PREFACE

"Hydrogen is the most important consistent of the universe."
– Gerhard Herzberg

Energy is one of the basic needs of human beings and is extremely crucial for continued development of human life. The global energy demand is increasing with increasing human population and modernization. The world at present relies on fossil fuels to meet its energy requirements. Presently available energy systems may not be able to make up the future energy requirements. The use of fossil fuel and nuclear energy, production and consumption, cause environmental degradation that is threatening human health and affects ecological balance. There fore, if the rapidly increasing global energy needs are to be met without damaging the environment, the paradigm has to shift to renewable energy.

Renewable energy sources that use indigenous resources have the potential to provide energy sources with almost zero emissions. Renewable energy sources such as solar energy, wind power, biomass and geothermal energy are abundant, inexhaustible and widely available. But they are very expensive. On the other hand, hydrogen is a high energy carrier source. Hydrogen is the cleanest, sustainable and renewable energy carrier. It has high energy content by weight, which is nearly three times that of gasoline.

The Hydrogen economy infrastructure is comprised of five key elements: Production, Delivery, Storage, Conversion and Applications. While Hydrogen production and conversion are already technologically feasible, its delivery and storage face serious challenges. A range of storage technologies that address this problem like compressed gas, liquefied hydrogen, metal hydride and carbon based system exist. Which choice is best, depends on several factors: the application, the energy density needed the amount to be stored and the storage time, the forms of energy available, maintenance requirements, capital and operating costs. For stationary systems, the weight and volume of the system used for Hydrogen storage is not a key factor. However, for mobile applications, such as fuel cell electric vehicles or hydrogen fuelled (internal combustion) cars, hydrogen

storage system has to be compact, light weight, safe and affordable. The salient features of metal hydrides are following:

- High hydrogen storage capacity
- Reversibility of hydride formation and deformation reactions
- Most portable in mobile application
- No loss of Hydrogen
- The cleanest fuel on Earth

Elemental Magnesium is a near ideal candidate material for storing Hydrogen as a solid metallic Hydride for fuel cell application. Pure Mg has a storage capacity of about 7.6% and an energy density of about 2.33 kWh/kg. Both these values are among the highest in the entire class of commercially available metallic Hydride formers. Also, it is lower cost material. However, the rate at which hydrogen absorbs and desorbs in Magnesium is low because of a number of reasons which includes low diffusivity of hydrogen on magnesium lattice, poor hydrogen dissociation characteristics on the surface of Mg to generate atomic hydrogen that can easily diffuse into the metal, and the fact that the hydrogen atoms bind too strongly to the Mg lattice, resulting in high enthalpy of formation. This translates into higher operation temperature of the Hydride cell. And also these characteristics result in poor diffusional kinetics and requirements of high temperatures for hydriding and dehydriding making Magnesium difficult to use for mobile power system applications such as in motor vehicles and power boats.

To improve the diffusion kinetics, approaches include incorporation of rapid diffusion channels in Mg by decreasing crystallite size and by blending in catalysts such as Ni, Fe, Sc, Mn, Al etc. To overcome the thermodynamic constraint in Mg based alloys, the addition of a catalyst can play an important role. The main objectives of catalyst addition are “overcoming the dissociation barrier for hydrogen” and “destabilization of the hydride phase”. The addition of Ni and other transition metals (Ti, V, Mn, Zr, and Fe)

also improves the hydrogenation behavior of Mg and decreases the activation energy for hydrogen desorption.

In the present study, Magnesium based alloy compositions have been synthesized with blending of various catalysts by mechanical alloying for optimal hydrogen storage.

The entire work is organized in the following chapters, which are briefly explained as follow:

- **Chapter 1** deals with the future renewable energy source, namely – Hydrogen. The needs of hydrogen in the field of renewable and environmentally friendly energy sources are explained. A brief description of hydrogen technologies (Production, Delivery, Storage, Conversion, and End–Uses/Applications) – is given. The obstacle to realize the hydrogen technology is neither production nor utilization, but rather effective and safe means of storing hydrogen. This implies the importance of hydrogen storage. The requirements of safe hydrogen storage are also presented. It is also shown that Magnesium based metal hydrides are promising for use as hydrogen storing materials. A motivation for the present work is also presented at the end of the chapter.

