Chapter 7

Summary and Conclusions

Abstract

This chapter contains summary including highlights of the most important results obtained in this work and conclusions.

The main objective of the present study is to synthesize and characterize metal hydrides for hydrogen storage media, in solid form. A general overview of the potential hydrogen storage methods with their possibilities and limitations is presented. Among the various metal hydrides, Magnesium is a potential option. However, desorption temperature of this metal hydride is very high and also, kinetics of hydrogen up-take and release are slow. Therefore, the present study focused on improving the hydrogen storage properties of Mg and low temperature based metal hydrides. This can be achieved by reducing the grain size to nano regime and / or addition of catalysts.

Initially, hydrogen absorption and desorption kinetics is conducted on pure Magnesium. The mean particle size of Magnesium particles is measured as 470 ± 159 μm without milling and after 40 h milling, it is obtained as 22.6 ± 8.6 μm. 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. Thereafter, a Mg_2Ni alloy with a mean particle size of 2.94 ± 0.8 μm (with crystallite size 8.75 nm) is synthesized. The maximum hydrogen up take is 3.31 mass % at 210 °C temperature. Desorption of hydrogen is started at 201 ºC and the maximum hydrogen release is 2.28 mass % at discharging temperature of 375 °C. A Mg–Fe–Mn–Ni alloy with a mean particle size (Mg) of 9 ± 1 μm and mean size of the satellite catalyst particulates (Ni, Fe and Mn) of 1.25 ± 0.3 μm is synthesized. The crystallite size of Mg phase is obtained as 21.73 nm. This alloy has a hydrogen uptake capacity of 6.65 wt% at 320 ºC and desorption capacity of 5 wt% at 377 ºC.

Ternary Mg based alloy compositions based on elemental species V and Ni have been synthesized using the route of high energy planetary ball milling. The chemical compositions of the alloy system investigated have more than or equal to 85 at% of Magnesium, 5 at% of Nickel, and 2.5 – 10 at% of Vanadium. Based on the work on ternary Mg–V–Ni compositions, the following conclusions are derived:

- Scanning electron microscope (SEM) analysis shows the optimized Mg–V–Ni alloy composition (coded MV2) as having a mean particle size (of the

Magnesium phase) of 12.3 ± 2 μm, and particle size of the satellite catalyst particulates of V and Ni in range 1.69 ± 0.3 μm to 0.36 ± 0.1 μm, respectively.

- Energy Dispersive X – Ray Spectrometer (EDS) analysis is conducted for the elemental analysis of the synthesized Mg–V–Ni alloy compositions. Results indicate the measured elemental compositions to match closely with the targeted compositions.

- The crystallite size of the synthesized Mg–V–Ni compositions is measured as 24.03 nm, 23.18 nm and 19.10 nm for MV1, MV2 and MV3 coded compositions, respectively, using X–Ray Diffractometer (XRD). This clearly indicates that the crystallite size / grain regime decreases, when the Vanadium concentration is increased. This is due to the catalyst effect (Vanadium and Nickel).

- Further, XRD analysis shows crystallite size of the optimized Mg–V–Ni (coded MV2) to be of the order of 24.88 ± 5.98 nm, confirming the presence of nano-scaled substructures/grain boundaries in the alloy composition. The crystallite size of optimized hydriding Mg–V–Ni alloy composition is of the order of 38.95 nm, which is 14 nm higher than the measured crystallite size of unhydrided composition.

- Hydriding studies are conducted as a function of temperature on the synthesized Mg–V–Ni compositions. The optimized composition (coded MV2) shows the highest hydrogen uptake with the fastest kinetics at a temperature of 265 ºC with 95 % of H_2 getting absorbed in first 3–5 minutes. The total absorbed value of hydrogen at 265 ºC is measured as 6.72 mass %.

- Desorption studies conducted at various temperatures in the range of 325 ºC to 375 ºC show that the desorption kinetics increased as temperature is increased, with the highest desorption kinetics occurring at 375 ºC. The estimated desorption at 375 ºC is measured as 5.02 mass%.

- The deviation in hydriding and dehydriding kinetics due to departure from Ideal gas behavior of hydrogen is computed. The percentage deviations in the hydriding kinetics data are obtained approximately as 3.25 %, 4.98 % and 4.48 % for Van–der–Waal, Redlich–Kwong and Redlich–Kwong–Soave equations, respectively, for the optimized MV2 coded composition. Similarly, the observed percentage deviation of hydrogen in the dehydriding kinetics data using ideal gas equation with respect to the above mentioned three real gas equations are obtained as 1.41 %, 1.27 % and 1.36 %, respectively, for the optimized MV2 coded composition.

