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Investigations on Microstructures of Ball–milled $MmNi_5$ Hydrogen Storage Alloy

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ABSTRACT

Five samples of $MmNi_5$ hydrogen storage alloy are prepared by ball–milling the $MmNi_5$ alloy at various speeds for different periods. For the first time, it has been shown that an optimum microstructure in terms of homogeneity, particle size, crystallite size and unit cell volume is necessary to give best hydrogenation properties. The alloy ball–milled at the speed of 100 rpm for 1 h duration shows optimum hydrogenation behaviour. This alloy is activated completely in the 2nd hydrogenation–dehydrogenation cycle with hydrogen storage capacity of 1.5 wt%, and 90% hydrogen absorption/desorption is recorded in 2 min; whereas the same for un–milled $MmNi_5$ alloy is 5th cycle, 1.4 wt% capacity and 5 min respectively. Optimum microstructure for the alloy ball–milled at 100 rpm for 1 h duration corresponds to homogeneous size distribution of particles with average value of 2 μm, crystallite size as 18 nm and unit cell volume as 87.7075 $Å^3$.

1. Introduction

Hydrogen storage materials are the most popular mode for storage of hydrogen energy in efficient manner. Among various hydrogen storage materials AB_5–type metal hydride is attractive due to its easy activation and operation at ambient condition [1]. Most often, hydrogen storage alloys are synthesized through radio–frequency induction melting or arc melting. To improve the hydrogenation properties of the state of the art alloy, new synthesis routes are adopted. Non–conventional synthesis by melt–spinning technique, results in enhanced hydrogenation properties of the hydrogen storage alloys by change in microstructure of the alloys [2,3]. Substitution of other elements in basic structure also influences hydrogenation properties [4]. Chumphongphan et al. have reported that substitution of Al and Mo in $CaNi_5$ alloy results in reduction of hydrogen storage capacity and plateau pressure [4].

Synthesis of hydrogen storage alloy by mechanical alloying leads to nanocrystalline structure with improved hydrogenation properties [5]. Talaganis et al. have found that low energy mechanical alloying of $LaNi_5$ with low temperature (600 °C) annealing procedure reduces the number of intermediate stages [6]. Electrode characteristics of nanocrystalline AB_5 compounds are also improved, when prepared by mechanical alloying [7]. In another work by Hurtado et al. mechanical milling of AB_5 alloy requires 70 h to reach the final stage [8]. Thus mechanical alloying needs larger time for synthesis of alloys.

Nanocrystalline materials with new and improved properties can also be prepared by ball–milling of alloy synthesized through arc–melting [9]. This process takes few hours in comparison to many hours needed for mechanical alloying. During ball–milling process the microstructure of the alloy changes continuously, leading to change in hydrogenation behaviour. Earlier studies on ball–milled hydrogen storage alloys have shown improved hydrogenation behaviour. Aoyagi et al. have investigated the effect of ball–milling on the hydrogen absorption properties of FeTi, Mg_2Ni and $LaNi_5$ and found fast rate of absorption of hydrogen in ball–milled alloys due to the creation of new surfaces [10]. Another study on the effects of ball–milling of $LaNi_5$ alloy, gives better discharge capacity of 307.1 mAh g^{-1} for milled alloy electrode in comparison to 154.5 mAh g^{-1} for un–milled alloy [11]. V. V. Sarma et al. have investigated the effect of ball–milling on $MmNi_{4.6}Fe_{0.4}$ alloy [12]. In their study they observed fast kinetics and improvement in hydrogen storage capacity of ball–milled alloy as 1.7 wt% in comparison to 1.5 wt% of un–milled alloy. Smaller particles with fresh surfaces, formed during ball–milling are the most likely cause of enhanced hydrogenation behaviour. Some microstructural evaluations of ball–milled $MmNi_5$ alloy have been done by Esquivel et al.; however, they have not studied the hydrogenation behaviour of ball–milled $MmNi_5$ alloy [13]. In a separate study by B. Joseph et al., it was found that long–time ball–milling of $LaNi_5$ caused the formation of some anomalous

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state, which was very resistant against hydrogen absorption [14]. Microstructural characterization has not been performed by them. Obregón et al. have prepared $MmNi_{5-x}Al_x$ hydrogen storage material through mechanical alloying and estimated the optimum milling and annealing time [15].

From the above discussion it is clear that ball–milling of $MmNi_5$ alloy may improve the hydrogenation properties. The speed and duration of milling affect the hydrogenation properties very much. It was mentioned by earlier researchers that microstructural changes caused by ball–milling were important for understanding the improvement in hydrogenation characteristics [10–15]. Few reports discuss the changes in hydrogenation behaviour after ball–milling; while others focus on the microstructure evaluation. However, no specific studies have been reported so far to explore the direct relation of microstructural changes due to ball–milling of alloy at different speed and duration of milling, which influence the hydrogenation properties of $MmNi_5$ alloy.

