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# Enhanced hydrogen storage in accumulative roll bonded Mg-based hybrid

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ABSTRACT

Magnesium based hybrids have potential applications for hydrogen storage in the solid state. Although magnesium can store a high amount of hydrogen (7.6 wt.%), high temperatures (~300 °C) and pressures (0.3–1 MPa) are required for the same. Additionally, the kinetics of absorption of hydrogen in bulk magnesium is slow. In the current work, Mg–$LaNi_5$-soot hybrids are synthesized by the accumulative roll bonding (ARB) process (30 roll passes, 50% reduction per pass). It is observed that the hybrid absorbs 5 wt.% hydrogen at 250 °C at a pressure of ~0.33 MPa (4.5 wt.% hydrogen at a plateau pressure of less than 0.08 MPa). After 30 ARB passes, the kinetics of absorption of the hybrid was 4.0 wt.% hydrogen in 30 s at 2 MPa, which is 3500% faster than the Mg (ARB) sample and 500% faster than Mg–$LaNi_5$ hybrid. This combination of operating parameters and enhanced hydrogen storage properties (high capacity at lower temperatures and pressures combined with rapid kinetics) offer exciting prospects towards applications, given that bulk samples can be synthesized in large quantities using the process developed. After 25 ARB passes there are more than $10^5$ layers in the hybrid and the layer thickness becomes less than ~24 nm. Hence, intimate mixing of the components of the hybrid, along with a fine microstructure and increased defect density in the hybrid, seems to play an important role in the enhancement of the hydrogen absorption properties.



## Introduction

Hybrids are emerging as promising materials for solid state hydrogen storage [1–4]. It is expected that hybrids will help to overcome some of the limitations found in monolithic materials used for hydrogen storage. These limitations specifically relate to a preferred combination of thermodynamic (temperature and pressure of absorption and desorption) and kinetic parameters (rate of absorption and desorption) [5].

Multiple techniques have been used by investigators to synthesize these hybrids. These include ball milling [6], sintering [7], sputtering [8] and conventional mechanical mixing [9]. Some of these processing routes (e.g. ball milling) not only help in the synthesis of the hybrid, but also help in microstructural engineering of the sample (i.e. achieving finer grain size, fine scale distribution of the second phase, higher dislocation density, etc.) [10,11].

One of the widely used methods for the synthesis of monolithic and composite materials for hydrogen storage is

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ball milling. Mg–$LaNi_5$ composites have been synthesized by ball milling by Terzieva et al. [12]. They have reported the absorption of 1.9 wt.% hydrogen in ~30 s at 300 °C and 1 MPa pressure in a Mg-30 wt.% $LaNi_5$ sample. Liang et al. [6] studied hydrogen storage properties in ball milled $MgH_2$-30 wt.% $LaNi_5$. They observed hydrogen storage capacity of ~3.7 wt.% at a plateau pressure of 0.2 MPa at 310 °C. They also reported ~1.4 wt.% hydrogen absorption in 30 s (1 MPa, 150 °C). To emphasize the effect of finer grain size on the hydrogen absorption, Fu et al. [13] synthesized Mg-5 wt.% $LaNi_5$ composites by ball milling under hydrogen atmosphere and reported higher hydrogen storage capacity (~4.6 wt.% at a plateau pressure of 0.04 MPa at 245 °C and ~4.8 wt.% at a plateau pressure of >0.1 MPa at 285 °C), coupled with reasonably good kinetics (>3.5 wt.% in 30 s a ~285 °C at 2 MPa). A point noteworthy of consideration is that the kinetic data, inferred from plots in literature, should be read with a degree of caution (given that the data set in most cases is in a time scale of 60 min). With increasing wt.% of $LaNi_5$ (5%, 15%, 35%) in the composite, a decrease in the amount of hydrogen absorbed is observed at the plateau pressure. It is to be noted that in all cases a 'strict' plateau is not observed (i.e. the plateau is 'sloping'). Sun et al. [1] synthesized Mg-X wt.% $LaNi_5$ (X = 20, 30, 40, 50) by ball milling followed by sintering. They have achieved best hydrogen storage capacity of ~4.3 wt.% (0.2 MPa plateau pressure at 300 °C) for the Mg-20 wt.% $LaNi_5$ composite. Liu et al. [14] prepared Mg-20 wt.% $LaNi_5$ composite using a laser sintering technique and they have observed appreciable hydrogen storage capacity (~4 wt.% at a plateau pressure of 0.15 MPa at 300 °C).