- **Chapter 2** explains the basic concept of solid state hydrogen storage. The reaction between gas phase hydrogen and a metal surface are illustrated using the one–dimensional Lennard–Jones potential of atomic H and molecular H_2. The formation of metal hydrides can be divided into the five elementary reactions, such as physisorption, dissociation of hydrogen molecules, surface penetration, diffusion and hydride formation, which is also explained. Based on the literature survey, state–of–the art report of most popular metallic hydrides (elemental, AB, A_2B, AB_2, and AB_5 type) is briefly presented. The computational formalism of absorbed/desorbed mass % of hydrogen using ideal gas law is explained. Computation of deviations due to departure from idealism using three different equations of state for real gases is also

presented. These equations are the Van–der–Waal, Redlich–Kwong and Redlich–Kwong–Soave equation, respectively. The reaction kinetics of the solid state hydrogen storage materials using different kinetics models, namely, first order model, shrinking core model, and Johnson–Mehl–Avrami model is also studied. Finally, explanations are presented on methods of predicting thermodynamic properties (ΔH and ΔS) of the metallic hydrides using the pressure composition isotherm curve method and Van't Hoff relationship.

- **Chapter 3** is focused on the materials and methodology used for studying metal hydrides. Main focus is on high energy ball milling for synthesis of the alloy compositions. Also, high-lights are presented on characterization techniques, namely tools for morphological, elemental analysis, quantitative analysis and structural analysis. The instrumentation used includes JEOL make scanning electron microscope (SEM) with attached energy dispersive X–ray spectrometer (EDS) and Bruker make X–ray diffractometer (XRD). Details are presented on the Sievert's apparatus for studying hydriding–dehydriding characterization of the synthesized alloy compositions. In the end, thermal analysis is conducted using differential scanning calorimetry (DSC), which is also discussed (for measuring the enthalpy and entropy of formation of the developed alloy compositions).

- **Chapter 4** presents results obtained on the ternary/quaternary Magnesium based alloy compositions studied. Pure Mg (without milling) shows reversible 0.43 mass% of H_2 uptake at a charging temperature of 303 °C. After 40 h milling, pure Mg shows 3.81 mass% of reversible H_2 uptake at a charging temperature of 303 °C. The ternary Mg–V–Ni alloy compositions show maximum 5.02 mass% of reversible H_2 at a charging temperature of 265 °C. It is also seen that 95% of hydrogen is absorbed within first 3 to 5 minutes. The ternary Mg–Pd–Ni alloy compositions show maximum 3.98 mass% of reversible H_2 at a charging temperature of 202 ºC and pressure of 10 bar. The quaternary Mg–Zr–Mn–Ni alloy compositions indicate fast kinetics, with 95% of hydrogen absorbed within the first 6 to 10 minutes. These compositions also indicate

very high hydrogen storage capacity greater than 7 mass% of hydrogen stored reversibly, at a charging temperature of 201 °C. The reaction kinetics model of each of the systems studied is also presented. Further, the formation enthalpy and entropy of each system is computed using Van't Hoff relationship and also by DSC technique.

- **Chapter 5** describes results on some low temperature alloy compositions, namely, Fe–Ti–Ni, V–Ti, and V–Ni. The Fe–Ti–Ni alloy composition shows 0.73 mass% of H_2 at a charging temperature of 103 °C only. However, this composition releases 0.14 mass% of H_2 at discharging temperature of 150 ºC, and rest of H_2 is released at higher discharging temperature. Similarly, the V–Ti alloy composition shows 1.75 mass% of H_2 uptake at charging temperature of only 100 ºC with release of 0.46 mass% of H_2 at discharging temperature of 154 ºC. The V–Ni alloy composition indicates 1.83 mass% of H_2 at only 83 ºC charging temperature, and release of 0.88 mass% of H_2 at discharging temperature of 148 ºC. The reaction kinetics study of each system is also presented.

- **Chapter 6** is a discussion on the novel applications of the developed metal hydrides. These are hydrogen storage, fuel storage (stationary and vehicular applications), electrical energy storage (battery and fuel cell applications), thermodynamic devices (heat pump, refrigerator and compressor) and other applications (catalysts for hydrogen reduction, sensor devices and purification).

- **Chapter 7** contains the summary including highlights of the most important results obtained in this work and conclusions.

The **references** are numbered in square bracket in text and are listed at the end of the respective chapters.