Hydrogen storage in Mg–Mg$_2$Ni–carbon hybrids

Anshul Gupta, Suboohi Shervani, Mohammad Faisal, Kantesh Balani, Anandh Subramaniam

Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

ARTICLE INFO

Article history:
Available online 25 December 2014

Keywords:
Accumulative roll bonding
Hybrid
Hydrogen storage
Pressure–composition isotherms
Kinetics

ABSTRACT

Mg-based hybrids have potential applications for hydrogen storage in the solid state. In the current investigation laminate hybrids were prepared keeping this objective in view. Mg$_2$Ni was synthesized from vacuum induction melting of metal ingots, which was further incorporated between the Mg layers by Accumulative Roll Bonding process (ARB). To improve the hydrogen storage properties, carbon (soot/graphite) was also deposited between the Mg layers. By using the ARB process, microstructure refinement was achieved, along with the incorporation of about 5 wt.% Mg$_2$Ni and 1.3 wt.% soot (or 5 wt.% graphite) in the hybrid. A total of 30 ARB passes were used in the process. The hydrogen absorption characteristics of the hybrid (through pressure–composition isotherms and absorption–time curves) were studied using a standard Sieverts apparatus. Absorption of about 6.2 wt.%H was observed at 300 °C at ~3.5 bar pressure in the Mg–Mg$_2$Ni–graphite hybrids (5.8 wt.%H at a plateau pressure of ~2 bar). Good kinetics of absorption was also observed, i.e. 4.5 wt.%H was absorbed in ~80 s at 300 °C under 20 bar H$_2$ pressure.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Amongst different classes of materials for solid state hydrogen storage, metal hydrides have received considerable attention [1]. Important classes of metallic systems for hydrogen storage include [2]: pure metals (e.g. Mg, Pd, etc.), AB compounds (e.g. TiFe, ZrNi, etc.), A$_2$B compounds (e.g. Mg$_2$Ni, Ti$_2$Ni, etc.) and AB$_5$ compounds (e.g. LaNi$_5$, CaNi$_5$, etc.). In addition to monolithic materials, hybrids have also been used for hydrogen storage [3]. Use of hybrids is expected to improve the hydrogen absorption and desorption properties, which include [4]: enhanced storage capacity, faster kinetics of absorption, lower temperature of absorption, etc.

Ball milling has been the preferred route for the synthesis of hybrids as the process produces powders, which have fine grain size, high dislocation density and a fine scale distribution of the phases [5]. Accumulative Roll Bonding (ARB) process, first proposed by Saito et al. [6], used conventional roll bonding technique [7] in a repeated manner, to impart large strain (true strain of 6.4) to the Al–Mg alloy. ARB process has been used to produce ultra-fine (sub-micron) grained materials [8,9] suitable for hydrogen storage applications [10]. Mg–Ni laminate composites, in the atomic ratio of 5:1 (Mg:Ni), prepared by accumulative roll bonding show considerably enhanced hydrogen storage capacity of ~5.5 wt.%H at 300 °C at ~5 bar pressure [11]. MgH$_2$–10 wt.%MgNiH$_4$ composites, synthesized by Dehouche et al. [12] by ball milling under argon atmosphere, show 5.5 wt.%H storage capacity at 300 °C at ~3.5 bar pressure and comparable hydrogen storage capacity at 250 °C at ~1.3 bar pressure. Bobet et al. [13] studied the effect of carbon (graphite) on hydrogen sorption properties of Mg–Mg$_2$Ni composites synthesized by ball milling under argon atmosphere. They reported ~5.2 wt.%H absorption in 30 min at 300 °C under 10 bar hydrogen pressure in Mg–15 wt.%Mg$_2$Ni–10 wt.%C composites. However, desorption kinetics was sluggish with desorption of ~1 wt.%H in 10 min at 300 °C under 1.5 bar hydrogen pressure [13].

The literature on hydrogen storage characteristics of Mg–C composites is limited. In Mg–30 wt.%C composite obtained by ball milling (under 10 bar hydrogen pressure), ~4.2 wt.%H storage capacity was reported at a plateau pressure of 2.8 bar (300 °C) [14]. The presence of ‘dangling carbon bonds’ is expected to play a role in the absorption of hydrogen in these hybrids [15]. Considerable literature also exists on the use of CNTs for hydrogen storage [16].

