Metal Hydrides for Energy Storage and Conversion Applications

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INTRODUCTION

Following the discovery of the first metal hydride (i.e., PdH_x) in 1866 until the middle of twentieth century, these materials were mostly scientific curiosities until they started being used by the nuclear power and weapons communities for various applications [1]. Starting in the 1970s, development of hydrides that were easily reversible at moderate temperatures (250 K – 600 K) and pressures (0.1 bar – 100 bar) stimulated much interest for their use in various energy storage and conversion systems [2]. A brief review is given here of various properties of metal hydrides that are most important in selecting and using them in applications involving the absorption and desorption of hydrogen gas. Recent attention is mainly on improving hydrogen storage for operating fuel cells in vehicles during the 21st century.

THE METAL HYDRIDE FAMILY

Hydrogen is a very reactive element and will form hydrides and solid solutions with thousands of metals and alloys as well as form chemical compounds or complexes with most other elements. An updated hydride "family tree" of the elements, alloys, and complexes [3] is shown in Fig. 1. Metal Hydrides (MH_x) can be classified in terms of the hydrogen bonding to the metal (i.e., metallic, ionic, or covalent with complexes being intermediate cases). For the alloy side of the tree, hydrogen is usually bound in the interstitial sites in a metallic state with usually minor distortions of the generally stable H-free alloy structures. As indicated in Fig. 1, most practical MH_x involve a combination of elements "A" that are strongly exothermic hydrogen absorbers (e.g., Mg, Ti, Zr, La, etc.) with elements "B" that are either endothermic or very weakly exothermic hydrogen absorbers (e.g., Ni, Fe, Co, Mn, etc.). There have been numerous studies on the formation, properties, and applications of MHx over the past 35 years as summarized in recent reviews [3,4]. In addition, a hydride database with an extensive reference list is available on the Internet [5].

APPLICATIONS OF MH_X

Listed in Table I are numerous applications for which metal hydrides have been or are being considered [2,6]. Various key properties along with candidate MH_x systems are given in Table I for each application. Many of the intermetallic compounds and solid-solution alloys can readily absorb and desorb hydrogen gas around room temperature and near atmospheric H_2 pressures. Unfortunately these hydrides can reversibly store only 1-3 wt.% H_2, which is not enough for most vehicle applications. On the other hand, covalent and ionic hydrides (e.g., MgH_2 and LiH, respectively) are capable of storing 7-12 wt.% H_2, but they must be heated above ~600 K to release gas at pressure ~1+ bar. These desorption temperatures are much higher than the ~350 K waste heat available from a Proton Exchange Membrane (PEM) fuel cell. However, recent progress has been with "catalyzed" complex hydrides [7] containing mixed ionic-covalent bonding which can reversibly store > 4 wt.% H_2 with operating temperatures below ~ 400 K. The current status of these and other novel hydrides will be described along with future goals.

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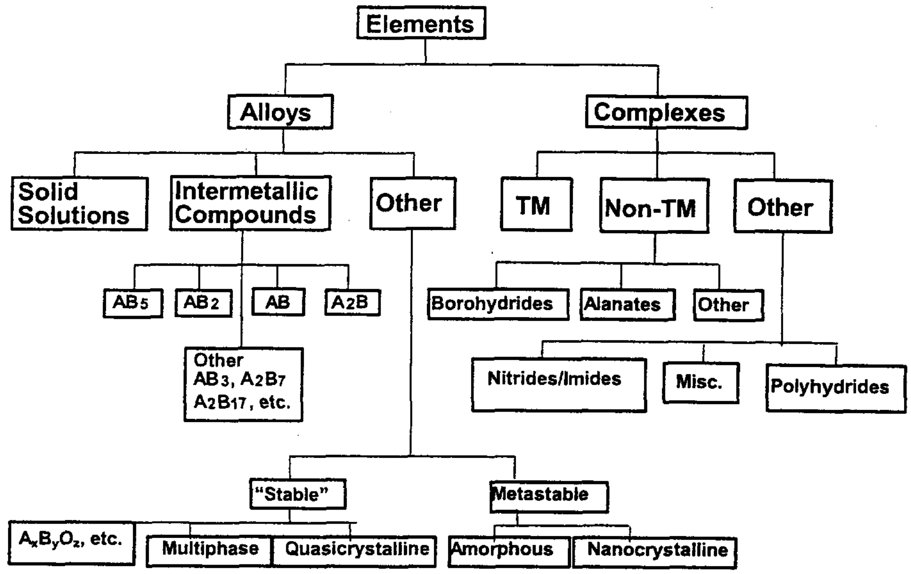

Figure 1 – Family tree of hydriding alloys and complexes, which is a slightly modified version to Sandrock's original scheme [3]. TM = transition metal

TABLE I. Energy Storage and Conversion Applications for Metal Hydrides.

Application	Required MH_x Attributes	Candidate Metal Alloys
Stationary fuel storage	P_d~1-10 bar, very low cost, use waste heat, H-capacity > 2 wt%, safety	TiFe, V-alloys, Mg-alloys, AB_2-alloys
Vehicular fuel storage (internal combustion/Fuel cells)	H-capacity > 5 wt%, cost, P_d~1-10 bar, use waste heat, fast kinetics, durability during cycling, safety, contamination	AB_2, Mg-alloys, alanates, (TiFe, AB_5 used in the past, but H-capacities too low)
Electrodes/Ni-MH batteries	Cost, reversible energy capacity, power density, activation, P_d < 1 bar	AB_5, AB_2, AB
Chemical heat pumps and refrigerators	Very fast kinetics, cost, H-capacity, P_d~1-5 bar, use waste heat	AB_5, AB_2, AB
Purification, chemical separation, & isotope separation (Fusion Energy)	Kinetics, Activation, impurity contamination, reaction efficiency, stability, durability, safety	Pd, V-alloys, Zr-alloys (AB_2, AB)
Reversible gettering (vacuum)	Very low pressure, kinetics, pumping speed, activation, durability	U, Zr-alloys (AB_2, AB, $A_xB_yO_z$)
Gas gap thermal switches	P_d <0.05 bar, fast kinetics, low power (~10 mW), durability during temperature cycling, contamination, reliability	ZrNi, U, Zr-alloys (AB_2, $A_xB_yO_z$)
Compressors (up to ~ 500 bar) for liquefaction or filling high pressure gas storage tanks	Thermal efficiency (i.e., high $\Delta P/\Delta T$ ratio), fast kinetics, cycling stability, safety, cost	V-alloys, AB_5, AB_2, AB
Sorption cryocoolers (space flight applications)	Fast kinetics, cycling stability, constant P_a absorption plateau, power, reliability	$LaNi_{4.8}Sn_{0.2}$, V-alloys, AB_5, AB_2