quad \Delta G_{562} \approx 10\ kJ/mol\ H_2 \qquad [16]$$

This may compared to reaction [15] where $\Delta G_{562} = 0$. The reason why disproportion is not favored in this system is because MgH_2 is relatively unstable ($\Delta G_{f562} = 0$) as compared to most other binary hydrides, e.g. Ti and La.

Mg_2NiH_4 undergoes a structural phase transition at approximately 503 K to form a low temperature (LT) and a high temperature (HT) phase. The HT phase is cubic (64) whereas the LT phase is monoclinic (65). Gavra et al. have found the monoclinic phase to have metal - like electrical conductivity whereas the orthorhombic phase is insulating (66).

Despite a structural similarity with Mg_2Ni, Mg_2Cu behaves quite differently; it disproportionates at > 523 K to form the binary hydride and a lower intermetallic compound (67) according to the following reaction:

$$2\ Mg_2Cu + 3\ H_2 \rightleftharpoons 3\ MgH_2 + MgCu_2 \qquad [17]$$

Where are $\Delta H_{298} = -72.5$ kJ/mol H_2, $\Delta G_{298} = -30$ kJ/mol H_2 and $\Delta S = -142$ J/(mol H_2 K). While this system is slightly more unstable than the corresponding Mg-H system, it stores only ~2.7 weight % available hydrogen. We note that the disproportionation of Mg_2Cu occurs quite rapidly at the rather low temperature of 573 K indicating substantial metal atom mobility. This is attributed to its low melting point of 841 K. However, no reaction occurs at room temperature at pressures up to 880 atm, as predicted by rule 3 above. Nor does a ternary hydride form, which would not require substantial metal atom rearrangement. It should be mentioned that disproportionation reactions can be useful tools for the determination of metallurgical thermodynamic data. For example, knowing ΔG_{f298} for Mg_2Cu, MgH_2 and the ΔG for reaction [17], the calculated ΔG_{f298} for $MgCu_2$ is -36 kJ, which is in good agreement with the literature value of -34 kJ (68).

Applications of Mg Alloy Hydrides

Several applications have been suggested for these hydrides but none have been reduced to practice. In almost all cases the base alloy was Mg doped with either Ni or Cu (present as Mg_2M) which acted as catalysts for the hydriding/dehydridng reaction (69). Hoffman et al. suggested the use of catalyzed MgH_2 for hydrogen storage in automotive applications (70) using the engine exhaust to supply the heat of decomposition. Later Toepler et al. (71) proposed to use dual bed storage in hydrogen powered vehicles to increase range and decrease weight. One bed consisted of $FeTiH_x$ operated at low temperature while a second, high temperature bed consisted of catalyzed MgH_2 with the heat of decomposition again supplied by the engine exhaust.

A high temperature heat storage system for electric utilities has been proposed (69). The system employs two hydride beds, a high temperature bed consisting of catalyzed MgH_2 and a low temperature bed consisting of $FeTi_{.8}Mn_{.2}$. The system stores heat at 608 K. A similar system employing catalyzed MgH_2 was recently demonstrated on a laboratory scale (72).

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Table 1

Thermodynamic Data of Representative Compounds[a]

Compound	Conversion	ΔH kJ(mol H_2)$^{-1}$	ΔS J(K mol H_2)$^{-1}$	Ref.
$LaNi_5H_x$	ß → α	−30.01	−108	19
$LaNi_5H_x$[b]	α → ß	−29.4		3
$LaNi_{4.6}Al_{0.4}H_x$	ß → α	−36.3	−109	37
$FeTiH_x$	γ → ß	−33.3	−104	51
$FeTiH_x$[b]	ß → α	−28.1	−106	51
Mg_2NiH_4	ß → α	−64.2	−122	63
MgH_2	ß → α	−74.2	−134	2
MgH_2[c]	ß → α	−77.1	−137	63
TiH_2	metal → δ	−133	−125	2
LaH_2	α ↔ ß	−206	−147	2