Some literature exists on the hydrogen storage characteristics of Mg–C composites as well. Zhou et al. [15] have prepared Mg-30 wt.% carbon (crystallitic form obtained from coal) composite by ball milling under hydrogen pressure of 1 MPa. They observed hydrogen storage capacity of ~4.2 wt.% at a plateau pressure of 0.28 MPa (at 300 °C). They have explained enhanced hydrogen absorption in Mg–C composites by the presence of carbon 'dangling bonds', which can absorb hydrogen. Konarova et al. [16] have observed reasonable hydrogen storage kinetics (2.1 wt.% in 30 s at 250 °C) in a $MgH_2$–C porous composite, synthesized by decomposition of an organomagnesium precursor under hydrogen. Jeloaica et al. [17] have reported that during interaction of hydrogen atom with graphite (0001) surface, both physiosorption and chemisorption of hydrogen take place. This leads to the elimination of the energy barrier required for the diffusion of hydrogen and thereby enhances kinetics. Wu et al. [18] have prepared $MgH_2$-5wt.% AP (as prepared SWNT containing metallic particles). They observed fast kinetics absorbing 5 wt.% hydrogen in ~30 s at 200 °C. They have identified the role of CNTs in acting as diffusion channels into the Mg matrix, thus enhancing the kinetics. Amirkhiz et al. [19] prepared SWNT-$MgH_2$ composite by co-milling for 1 h. They proposed that SWNT functions as a "hydrogen pump" by penetrating into the thin surface hydroxide shell on the surface Mg. A general conclusion on the role of carbon enhancing the kinetics is related to the unique electron characteristics of carbon and the morphology effect [19]. Wu and Cheng [20] studied the effect of carbon on hydrogen storage properties. They have stated that small radius curvature carbon show appreciable catalytic effect when mechanically milled with Mg due to the presence of sp and $sp^2$ hybridization and thus the delocalized $\pi$ electrons may interact with hydrogen atoms and molecules.

In the past decade, many severe plastic deformation techniques, including ARB [21–23], have gained prominence as synthesis techniques to fabricate hydrogen storage materials [24]. Dufour and Huot [25] prepared an Mg–Pd composite by ARB. The hydrogen storage characteristics of these composites are not as good as some of the $LaNi_5$ containing composites discussed earlier. The Mg–Pd composite absorbs ~1 wt.% hydrogen at a plateau pressure of 0.4 MPa at 350 °C with a sloping plateau. Mohsen et al. [26] have synthesized Mg-22 at.% Ti layered composites via accumulative roll bonding. These composites show hydrogen storage capacity of ~3 wt.% at a plateau pressure of 0.6 MPa at 350 °C and reasonable kinetics of ~0.8 wt.% in 60 s (at 2 MPa and 350 °C). Botta et al. [27] have synthesized an Mg sample using several cold rolling passes. It showed limited absorption of 0.5 wt.% hydrogen in 30 s (350 °C, 2 MPa). Large amounts of strain due to severe plastic deformation techniques lead to refinement in grain size [28] and creation of non-metallurgical bonded interfaces [26]. Also, a number of defects such as dislocations, vacancies are also increased during the process [11]. Therefore, the effect of grain refinement, defects and synergistic combination of chemisorptions and physiosorption help in achieving enhanced kinetics of hydrogen storing material via ARB in Mg–$LaNi_5$-Carbon(soot) hybrids.

The current work aims at the following: (i) synthesis of Mg based hybrids (containing $LaNi_5$ and soot) by accumulative roll bonding (ARB), (ii) characterization of the material for hydrogen absorption and desorption properties via pressure-composition-isotherms (PCI) and wt.%H versus time plots. The overall goal is to: (i) push the amount of hydrogen stored in the hybrid to that obtained by routes like ball milling, (ii) reduce the absorption pressure and temperature (with respect to other bulk samples), (iii) increase the desorption pressure (to >0.1 MPa), (iv) enhance the absorption and desorption kinetics (to bring it on par with ball milled samples). One synthesized sample will also be tested for cyclability (i.e. storage of Hydrogen with multiple absorption–desorption cycles).

An important point to note with respect to the hydrogen absorption capacity is that, often in the literature, the maximum hydrogen absorption capacity is quoted, instead of the hydrogen absorption at the plateau pressure. From a perspective of applications of these materials for hydrogen storage, the absorption at the plateau pressure is the relevant parameter, which should be considered. Hence, in the current work, the hydrogen absorption capacity at the plateau pressure is quoted. For cases in the literature, where the absorption at plateau pressure is not quoted, the value is deduced from their reported experimental curves.

## Experimental details

Mg–$LaNi_5$-Soot hybrids were synthesized by an accumulative roll bonding (ARB) process (as schematically illustrated in Fig. 1). Magnesium sheets (0.8 mm uniform thickness) were prepared from starting sheets of 5 mm thickness (cut from

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