The current work aims at achieving the following: (i) synthesis of Mg–Mg$_2$Ni–soot/graphite laminated hybrids by accumulative roll bonding (ARB), and (ii) determination of hydrogen absorption and desorption properties (pressure–composition isotherms (PCI) and wt.%H vs. time plots). The importance of the work is that, hybrids with good storage capacity and fast kinetics can be synthesized using a ‘bulk’ technique, amenable for easy scaled-up production. The hydrogen absorption capacity cited in the current work is at the plateau pressure, which is appropriate from an applications perspective.

* Corresponding author. Tel.: +91 512 259 7215.
E-mail address: anandh@iitk.ac.in (A. Subramaniam).

http://dx.doi.org/10.1016/j.jallcom.2014.12.101
0925-8388/© 2014 Elsevier B.V. All rights reserved.
2. Experimental details

Accumulative Roll Bonding (ARB) process was used for the synthesis of Mg–Mg₂Ni–soot/graphite hybrids (process outline illustrated in Fig. 1). In the first step, 5 mm thick magnesium sheets (cut from the 99.9% pure Mg ingots, procured from International Magnesium Group, USA, using power-hacksaw) were reduced to 0.8 mm thickness by multi-pass cold rolling. Mg–Ni alloy was prepared by induction melting of Mg ingots and Ni shots (99.9% pure, 3-5 mm diameter and 2 mm length, procured from Alfa Aesar, USA) in the atomic ratio of 2:1 under argon (99.99%) atmosphere. The alloy ingot powder (powdered using a mortar and pestle) and soot (from kerosene lamp) were incorporated between the Mg layers before rolling (7.8 HP driving motor and 5” diameter rolls made of high carbon steel and rotating at 72 rpm). In some samples soot was replaced by powdered graphite. The samples were wire brushed and cleaned with ethanol before every roll pass to enhance bond strength between magnesium sheets. The rolling process (with 50% reduction per pass) not only bonds the sheets, but also acts like a severe plastic deformation process. After rolling, the sample was cut into two halves, stacked and rolled again with further incorporation of Mg₂Ni (for the first 10 ARB passes) and soot/graphite (for the first 25 ARB passes). At the end of the process (Fig. 1), a total of ~5 wt.% Mg₂Ni and ~1.25 wt.% soot (or 5 wt.% graphite) was incorporated. Mg–Mg₂Ni (fraction of Mg₂Ni being 5 wt.%) sample was also prepared by ARB (keeping the process parameters constant) as a reference sample for illustration of the hydrogen absorption characteristics with Mg–Mg₂Ni–carbon hybrids. The amount of material incorporated per pass is limited by the fact that incorporation of a large amount of second phase leads to poor bonding between the sheets on cold rolling. Further, the total number of passes in ARB is also limited, as the sample tends to crack and fragment upon cold rolling.

The samples were characterized for hydrogen absorption using a commercial Sieverts apparatus (AMC Corporation, USA) to obtain pressure–composition isotherms (PCI) and to acquire kinetics data (wt.%H vs. time plots). Hydrogen of 99.99% purity was used in all the measurements. Temperature of the system was measured using type K thermocouple in conjunction with Omega Controllers (PCI) and to acquire kinetics data (wt.%H vs. time plots). Hydrogen of 99.99% purity was used in all the measurements. Temperature of the system was measured using type K thermocouple in conjunction with Omega Controllers (CN2841) with an accuracy of ±0.2 °C under equilibrium conditions and stability better than ±0.05 °C. Pressure transducers (Honeywell TJE) which have resolution of 0.5 mbar for measurements up to 10 bar and 10 mbar for measurements up to 200 bar. Approach to equilibrium was monitored using the change in slope of temperature with time (0.00245 psi/s) in the sample chamber. The equilibrium of the gas is considered fully established when these two values together reach nearly zero for at least 2 min.

Around 100 mg of sample was loaded in sample chamber (SS316L, 2 cc volume) and evacuated for 30 min at 350 °C under rotary vacuum. The samples were subsequently activated by repeatedly cycling under 20 bar hydrogen pressure and 0.1 bar vacuum for half an hour each at 300 °C.

3. Results and discussions

Fig. 1 in Supplementary information shows X-ray diffraction pattern of as cast Mg–Ni alloy in atomic ratio 2:1. The phase analysis carried out using XRD shows presence of Mg₈Ni along with MgNi₂ and Mg as confirmed from energy dispersive spectroscopy in conjunction with scanning electron microscopy (Fig. S2 and Table S1 in Supplementary information). The volume fraction of phases calculated from the scanning electron micrograph (Fig. S2 in Supplementary information) using point count method is about 69% of Mg₈Ni, 12% of MgNi₂ and 19% of eutectic (consisting of Mg and Mg₂Ni).