a – Via PCT measurement
b – Calorimetric measurement
c – Catalyzed

Table 2
Crystallographic Data

Compound	Symmetry	Space gp.	Lattice Parameters a	 b	 c	Ref.
$LaNi_5D_7$	hex.	$P6_3mc$	5.412		8.559	38,39
$\beta_1FeTiD_{.98}$	ortho	Pmcm	2.956	4.543	4.388	54
$\beta_2FeTiD_{1.37}$	ortho	Pmcm	3.088	4.515	4.391	55
$\beta_2FeTiH_{1.40}$	ortho	Pmcm	3.094	4.513	4.391	57
$FeTiD_{1.90}$	ortho	cmmm	7.029	6.233	2.835	58,59
Mg_2NiH_4(HT)	cubic		6.490			64
Mg_2NiH_4(LT)	monoclinic	C2/c	14.363	6.4052 $\beta = 113.6$	6.4863	65

Table 3
Energy Density Comparison of Automotive Power Sources
Actual and Proposed(69)

Power Source	Energy Density whr/kg	Conversion Efficiency %	Net whr/kg
Pb/acid Battery			
Present	30	70	21
Advanced	50	70	35
Li/MS Battery	150	70	105
$FeTiH_{1.7}$[a,b]	516[c]	30	154
Mg_2NiH_4[a,b]	1121[c]	30	336
MgH_2(10% Ni)[a,b]	2555[c]	30	767
Gasoline[a]	12880[c]	23	2962

a - No allowance for container weight.
b - Based on available hydrogen i.e., $FeTiH_{1.7} \rightarrow FeTiH_{0.1}$, $Mg_2NiH_4 \rightarrow Mg_2NiH_{0.3}$
$MgH_2 \rightarrow MgH_{0.5}$
c - Based on lower heat of combustion.

Figure Captions

Figure 1: Ideal Presure-Temperature-Composition diagram. The length of the pressure plateau (AB) is the effective hydrogen storage capacity.

Figure 2: Pressure-Composition isotherms for the LaNi5/H system (19).

Figure 3: Variation of equilibrium dissociation pressure of $LaNi_x$.

Figure 4: Sub-surface phase composition of $LaNi_5H_x$ as a function of reaction pathway.

Figure 5: Correlation of Ln $P_{\alpha\beta}$ with cell volume (37).

Figure 6: Pressure-Composition isotherms for the FeTi/H system (51).

Figure 7: Pressure-Composition isotherms for the Mg_2Ni/H system (63).

Figure 8: Pressure-Composition isotherms for the Mg_2Ni + Mg/H system (63). The arrow indicates where the break in isotherm should occur based on initial amount of the Mg and Mg_2Ni phases.

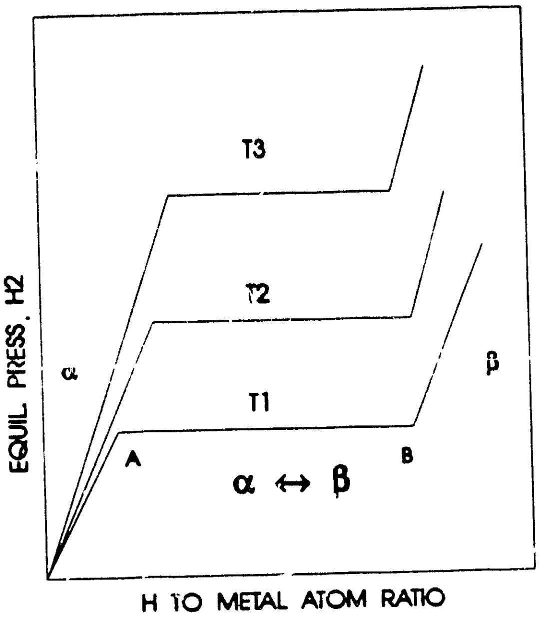

Figure 1: Ideal Presure-Temperature-Composition diagram. The length of the pressure plateau (AB) is the effective hydrogen storage capacity.

