


**AUTHOR QUERY FORM**

 ELSEVIER	<b>Journal:</b> HE  <b>Article Number:</b> 7355	<b>Please e-mail or fax your responses and any corrections to:</b>  <b>E-mail:</b> <a href="mailto:corrections.essd@elsevier.tnq.co.in">corrections.essd@elsevier.tnq.co.in</a>  <b>Fax:</b> +31 2048 52789
-----------------------------------------------------------------------------------------------	-------------------------------------------------------	-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult <http://www.elsevier.com/artworkinstructions>.

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof.

<b>Location in article</b>	<b>Query / Remark: Click on the Q link to find the query's location in text Please insert your reply or correction at the corresponding line in the proof</b>
<b>Q1</b>	Please verify page range in Ref.[5c]

Thank you for your assistance.

Available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

# An experimental investigation on the poor hydrogen sorption properties of nano-structured $\text{LaNi}_5$ prepared by ball-milling

B. Joseph<sup>a,b,\*</sup>, B. Schiavo<sup>b,c</sup>, G. D'Alì Staiti<sup>b,c</sup>, B.R. Sekhar<sup>d</sup>

<sup>a</sup>Dipartimento di Fisica, Università di Roma "La Sapienza", P. le Aldo Moro 2, 00185 Roma, Italy

<sup>b</sup>Istituto Tecnologie Avanzate, Base di ASI Luigi Broglio, Strada Statale 113, Trapani 9100, Italy

<sup>c</sup>Dipartimento di Fisica e Tecnologie Relative, Università di Palermo, Viale delle Sicenze, Palermo 90100, Italy

<sup>d</sup>Institute of Physics, Sachivalaya Marg, Bhubaneswar 751 005, India

## ARTICLE INFO

### Article history:

Received 23 March 2010

Received in revised form

17 December 2010

Accepted 18 January 2011

Available online xxx

### Keywords:

Hydrogen storage materials

Nanostructuring

Atomic disorder

## ABSTRACT

Nano-structured  $\text{LaNi}_5$  hydrogen storage materials prepared by ball-milling is analysed using differential scanning calorimetry (DSC) and x-ray photoelectron spectroscopy (XPS). DSC results indicate a partial elimination of defects at 500 °C in a more efficient way for the short-time ball-milled powders compared to the long-time ball-milled ones. XPS results show, almost no change in the core-level electronic structure for La and Ni of  $\text{LaNi}_5$  in the bulk and the nano-structured forms, but gives an indication that the self-restoring mechanism of the active surface observed in the bulk sample (Siegmann et al. Phys. Rev. Lett. 40, 972) may not be occurring in the nano-powders. Results from the X-ray diffraction and the local structural studies together with the above observations suggest that the reduced unit-cell volume and the enhanced atomic disorder in the nano-structured  $\text{LaNi}_5$  causes a larger energy barrier for the hydrogen sorption reactions of the long-time ball-milled samples.

© 2011 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

For hydrogen to be a viable substitute for the hydrocarbon based fuels there is a need to find out a suitable storage material for the solid state storage of hydrogen, for which a world wide research effort is going on for last several years [1]. Nano-structuring seems to offer some positive directions in this regard [2–6]. Ball-milling is the most widely used nano-structuring technique for the tailoring of hydrogen sorption properties of materials [3,4]. Ball-milling is very attractive due to its easy scale-up possibility from the laboratory to the industrial level [7]. Earlier studies on Mg [4], and a few recent studies on  $\text{MgH}_2$  and Mg together with other additives etc. [5,6], clearly show the advantages of ball-milling in particle size tuning for the hydrogen storage purpose. Such improvements in the properties, recently lead to the synthesis of pellets of  $\text{MgH}_2$ -

