

A Review on Mg-based Metal Hydrides for Hydrogen Storage Applications

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Abstract- In the recent years, many researchers have been worked on hydrogen storage in metal hydrides. Hydrogen storage in solid is new and safest way to store hydrogen in the forms of pressurized gas and cryogenic liquid. The magnesium (Mg) based hydride materials have been believed to one of the best capable hydrogen storage materials because of cost-effective and high hydrogen storage capability. The slow hydrogen absorption - desorption rate and high hydrogen absorption - desorption temperature bind these materials to use in the hydrogen storage applications. This review article overviews the current status of Mg-based metal hydrides thin films used for hydrogen storage. The Mg-based thin films metal hydrides like Mg-M (M-Ti, Ni, Mn, Co, Al) have been attracted much attention for hydrogen storage in last few years, because these materials have good storage of hydrogen having great reversible process, up to 7.6 wt%. Electrodes based on thin films inspire to see progress on magnesium based fuel cells. In addition, changes in electronic state of Mg-based materials reveals, after hydrogenation by means of metal-isolator transition, these materials may be used in many other applications viz. optical sensors, solar collectors, hydrogen sensors, smart windows, semiconductor electronics and solar cells.

Keywords- Thin film, Metal hydrides, Mg-based hydrides, Hydrogen storage

1. INTRODUCTION

Hydrogen is the one of the utmost abundant elements on the earth that grooves whole renewable fuels concerning reversibility, compatibility and energy density. Attention towards hydrogen as a fuel has been developed expressively in recent years. Looking to the potency hydrogen as a storage purpose, utilization of it enhanced, simultaneously. Hydrogen storage is real challenge for acknowledging "hydrogen economy" that will resolve the basic issues of mankind like energy depletion, air contamination, emission greenhouse gases and environmental changes. Many metals and intermetallic composites have reversible capability to absorb large amounts of hydrogen [1, 2]. Recent years study reveals that, use of hydrogen is estimated

to become the cleanest energy vector of the future and hydrogen has been planned as an energy carrier and petroleum substitute fuel. As hydrogen burn in air, it produces a clean energy. By In comparing with gas as liquid storage mechanism of hydrogen, solid form is the most advisable and practical approach, because hydrogen can be stored more per unit volume compare to gas as liquid, hence the higher pressure achieved [3]. During the past years, carbon free fuels have been in demanded by the commercial as well as the industry. The pure hydrogen (non carbon fuel) combined with oxygen; it produces electrical energy, in case of Fuel cell. Owing to the abundantness and evenly distribution of hydrogen leads relief in terms of security of energy. However, the high energy content (120 MJ/kg) of hydrogen also a favourable factor compare to three times of petrol (44 MJ/kg) [4, 5]. Hydrogen storage has established gradually importance due to the increasing energy demand in worldwide. The alloys of metals for storage of hydrogen in hydride can be used because that can absorb and hold large amount of hydrogen through bonding with hydrogen. Thin film form of any material leads to born the new era of applications with numorpus size, because of the controllable Electrical, optical, magnetical, and mechanical properties. In case of the metal hydride thin film, inspite of huge hydrogenation, the crystal structure remains enormously stable [6]. In a completely clean-energy theory, the hydrogen is the perfect resources storage of energy for the conversion and transportation. Though, appropriate storage facilities of hydrogen for portable devices are difficult, due to the low inherent density and boiling point i.e 90 g/m³ and 20.4 K at 1 atom. Respectively. However, there will be a safety issues, in case of safety purpose for hydrogen fuel utilization in the form of gas or liquid, in the mobile vehicles [7]. Solid state storage is an alternative storage technique for storage of hydrogen by means of adsorption or absorption phenomena. Metal hydrides shows its capability in the category of solid state storage metal due to its capability to handle the large volume and high mass density, which is required for long term stability [8]. A Van der Waals

