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Full Length Article

Role of $NiMn_{9.3}Al_{4.0}Co_{14.1}Fe_{3.6}$ alloy on dehydrogenation kinetics of MgH_2

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Abstract

Hydriding and dehydriding properties of MgH_2 - x wt. % $NiMn_{9.3}Al_{4.0}Co_{14.1}Fe_{3.6}$ ($x = 10$, 25, 50) nanocomposites have been investigated in present work. Doped alloy was prepared by arc melting method and ball milled with MgH_2 to get nanocomposites. Onset temperature as low as 180 °C was observed for MgH_2-50 wt% system which is 80 °C lower than the as-milled MgH_2 giving 131.34 KJ/mol activation energy. Structural analysis shows tetragonal, orthorhombic and monoclinic phases for MgH_2, $Al_{60}Mn_{11}Ni_4$ and Mg_2NiH_4. Morphology by SEM were undertaken to investigate the effect of hydrogenation on nanostructured alloy. DSC studies show a single broad exothermic peak in the temperature range 48 °C–353 °C after alloy addition in MgH_2. These results indicate that the hydrogenation properties of MgH_2 nanocomposite have been improved compared to the as-milled MgH_2.

Keywords: Hydrogen storage; Activation energy; Mg based nanocomposites; Phase structure; TGA.

1. Introduction

World over scientists, politicians and administrators are worried over the present energy scenario couple with the depletion of fossil fuels and environmental degradation. This led them to work for clean energy and hydrogen has been identified as an ideal candidate for a sustainable energy future. Hydrogen storage is one of the most important key issues for its becoming a viable solution for depleting energy resources [1]. Hydrogen can be stored as compressed gas, liquid form and in solids using reversible metal hydrides which are considered to be safe and practical materials [2]. AB_5 type intermetallic hydrides are considered as an efficient method of hydrogen storage. MgH_2 is an attractive energy storage material due to high theoretical hydrogen storage capacity of about 7.6 wt%, light weight, high abundance and low cost. Unfortunately MgH_2 suffers from high temperature hydrogen discharge, slow hydrogen sorption kinetics and a high reactivity with oxygen which makes it unsuitable for commercial applications [3]. Ball-milling /mechanical millin are the most popularly adopted method which creates a fresh surface and structural defects in the material [4,5]. The formed defects and grain boundaries allow easy diffusion of hydrogen from the surface to the bulk material [6]. However, this method has limitations to achieve nanocrystallite size that is required (<5 nm) for destabilization of MgH_2 [7].

Recently solid state hydrogen storage in metal hydrides constitutes a major research activity [8–10] because of its importance in renewable energy sources. Li et al. [11] investigated $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloy and found decrease in hydrogen storage capacity. $LaNi_{3.6}Mn_{0.3}Al_{0.4}Co_{0.7}$ alloy was improved by the addition of Co, Mn and Al by Briki et al. [12]. which led to a significant reduction of hysteresis in hydriding and dehydriding (H/D). (H/D) cycles on the structural and

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morphological properties of $MmNi_{4.22}Co_{0.48}Mn_{0.15}Al_{0.15}$ alloy was studied by Zareii et al. [13] who found and absorption plateau pressures to be ~0.51, 1.22 and 2.49 bars at 293, 313 and 333 K with a maximum hydrogen storage capacity of about 5.78 at 293 K. Exchange and limit current density and diffusion capability of La-Mg-Ni-based hydrogen storage alloys were improved by proper Mn and Ni content [14].

Effect of partial substitution of Co or Al for Ni in $La_2Mg(Ni_{0.8\text{-}x}Co_{0.2}Al_x)_9$ ($x = 0$–0.03) alloys was studied by Liao et al. [15] who found that increase of Al content leads to an increase in the cell volume and the hydride stability which causes the decrease in cell volume expansion on hydriding. In case of $MmNi_{3.55}Co_{0.75}Mn_{0.7\text{-}x}Al_x$ alloy Al substitution for Mn can lower the hydride formation pressure and reduce the hysteresis between the hydrogen absorption and desorption pressure [16]. The effect of iron substitution on the electrochemical behavior of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75\text{-}x}Fe_x$ (0-x-0.55) compounds was reported by Khaldi et al. [17] who found that the value of hydrogen diffusion coefficient decreases when increasing iron content in the alloy. Cheng et al. [18] in the year 2008 studied partial substitution of Al for Ni in $LaNi_{4.25}Al_{0.75}$ alloy improving the cyclic performance and decreases plateau pressure of the hydride. Influence of 1–10 at.% Co or 5 at.% Pd additives in $LaMg_2Ni$ and its hydrogen reactivity in $La_{25}Mg_{50}Ni_{25}$ alloys was studied by Teresiak et al. [19]. Influence of 1–10 at.% Co or 5 at.% Pd additives in $LaMg_2Ni$ and its hydrogen reactivity in $La_{25}Mg_{50}Ni_{25}$ alloys was studied by Teresiak et al. [19].