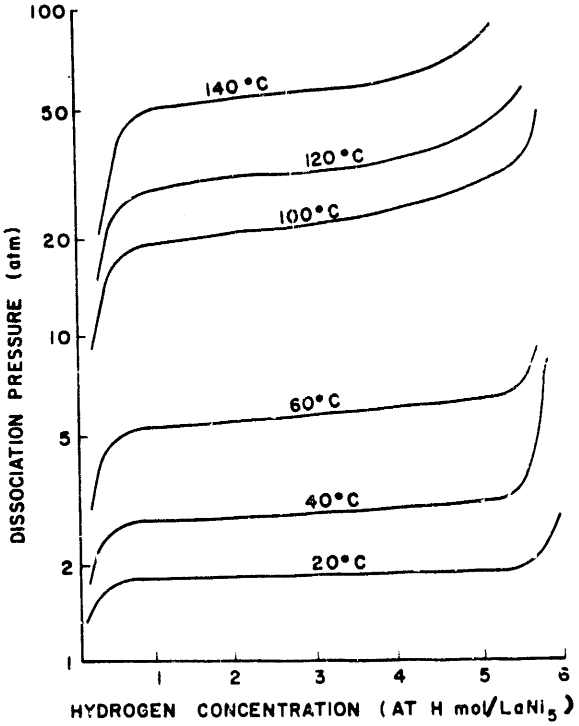

Figure 2: Pressure Composition isotherms for the $LaNi_5/H$ system (19).

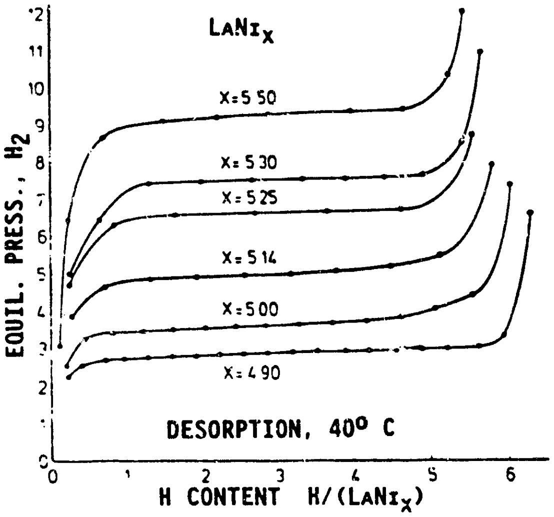

Figure 3: Variation of equilibrium dissociation pressure of $LaNi_x$ as x varies (41).

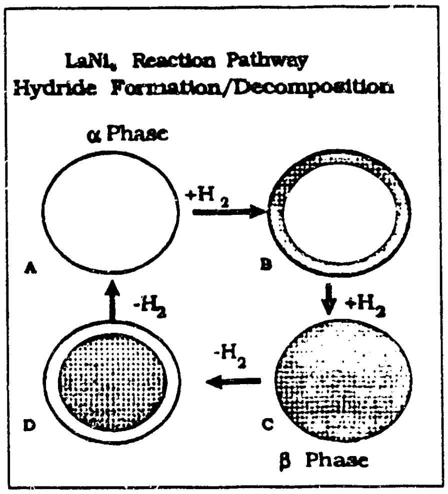

Figure 4: Sub-surface phase composition of $LaNi_5H_x$ as a function of reaction pathway (35).

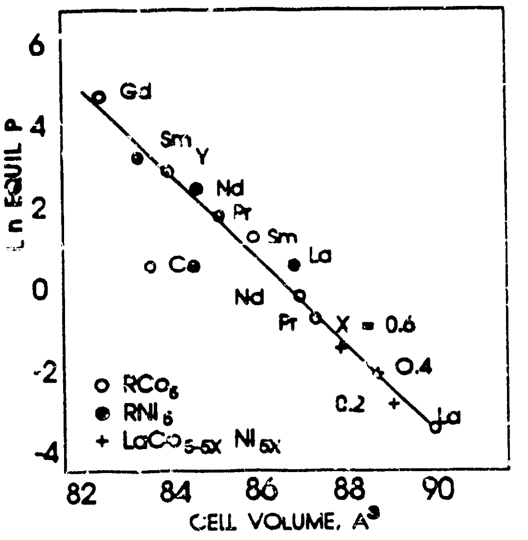

Figure 5: Correlation of equilibrium plateau pressure with cell volume (37,20).