- First order chemical kinetics models based on particular and complimentary function (full) solutions of a lumped first order differential equation show reasonable fits to the charging and discharging kinetics with coefficients of determination of 0.81 and 0.80, respectively.

- A spherically symmetric, steady state, diffusion model using first order reaction rate kinetics (Shrinking Core Model) has been successfully used to explain the charging kinetics of the optimized MV2 coded composition. Using a minimum variance non-linear optimization scheme, the best fit corresponding to mass transfer coefficient in gas phase, k_α as 1×10^{-6} m/s and reaction rate constant, k_r as 9×10^{-6} m/s has been obtained.

- A generalized case of random nucleation and growth, Johnson–Mehl–Avrami (JMA) model has been used to explain the charging kinetics of the optimized MV2 coded composition. For the JMA full linear regression model, a co-efficient of correlation, R^2 is obtained as 0.9981, and Avrami exponent, n is obtained as 1.72.

- The formation enthalpy and entropy of hydriding have been determined for optimized MV2 coded composition using Van't Hoff analysis and calorimetric techniques using a Differential Scanning Calorimeter (DSC). The values of ΔH_o is obtained as 76.8 ± 6.2 kJ/mole of H_2 and ΔS_o as 135 ± 6.9 J/mole of H_2 K using Van't Hoff analysis and these values match closely with the results of

DSC ($\overline{\Delta H}$ of 71.6 ± 5.8 kJ/mole of H_2 and $\overline{\Delta S_{pseudo}}$ of 127.1 ± 6.5 J/mole K), validating the basis of the Van’t Hoff analysis.

- It is to be noted that the pseudo entropy is computed under “far from equilibrium” conditions and, hence, is not expected to be close to the entropy obtained using Van’t Hoff analysis.

Ternary Mg based alloy compositions based on elemental species Pd and Ni have been synthesized using the route of high energy planetary ball milling. The chemical compositions of the alloy system investigated have more than or equal to 94 at% of Magnesium, 5 at% of Nickel, and 0.1 – 1 at% of Palladium. Based on the work on ternary Mg–Pd–Ni compositions, the following conclusions are derived:

- SEM analysis shows the synthesized Mg–Pd–Ni alloy compositions as having a mean particle size (of the Magnesium phase) of 14.3 ± 2.9 μm, 12.8 ± 2.4 μm, and 11.3 ± 2.2 μm for MP1, MP2 and MP3 coded compositions, respectively.

- EDS analysis is conducted for elemental analysis of the synthesized Mg–Pd–Ni alloy compositions. Results indicate the measured elemental compositions match closely with the targeted compositions.

- The crystallite size of the synthesized Mg–Pd–Ni compositions is measured as 23.85 nm, 22.55 nm and 19.28 nm for MP1, MP2 and MP3 coded compositions, respectively, using XRD technique. This clearly indicates that the crystallite size / grain regime decreases, when the Palladium concentration is increased. This is due to the catalyst effect (Pd and Ni).

- Further, XRD analysis shows that the crystallite size of the optimized Mg–Pd–Ni (coded MP2) to be of the order of 22.54 ± 0.97 nm, confirming the presence of nano-scaled substructures / grain boundaries in the alloy composition. The crystallite size of optimized hydrided MP2 coded composition is of order of 34.62 nm, which is 12 nm higher than the measured crystallite size of unhydrided composition.

- Hydriding studies are conducted as a function of temperature on the synthesized Mg–Pd–Ni compositions. The optimized composition (coded MP2) shows the highest hydrogen uptake with the fastest kinetics at a temperature of 200 ºC with 90 – 95 % of H_2 getting absorbed in first 20 minutes. The total absorbed value of hydrogen at 200 ºC and 20 bar charging pressure is measured as 5.95 mass % for MP2 coded composition.

- Desorption studies conducted at various temperatures in the range of 300 ºC to 375 ºC shows that the desorption kinetics increased as the temperature is increased. The estimated desorption at 350 ºC is measured as 4.48 mass%.

- Moreover, ternary Mg–Pd–Ni alloy composition also shows 3.98 mass% of reversible H_2 at a charging temperature of 202 ºC and pressure of 10 bar only.