based composites as practical material for solid state hydrogen storage, showing encouraging cycling properties [8]. Due to its excellent room temperature hydrogen storage properties,  $\text{LaNi}_5$  continue to attract lot of interest, although the weight percentage of hydrogen stored in it is relatively low. In several earlier studies, partial substitution of La [9] or Ni [10,11] has been attempted for increasing the performance of this compound and is found to have positive results in many cases. Although there are several studies reported on this system, a systematic study on the ball-milling effect of the parent  $\text{LaNi}_5$  compound were reported only recently, where we found that the long-time ball-milling of the bulk  $\text{LaNi}_5$  results in the formation of an – anomalous-state resistant to hydrogen sorption reactions [12]. In this contribution we report the results of the differential scanning calorimetry (DSC) and X-ray photoelectron spectroscopy (XPS) measurements carried out

\* Corresponding author. Dipartimento di Fisica, Università di Roma "La Sapienza", P. le Aldo Moro 2, 00185 Roma, Italy.

E-mail address: [boby.joseph@gmail.com](mailto:boby.joseph@gmail.com) (B. Joseph).

0360-3199/\$ – see front matter © 2011 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

doi:10.1016/j.ijhydene.2011.01.090

on the nano-structured  $\text{LaNi}_5$  samples prepared by ball-milling in comparison to the bulk (un-milled) powders. These results together with the results from the X-ray diffraction and the local structural studies [13,14], indicate that the resistance to the hydrogenation of the nano-structured  $\text{LaNi}_5$  is mostly due to the slightly reduced unit-cell volume and large atomic disorder present in these systems compared to the bulk  $\text{LaNi}_5$ .

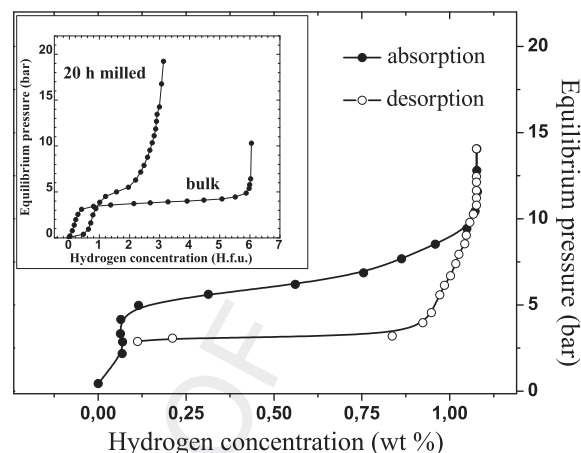
## 2. Experimental details

Hydrogen storage grade  $\text{LaNi}_5$  samples from Aldrich were used for the present study. Milling of these samples were carried out using an FRIETSCH planetary miller (Pulverisette 6), using a hardened steel vial and stainless steel balls, at a speed of 240 rotations-per-minute with a ball to powder ratio around 10. Milling was carried out in cycles of 20 min milling time and 20 min pause-time to avoid the heating of the sample during the milling process. Samples were prepared with milling times 2, 5, 10, 15, 20 and 100 h. For studying the annealing effects, part of the 20 h ball-milled samples were annealed under high vacuum ( $10^{-6}$  mbar) at  $500^\circ\text{C}$  for 30 min. Pressure composition isotherms (PCI) were measured using Sieverts'-method using an automated apparatus (PCTPro2000, Setaram). DSC measurements were carried out using a Mettler-Toledo DSC apparatus. All the DSC measurements were carried out in ambient atmosphere from 50 to  $500^\circ\text{C}$  with a heating rate of  $20^\circ\text{C}/\text{min}$ . All the sample handlings required for the ball-milling, PCI, and DSC, were carried out in an argon filled glove box (Mbraun) to prevent possible air contact. Samples handling for the other measurements were carried out in a glove bag in  $\text{N}_2$  atmosphere. XPS measurements were carried out on the bulk and the 100 h ball-milled sample using an UPS-XPS system (Omicron) using Mg  $K_{\alpha}$  photons. Samples were also analysed for the Fe impurities using the proton induced x-ray emission (PIXE) using 3 MeV protons from a 3 MV tandem Pelletron accelerator (9SDH, NEC USA). Samples for XPS and PIXE were prepared by pelletizing an equal mixture (weight) of  $\text{LaNi}_5$  and high purity graphite. Without the addition of graphite powder, the milled powders were not forming a stable pellet using a standard laboratory hydrostatic pellet maker. Before the XPS measurements, samples were degassed under ultra high vacuum ( $\sim 10^{-10}$  mbar) for more than 12 h.