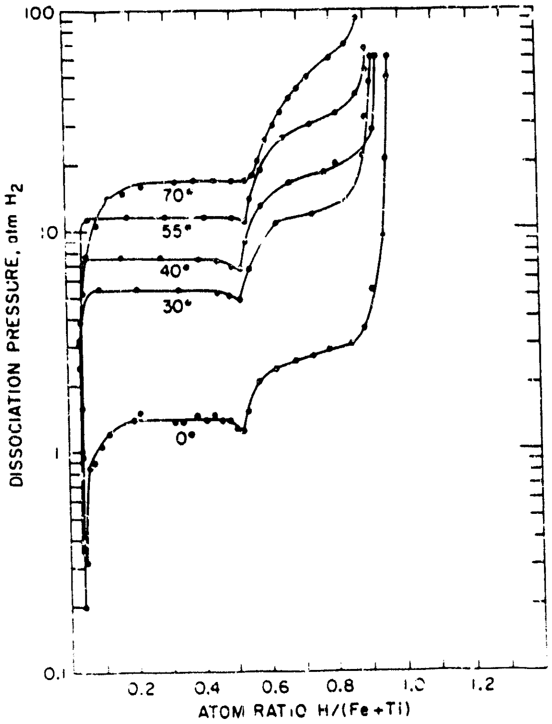

Figure 6: Pressure-Composition isotherms for the FeTi/H system (51).

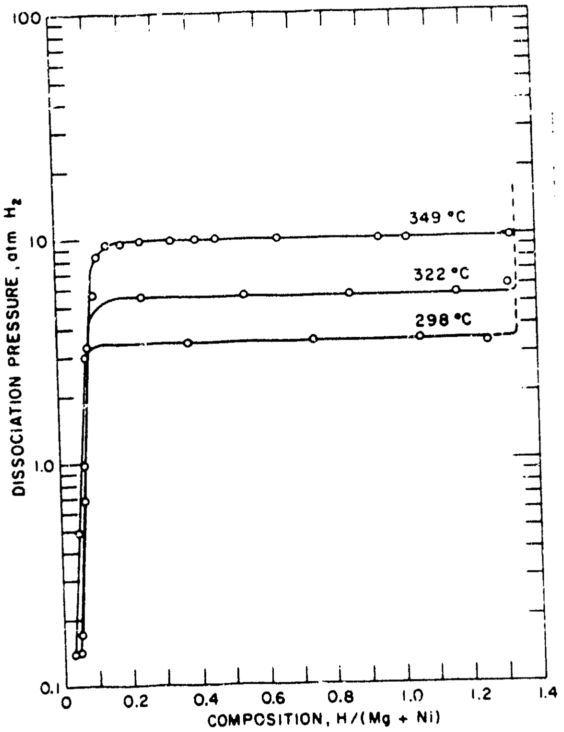

Figure 7: Pressure-Composition isotherms for the Mg_2Ni/H system (63).

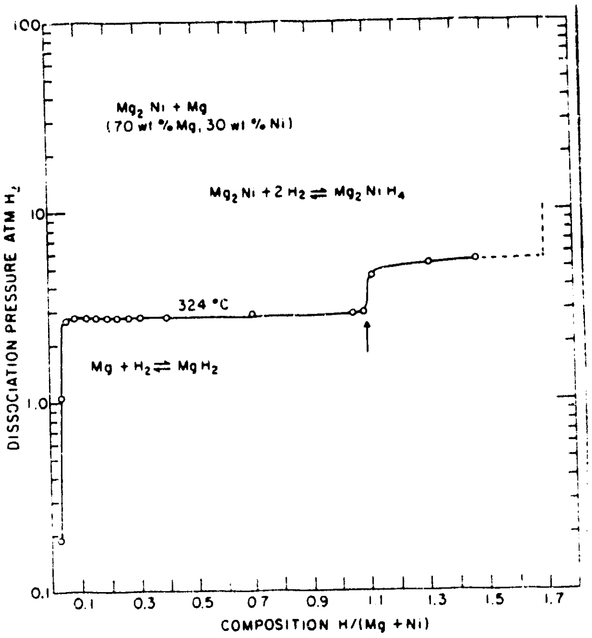

Figure 8: Isotherm for two phase alloy (63). The arrow marks break in isotherm calculated from Mg/Mg_2Ni phase ratio.

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