- The deviation in hydriding and dehydriding kinetics due to departure from ideal gas behavior of hydrogen is also computed. The percentage deviations in the hydriding kinetics data are obtained as 4.78 %, 4.55 % and 4.85 % for Van–der–Waal, Redlich–Kwong and Redlich–Kwong–Soave equations, respectively, for the optimized MP2 coded composition. Similarly, the observed percentage deviation of hydrogen in the dehydriding kinetics data using ideal gas equation with respect to the above mentioned three real gas equations are obtained as 4.46 %, 4.44 % and 4.46 %, respectively, for the optimized MP2 coded composition.

- First order chemical kinetics models based on particular and complimentary function (full) solutions of a lumped first order differential equation show reasonable fits to the charging and discharging kinetics, respectively with coefficients of determination of 0.88 and 0.89, respectively.

- Shrinking Core Model has been successfully used to explain the charging kinetics of the optimized MP2 coded composition. Using a minimum variance non-linear optimization scheme, the best fit corresponding to mass transfer coefficient in gas phase, k_α as 1×10^{-6} m/s and reaction rate constant, k_r as 9×10^{-6} m/s has been obtained.

- A generalized case of random nucleation and growth, Johnson–Mehl–Avrami (JMA) model has been used to explain the charging kinetics of the optimized MP2 coded composition. For the JMA full linear regression model, a co-efficient of correlation, R^2 is obtained as 0.9932, and Avrami exponent, n is obtained as 0.57.

- The formation enthalpy and entropy of hydriding have been determined for optimized MP2 coded composition using Van’t Hoff analysis and calorimetric techniques using a Differential Scanning Calorimeter (DSC). The values of ΔH_o is obtained as 71.9 ±5.6 kJ/mole of H_2 and ΔS_o as 126.3 ± 6.1 J/mole of H_2 K using Van’t Hoff analysis and these values match closely with the results of DSC ($\overline{\Delta H}$ of 68.2 ± 5.3 kJ/mole of H_2 and $\overline{\Delta S_{pseudo}}$ of 116.9 ± 5.6 J/mole K), validating the basis of the Van’t Hoff analysis.

- It is to be noted that the pseudo entropy is computed under “far from equilibrium” conditions and, hence, is not expected to be close to the entropy obtained using Van’t Hoff analysis.

Quaternary Mg based alloy compositions based on elemental species Zr, Mn and Ni have been synthesized using the route of high energy planetary ball milling. The chemical compositions of the alloy system investigated have more than or equal to 81 at% of Magnesium, 5 at% of Nickel, and 2.5 – 7 at% of (Zr–Mn). Based on the work on ternary Mg–Zr–Mn–Ni compositions, the following conclusions are derived:

- SEM analysis shows the synthesized Mg–Zr–Mn–Ni alloy compositions as having mean particle size (of the Magnesium phase) of 16.9 ± 4.6 μm, 13.6 ± 3.9 μm, and 11.8 ± 3.7 μm for MZ1, MZ2 and MZ3 coded compositions, respectively.

- EDS analysis is conducted for the elemental analysis of the synthesized Mg–Zr–Mn–Ni alloy compositions. Results indicate the measured elemental compositions match closely with the targeted compositions.

- The crystallite size of the synthesized Mg–Zr–Mn–Ni compositions is measured as 22.29 nm, 17.36 nm and 11.32 nm for MZ1, MZ2 and MZ3 coded compositions, respectively, using XRD technique. Increasing addition of Zr and Mn particulates provide zener pinning centres for grain boundaries and hence reversion of refined grains is prevented. As a consequence, grain size reduces and increased high velocity hydrogen transport channels become available for diffusion of hydrogen into the particles. This increases the absorption kinetics.

- Further, XRD analysis shows crystallite size of the optimized Mg–Zr–Mn–Ni (coded MZ2) to be of the order of 17.69 ± 1.3 nm, confirming the presence of nano-scaled substructures / grain boundaries in the alloy composition. The crystallite size of optimized hydrided MZ2 composition is of order of 42.27 nm, which is 24 nm higher than the measured crystallite size of unhydrided composition.

- Hydriding studies are conducted as a function of temperature on the synthesized Mg–Zr–Mn–Ni compositions. The optimized composition (coded MZ2) shows the highest hydrogen uptake with the fastest kinetics at a temperature of 200 ºC with 90 – 95 % of H_2 getting absorbed in first 20 minutes. The total absorbed value of hydrogen at 200 ºC and 30 bar charging pressure is measured as 6.37 mass % for MZ2 coded composition.

- The MZ2 coded composition investigated shows a maximum hydrogen uptake capacity of 7.57 wt% at 201 ºC and desorption capacity of 7.36 wt% at 350 ºC. The charging/discharging kinetics of the investigated system shows that 85 % – 90 % of hydrogen is absorbed and desorbed within first 10 minutes, indicating rapid hydriding / dehydriding kinetics, clearly associated with catalytic action of Ni, Zr and Mn.