interaction at the metal surface is responsible for the hydrogen absorption. The H_2 molecules dissociate into hydrogen atoms at the metal's surface followed by the absorbed and dispersed chemically on the surface. In the chemical element diffusion, generally octahedral and tetrahedral opening sites responsible for the movement of atoms that cause the formation of the binary compound by means of nucleation and growth [9]. Being thin films, the majority adsorption and absorption takes place on the surface only. In addition to that if the films are nanostructured, and then the surface to volume ratio increases significantly. This is the reason behind the major use of metal hydride nanostructure thin films as a solid hydrogen storage device. Moreover there is a huge command on the thickness and the tailoring process can be achieved [10-14]. In case of Magnesium, though it has slow kinetics, is significant material for hydrogen storing application. High binding energy and high temperature (573-625K) are the big challenges of hydrogen storage in magnesium. The dissociation activity of Alloy of Mg (due to d- electron in transition metals) was considerably evaluated [15]. Mg-based nanostructured thin film (metal hydrides) also is used seed layered thin films. In preparing the thin film, the layer thickness and adaptability might be controlled to tailor both the degree of crystallization and composition of the metal film and boundaries, for example, particle size, geometry, morphology, oxygen content and material preparation may emphatically impact the hydrogenation/dehydrogenation mechanism. The thin film has a simple geometry and therefore offers an appropriate direction to analyze the hydrogenation and dehydrogenation process and assets of metal hydrides [16].

2. Mg-BASED HYDRIDES

The Mg-based thin film metal hydrides have been considered to be favourable for the storage of hydrogen in solid state due to their large hydrogen storage capability and relatively low cost. Nanostructure Mg-based geometry considered more due to its high resistance tendency towards the diffusion of hydrogen towards the grains of particles or to the charges of the boundaries of particles. However, the higher development enthalpies of Mg hydrides and its composites, the hydrogen absorption/desorption begins just at high temperature (623-673K) and for the total hydrogenation it takes up to a couple of hours. Thus, current research focused towards the reduction of absorption/desorption temperature of hydrogen and improving in the kinetic performance of Mg without any significant change [17, 18]. Mg-hydride, MgH_2 , is particularly exciting because of its high values of reversible hydrogen storage capacity (7.6 wt %) [8]. Then again, Mg forms a very stable hydride because

of the solid Mg-H ionic bonds, bringing about a nearly high enthalpy, $\Delta H = -75$ KJ/mol [19]. It implies a high temperature (350°C) is commonly needed to achieve hydrogen desorption at an enough high pressing factor (>1 atm) [20]. Magnesium and its alloys, because of their outstanding physical and chemical properties like biocompatibility, low density, great damping presentation, recyclability, huge hydrogen storage capacity, high specific capacity for batteries (theoretical), are considered to have good application possibilities in the fields of aerospace, transportation, biomedical and energy sectors. For the most part it is viewed as that the Mg/Pd thin film has amended hydrogen absorption/desorption kinetics, yet the cost of Pd is high enough to handle, hence enormous scope of utilization of Mg/Pd thin film in everyday life applications. However, the exploration on non-palladium covered Mg film shows up because of minimal expense. The compounds example like Mg_2NiH_4 , Mg_2CoH_5 , Mg_2FeH_6 are exciting substitutes to pure magnesium hydride, which compromise hydrogen storage capacity in respect to volume or mass and different equilibrium pressures. To explore the solid state hydrogen storage opportunity in Mg/Co thin film, the Mg/Co thin films have been prepared in our earlier work and studied the variation in optical bandgap after hydrogenation. The reason behind is the accumulation of hydrogen at interface of thin film. Then it collects the electrons, as per anionic model, from the Mg/Co thin film. Variation in bandgap also represents the phase changes from metal to semiconductor [21]. The optical band gaps of various Mg based metal hydrides are shown in Fig. 1, 2 and 3. It has been noted that huge modification in optical properties after hydrogenation in the mixed metal thin films (Mg based thin films having a transition elements), example like transmittance, reflectance and optical bandgap.