Zhang et al. [20] found that the Mn partial substitution for Ni decreases the plateau pressure without reducing its hydrogen storage capacity. It has been reported by Jiang et al. [21] that appropriate substitution of Ni with Mn could increase the electrochemical discharge capacity and the hydrogen absorption rate of $ReNi_{2.6\text{-}x}Mn_xCo_{0.9}$ ($x = 0$–0.9) alloys. Zhang et al. [22] investigate the kinetic mechanism of hydriding reaction in α phase (solid solution) region for cubic Laves $Ho_{1-x}Mm_xCo_2$ alloys. The results indicate that the hydrogen absorption kinetics in α phase region is controlled by hydrogen diffusion into the bulk. The activation energies calculated using Chou model with the least square method are in the range of 29.4–53.5 kJ/mol H_2. Li et al. [23] studied the Mg–3 mol% $LaNi_3$ composition by hydrogen combustion synthesis (HCS) method and investigated effects on the hydrogenation properties, analyzed changes from the relationship between the microstructure, crystalline state and the energy injected into the composite from the external high magnetic field. Rate-controlling step of hydrogen diffusion in Mg–30 wt.% $LaNi_5$ at temperatures ranging from 302 to 573 K, while that of Mg–50 wt.% $LaNi_5$ changed from surface penetration to hydrogen diffusion with increasing initial hydrogen pressure ranging from 0.2 to 1.5 MPa [24]. It was found that activation energies calculated by Chou model for hydrogen absorption in Mg–30 wt.% $LaNi_5$ were 25.2 and 28.0 kJ/mol. H_2 calculated by Chou model. Li et al. [25] studied the hydriding/dehydriding of $(LaNi_5)_{1-x}Mg_x$ ($x = 0$, 0.018, 0.041, 0.063) and the results indicate that the hydriding kinetics of $(LaNi_5)_{1-x}Mg_x$ alloys are controlled by diffusion of hydrogen atom in hydride. The addition of small amount of magnesium improves the kinetic performance of $LaNi_5$ slightly.

In present work $NiMn_{9.3}Al_{4.0}Co_{14.1}Fe_{3.6}$, prepared for the first time is added to MgH_2 to form nanocomposite and studied its structural and hydrogen storage properties. However alloys suffer from disadvantages like difficult activation treatment, poor-kinetics and high desorption temperature.

2. Experimental

2.1. Alloy preparation

$NiMn_{9.3}Al_{4.0}Co_{14.1}Fe_{3.6}$ alloy was prepared using Arc-melting method in argon atmosphere by re-melting 3 times the stoichiometric amounts of 99.5% purity of elements to get homogeneous composition. The ingot was then annealed in a sealed evacuated quartz tube for one week at 1173 K after which it was crushed to get alloy for study.

2.2. Preparation of MgH2-alloy composite

The MgH_2-x wt% $NiMn_{9.3}Al_{4.0}Co_{14.1}Fe_{3.6}$ ($x = 10$, 25, 50) composites were milled mechanically under 0.1 MPa Ar pressure for 10 h (300 rpm) using a FRITSCH P7 ball milling machine. This process was completed on the basis of 5 min rest and 15 min work pattern and the 10:1 ratio of ball to powder and MgH_2 was fixed for mechanical milling. The high purity Ar gas (99.99%) was used to avoid the oxidation and hydrogenation during the mechanical milling.

2.3. Activation of nanocomposites

Two grams of MgH_2+x wt% ($x = 10$, 25, 50) nanocomposite was kept in sample holder of 1″ diameter Cu tube with thermocouple and heater. Initially the composite was evacuated to 10^{-5} mbar vacuum, flushed with 99.95% pure hydrogen at 3 bar pressure, again evacuated to 10^{-5} mbar vacuum and heated to 398 K for 3 h. At this point cool the sample introduced hydrogen and heats it to 398 K for 3 h in hydrogen environment. Considerable time was allowed to heat the sample till an equilibrium temperature is reached. Now evacuate alloy to 10^{-5} mbar pressure and cool it to room temperature.

In second cycle after cooling the composite material to room temperature hydrogen at 3 bar was introduced in the cell where the composite start absorbing hydrogen resulting in decrease in pressure in the cell. This process was repeated for five cycles till the activation process completes and the pressure in the reactor comes to a constant value showing the formation of the hydride material with full saturation [26].

2.4. Characterization of composite

Structural characterization was performed with the help of X-Ray Diffraction (XRD) technique with Cu-Kα radiation (operated at 45KV, $\lambda = 1.54$ Å in 2θ range of 20–90°).

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