- Desorption studies conducted at various temperatures in the range of 320 ºC to 375 ºC shows that the desorption kinetics increased as temperature is increased. The estimated desorption at 350 ºC is measured as 5.75 mass%.

- The deviation in hydriding and dehydriding kinetics due to departure from ideal gas behavior of hydrogen is also computed. The percentage deviations in the hydriding kinetics data are obtained as 3.32 %, 4.24 % and 4.61 % for Van–der–Waal, Redlich–Kwong and Redlich–Kwong–Soave equations, respectively, for the optimized MZ2 coded composition. Similarly, the observed percentage deviation of hydrogen in the dehydriding kinetics data using ideal gas equation with respect to the above mentioned three real gas equations are obtained as 0.16 %, 0.16 % and 0.71 %, respectively, for the optimized MZ2 coded composition.

- First order chemical kinetics models based on particular and complimentary function (full) solutions of a lumped first order differential equation show reasonable good fits to the charging and discharging kinetics, respectively with coefficients of determination of 0.98 and 0.96, respectively.

- Shrinking Core Model has been successfully used to explain the charging kinetics of the optimized MZ2 coded composition. Using a minimum variance non-linear optimization scheme, the best fit corresponding to mass transfer coefficient in gas phase, k_α as 0.5×10^{-6} m/s and reaction rate constant, k_r as 16×10^{-6} m/s has been obtained.

- A generalized case of random nucleation and growth, Johnson–Mehl–Avrami (JMA) model has been used to explain the charging kinetics of the optimized MZ2 composition. For the JMA full linear regression model, a co-efficient of correlation, R^2 is obtained as 0.9771, and Avrami exponent, n is obtained as 1.31.

- The formation enthalpy and entropy of hydriding have been determined for optimized MZ2 coded composition using Van’t Hoff analysis and calorimetric techniques using a Differential Scanning Calorimeter (DSC). The values of ΔH_o is obtained as 80.9 ± 6.6 kJ/mole of H_2 and ΔS_o as 128.5 ± 6.9 J/mole of H_2 K using Van’t Hoff analysis and these values match closely with the results of DSC ($\overline{\Delta H}$ of 74.4 ± 6.1 kJ/mole of H_2 and $\overline{\Delta S_{pseudo}}$ of 119.5 ± 6.5 J/mole K), validating the basis of the Van’t Hoff analysis.

- It is to be noted that the pseudo entropy is computed under “far from equilibrium” conditions and, hence, is not expected to be close to the entropy obtained using Van’t Hoff analysis.

Finally, some low temperature compositions, namely, Fe–Ti–Ni, V–Ti, and V–Ni are also studied. The Fe–Ti–Ni composition with a mean particle size of 8.37 ± 5.7 μm is synthesized. This composition has a hydrogen uptake capacity of 0.73 mass% 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, V–Ti composition with a mean particle size of 6.24 ± 2.6 μm is synthesized. This composition has a hydrogen uptake capacity of 1.75 mass% of H_2 uptake at a charging temperature of only 100 ºC and release of 0.46 mass% of H_2 at discharging temperature of 154 ºC. The V–Ni composition with a mean particle size of 12.5 ± 2.9 μm is synthesized. This composition has a hydrogen uptake capacity of 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.

Scope for Further Study

In this study, Magnesium based alloy compositions have been synthesized with blending of various catalysts by mechanical alloying. Desorption temperature of MgH_2 is improved by 50 °C with respect to pure Mg. But, it is still very high (nearly, 300 °C) for mobile applications. Magnesium hydride becomes less stable with decreasing crystallite size. It is shown that desorption temperature of MgH_2 is improved, with Mg based nano cluster smaller than 20 Magnesium atoms. For example, a MgH_2 crystallite of 0.9 nm corresponds to a desorption temperature of only 200 °C. This knowledge can be extended to synthesize nano clusters of Mg even further reduced sized.

Research can be extended to develop Mg based complex metal hydride to reduce the temperature barrier. For example, $Mg(AlH_4)_2$ contains 9.6 mass% of hydrogen and decomposes below 200 °C. Moreover, a prototype hydrogen storage pressure vessel to store hydrogen as a solid state form (metal hydride) with appropriate control systems for powering a portable genset can be studied. Such a system, involving hydrogen storage concept is being considered as an important application in electric utility systems. There remain a significant number of research and development problems still to be solved, before the concept is economically viable.