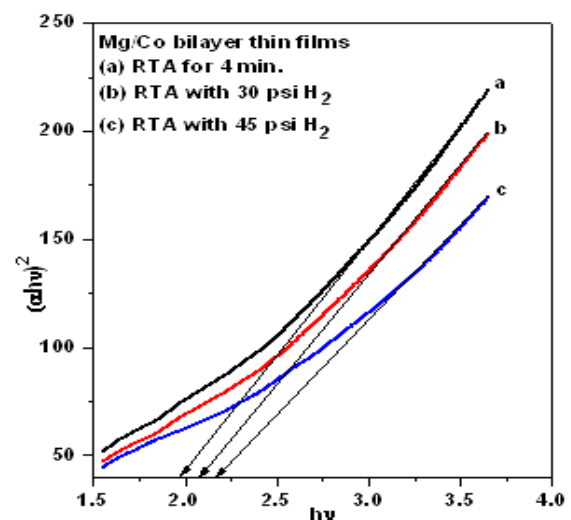


Fig. 1 Optical bandgap spectra of Mg/Co bilayer thin film [21].

Similar results have been reported for magnesium transition-metal alloys like Mg_2CoH_5 , $Mg_6Co_2H_{11}$,

Mg₃MnH₇ and Mg₂FeH₆. All of these studies based on the optical DFT calculation, that indicates significantly about the semiconductor base [22-24]. It has been also reported the influence of hydrogenation of Mg/Mn bilayer thin film on optical bandgap. This study reveals that the band gap increases with hydrogenation process. The overall bring out suggest the storage of hydrogen in Mg/Mn thin film [25].

Table 1: Variations in Optical bandgap of Mg/Mn and Mg/Co thin films with hydrogenation [21, 25].

Hydrogen pressure	Mg/Mn thin films (eV)	Mg/Co thin films (eV)
Without H ₂	2.0218	1.9693
At 30 psi H ₂	2.0844	2.0679
At 45 psi H ₂	2.1397	2.1605

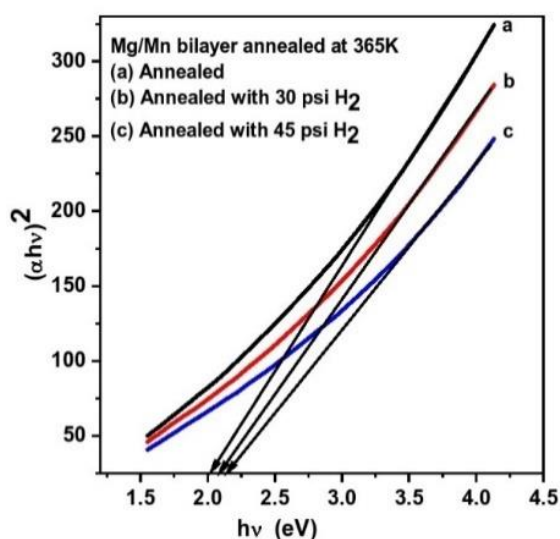


Fig 2 Optical band graph of annealed hydrogenated Mg/Mn bilayer thin films [25].

It has been investigated that alloys Mg₂TMH_x (TM = Ni, Co, Fe) have largest hydrogen storage capacities and these also have very high (3.6-5.6%) gravimetric capacities. Among different Mg-based hydrogen storage composites, Mg-Ni hydrogen storage compounds are the most considered ones. An Mg-Ni system has nearly high hydrogen storage capacity, yet moreover has better hydrogen absorption/desorption action. However, Ni is a particular case of interested due to prominent catalytic effect regardless of electro-negativity. And it has been assumed that the development of the Mg-Ni compound may assume a significant part in improving the hydriding/dehydriding kinetics of the Mg-Ni system [26-31]. The Mg-Ni-H system has been examined for a long time, generally due to the large capacity with regard to hydrogen storage 3.6 wt% hydrogen as Mg₂NiH₄ [32]. Among the different additives materials, the transition metals are better

catalytic performances on MgH₂ including their derivatives [33]. It have been investigated that different catalytic effects of 3d-TMs (TM; Ti, V, Mn, Fe, Ni, etc.) on the reaction kinetics of Mg-H system and the Mg-Ti composite in the ball-milled shows incredible quick hydrogen absorption rate [34-37]. This may also because of the decrease in electronegativity from Ti to Mo. Moreover as the formation enthalpy goes higher the dehydration kinetics spoiled. The hydrogen storage properties for Mg/Ti thin films have been investigated in our previous work and found optical bandgap 2.08 eV before hydrogenation of the films. After hydrogenation the bandgap was found to be increased upto 2.22 eV, the variation in bandgap indicates the possibility of storing of hydrogen in Mg/Ti thin films [38].