Fig. 2 shows PCI curves for ARB synthesized hybrids (Mg–Mg₂Ni and Mg–Mg₂Ni–soot/graphite). The Mg–Mg₂Ni hybrid absorbs 3.4 wt.%H at 300 °C at 3.5 bar pressure, while the Mg–Mg₂Ni–soot hybrid absorbs 5.4 wt.%H at 3.3 bar pressure (4.4 wt.%H at a plateau pressure of ~2.5 bar). The Mg–Mg₂Ni–graphite hybrid absorbs considerably higher amount of hydrogen: 6.2 wt.%H at 300 °C at 3.5 bar pressure (5.8 wt.%H at a plateau pressure of ~2.3 bar) and 5.7 wt.%H at 250 °C at 1.2 bar pressure (5.3 wt.%H at a plateau pressure of ~0.6 bar). These results exceed those obtained for ball milled composites incorporating hydrides of Mg–Mg₂Ni synthesized by Dehouche et al. [12].

Fig. 3 shows PCI curves obtained at three temperatures (absorption): 260 °C, 270 °C and 300 °C for the Mg–Mg₂Ni–graphite hybrid. The desorption isotherm measured in each case showed that the process is reversible but the preliminary data were determined under non-equilibrium conditions and thus have been omitted from this report. As expected the plateau pressure for absorption increases with increasing temperature. Van’t Hoff plot
and respectively. These values are nanocrystals, J. Alloys Comp. enhances the kinetics of absorption and desorption. This is consistent with previous observations [15]. It is to be noted that carbon significantly enhances the kinetics of absorption and desorption. This is consistent with previous observations [15].

4. Summary and conclusions

Accumulative Roll Bonding (ARB) synthesized Mg–Mg2Ni–soot/graphite hybrids offer attractive hydrogen storage properties both in terms of storage capacity (e.g. the Mg–Mg2Ni–graphite sample absorbs 6.2 wt.%H at 300 °C at 3.5 bar pressure and 5.7 wt.%H at 250 °C at 1.2 bar pressure) and absorption kinetics (e.g. the Mg–Mg2Ni–graphite sample absorbs 4.5 wt.%H in 80 s at 300 °C under 20 bar hydrogen pressure). Carbon (soot/graphite) plays an important role in enhancing both the absorption capacity as well as the kinetics. The samples with graphite show better hydrogenation properties, due to the higher volume fraction of the carbon present. The cyclicity of the Mg–Mg2Ni–graphite hybrid is also good-stable reversible absorption was seen till six cycles. The most important feature of the process developed for the synthesis of the hybrids is that it is easily amenable for scaled-up production.

Fig. 4. Plot of wt.%H absorbed (20 bar H2 pressure, solid lines-filled markers) and desorbed (0.1 bar vacuum, dashed lines-empty markers) with time for: Mg–Mg2Ni and Mg–Mg2Ni–soot/graphite hybrids at 300 °C.

[InP vs. 1/T] drawn from the PCI data obtained at these three temperatures is shown in inset. The enthalpy and entropy of absorption calculated using linear regression analysis are −73.42 kJ/mole H2 and −133.11 J/K mol H2 respectively. These values are similar to those for absorption of hydrogen in magnesium (as cited in literature [17,18]). This point is noteworthy as graphite/soot in the composite is playing an important role in the enhancement of hydrogen storage capacity. Some aspects of the role played by carbon (as a catalyst) in hybrids have been investigated before [19], however more work needs to be done to understand the precise mechanisms, which are operative.

Fig. 4 shows wt.%H absorbed (and desorbed) with time for Mg–Mg2Ni and Mg–Mg2Ni–soot/graphite hybrids. At 300 °C and under 20 bar hydrogen pressure, it is seen that the Mg–Mg2Ni hybrid absorbs 0.7 wt.%H in 80 s, while the Mg–Mg2Ni–soot hybrid absorbs 3.4 wt.%H in 80 s and the Mg–Mg2Ni–graphite hybrid absorbs 4.5 wt.%H in 80 s. Further, it is noted from the figure that, the desorption kinetics of Mg–Mg2Ni–soot/graphite hybrids is not as good as absorption. Given the ‘bulk’ nature of the samples these values represent fast kinetics of absorption (and desorption) and exceed the values obtained for even ball milled samples prepared by Bobet et al. [13]. It is to be noted that carbon significantly enhances the kinetics of absorption and desorption. This is consistent with previous observations [15].

Acknowledgments

The authors would like to thank Department of Science and Technology, Government of India for funding of the project under the Technology Systems Development Programme.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2014.12.101.

References