In present study hydrogen storage alloys are prepared through ball–milling of $MmNi_5$ alloy at different speed and duration of milling. Since earlier studies on ball–milled $MmNi_5$ alloy have not reported the correlation of microstructure with hydrogenation behaviour, present investigation is aimed to explore the systematic change in the microstructure of the ball–milled $MmNi_5$ alloy. For the first time in the present study it has been shown that an optimum microstructure is required to obtain optimum hydrogenation properties. Efforts have been made to investigate those microstructural changes, which may cause improvement in the hydrogenation behaviour of hydrogen storage alloy after ball–milling. These microstructural changes have been correlated with hydrogenation behaviour of ball–milled $MmNi_5$ alloy. The reasons behind this improvement are explored.

2. Experimental details

2.1. Synthesis

$MmNi_5$ alloy was synthesized by taking stoichiometric ratio of mischmetal (La 22%, Ce 52%, Nd 15%, Pr 11%) and nickel. This mixture was pelletized and melted in 18 kW radio– frequency induction furnace in ambient argon. The as–synthesized alloy was pulverized into powder (<150 μm) using a pestle and a mortar in the air. After that the powder was ball–milled in self–constructed ball–mill using stainless steel balls at different speed (100–400 rpm) for different time of milling (15 min to 2 h) in ambient argon. Ball to powder weight ratio was kept at 100:1. The diameter of the stainless steel ball was 12.6 mm. The cylinder used in grinding process had volume of 890 cm^3. Five samples of hydrogen storage alloys were prepared at different speed and time of milling, as shown in Table 1.

2.2. Structural and microstructural characterization

All the five samples prepared in this manner were subjected to X-ray diffraction (XRD) analysis employing a Philips X-ray diffractometer (PW1710) equipped with graphite monochrometor and working with CuKα radiation (λ = 1.5418 Å). The microstructures were examined by scanning electron microscopy (SEM) through a Philips XL–20 series SEM with 30 kV secondary electrons.

Table 1
Nomenclature of the alloys.

S.No.	Name of alloy	Speed of ball–mill (rpm)	Time of milling
1	Alloy 1 (un–milled)	–	–
2	Alloy 2	200	15 min
3	Alloy 3	200	30 min
4	Alloy 4	100	1 h
5	Alloy 5	400	2 h

2.3. Hydrogenation behaviour

The hydrogenation properties were studied by monitoring activation curves, absorption–desorption pressure–composition isotherms (P–C–T) and absorption–desorption kinetics at the temperature of 300K. The hydrogen storage alloy was put in the hydrogen reactor and the reactor was evacuated at a pressure of 10^{-5} MPa. After that it was filled with hydrogen gas. The absorption of hydrogen in the hydrogen storage alloy was reflected by decrease in the initial hydrogen pressure in the reactor. The amount of hydrogen desorbed was monitored by volume displacement method [16].

3. Results and discussions

3.1. Structural and microstructural characterization

X-ray diffraction (XRD) patterns of all the five samples are shown in Fig. 1. XRD analysis by Fig. 1 reveals single–phase $CaCu_5$–type hexagonal structure for all the samples. The calculated value of lattice parameters and unit cell volume of all the five samples are given in Table 2. These values indicate that the lattice parameters ‘a’ and ‘c’ are almost constant for all the samples; however, a maximum increase of 0.36% is observed in the unit cell volume of alloy 4 as compared to un–milled alloy. A close insight into the XRD patterns depicts broadening of the XRD peaks continuously from alloy 1 to alloy 5. As the speed (rpm) and duration of ball–milling

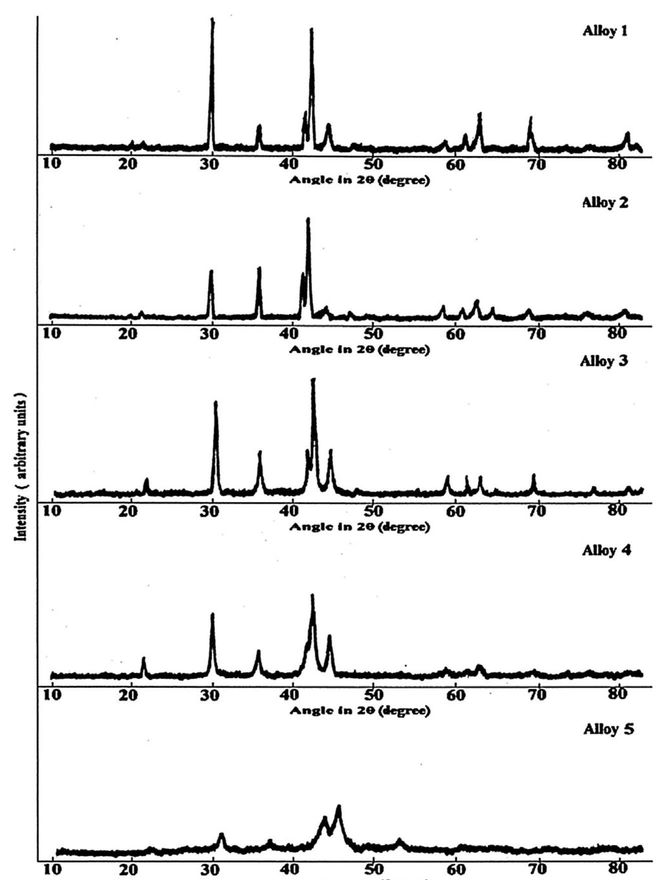

Fig. 1. X-ray diffractogram (XRD) of all the five alloys.