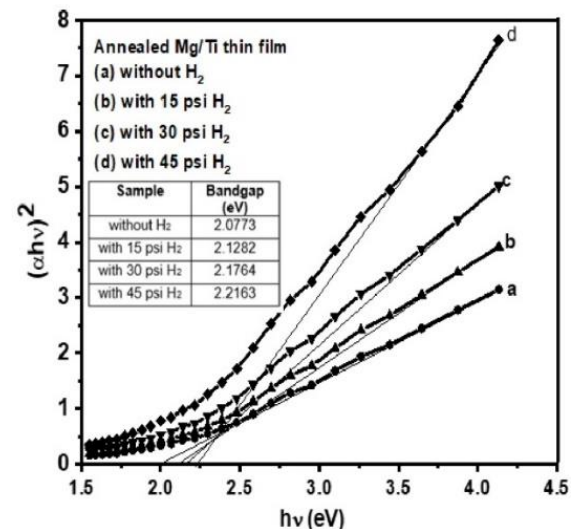


Fig.3 Optical bandgap spectra of annealed hydrogenated Mg/Ti bilayer thin film [29].

In late investigation it has been discovered that if Mg element replace with Al element and increment of the expansion of Al shows that the hydrogen storage capability of the alloy is came down. This occurs because of the replacement of Mg with Al decreases the development of the hydrogen absorbing phase of Mg₂Ni. But, the hydrogen absorption/desorption rate of Mg₂Ni after addition of Al element increases and the hydrogen absorption temperature decreases with the increase of Al percentage [39-43]. The incorporation of Al actuates development of non-hydrogen adsorption/adsorption phases Al₃Ni₂ and Mg₃AlNi₂ respectively in the Mg₂Ni hydrogen storage alloy. The developed new phases, in case of alloy, give huge hydrogen diffusion due to increase the grain boundaries and defects. The hydrogen adsorption-desorption properties of the alloy can essentially be improved by the synergistic hydrogen adsorption of Mg₃AlNi₂ and Mg₂Ni. It has also been reported that after adding the Al element, a dense layer of Al₂O₃ is created on the surface of the material and also corrosion resistance is enhanced [44,45]. Among Mg-based alloys Mg/Al alloy also has the

benefits of good hydrogen storage capacity having a cost effective approach, which decides the chance of its utilization as a thin-film structure to meliorate the hydrogen storage in Mg/Al thin film [46, 47]. It has been reported by the researchers that after hydrogenation, Mg/Al gradually changes to Mg(AlH₄)₂ hydride [48]. Involving of Mg-based materials thin films, various applications proposed to utilize Mg-based thin film structures effectively such as fuel cells, hydrogen storage, hydrogen sensors, smart windows, semiconductor electronics devices, data storage and, solar cells [49-53].

3. CONCLUSION

Mg-based metal hydrides materials are potential candidate for hydrogen storage applications. This leads to grown the hydrogen economy due to its several prominent advantages. The hydriding and dehydriding kinetics of Mg-based metal hydrides are suitable to various metal hydride devices and applications, peculiarly in energy conversion/conservation devices; viz. refrigerators, heat pumps, automobiles, batteries, thermal energy storage and power generators. Thin film form of hydrogen storage materials can efficient due to the controlled microstructure (nanocrystalline or amorphous) of the material. Hence, hydrogen absorption-desorption activities improves. The Mg-based hydrogen storage materials include abundant variety of alloys, composites and compounds. The present survey provides motivation to new significant turns of events and exhilarations for the years too soon producing substantial hydrogen storage applications. Mg-based materials attract a great deal interest for hydrogen storage with a lot increased energy densities than conventional phase changed based materials. In the future the compositing Mg film with added hydrogen storage materials are the thrusts research directions to obtain Mg-based alloy thin films with splendid kinetics. The formation of the Mg-based thin film materials such as Mg/Ni, Mg/Al and Mg/Ti system might play a crucial character for ameliorating the hydriding and dehydriding kinetics.

4. ACKNOWLEDGEMENT

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