## 3. Results and discussion

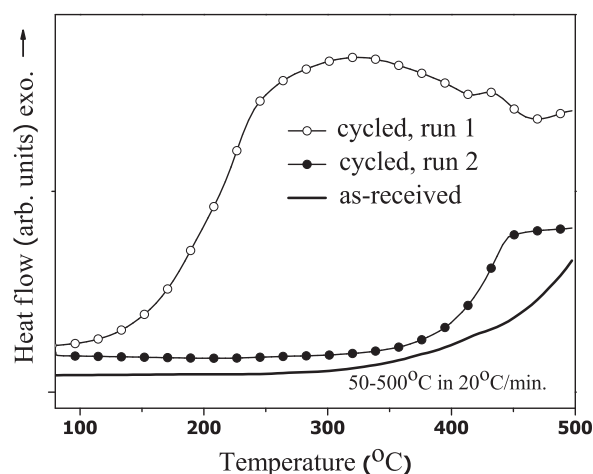
### 3.1. Hydrogen absorption studies

As mentioned in the introduction, unlike several other potential hydrogen storage materials [4–6], long-time ball-milling is found to have an adverse effect on the hydrogen sorption properties of  $\text{LaNi}_5$  [12]. Fig. 1 shows the rehydrogenation and dehydrogenation PCIs of the 20 h milled and  $500^\circ\text{C}$  30 min high vacuum annealed  $\text{LaNi}_5$  powders. Inset of this figure shows the rehydrogenation PCIs for the as-milled and the un-milled samples. In the as-milled state, the sample reveals a smaller plateau region compared to the un-milled, indicating a substantial reduction in the hydrogen absorption capacity. Also the plateau pressure is found to be higher,

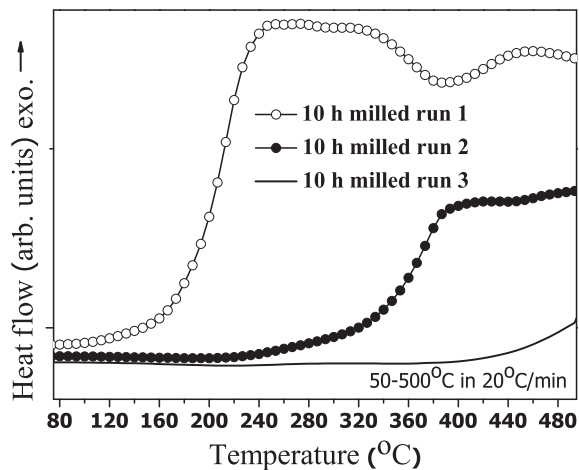


**Fig. 1** – PCIs for the 20 h milled and  $500^\circ\text{C}$  30 min annealed  $\text{LaNi}_5$  samples. Solid circles correspond to the rehydrogenation while open circles indicate the dehydrogenation. Inset shows the rehydrogenation curves for the bulk (un-milled) and 20 h milled  $\text{LaNi}_5$ .

indicating an increased energy barrier for the absorption reaction. This behaviour is opposite to that observed for the Mg compounds where ball-milling is found to enhance the hydrogen sorption kinetics [4–6]. Further increase in the milling time is found to decrease the absorption capacity to further lower values [12]. It is to be noted that the ball-milled samples showed almost all the diffraction peaks as the un-milled sample, but with reduced intensity and enhanced widths [13], indicating that the ball-milling has resulted only in particle size reduction and enhancement in disorder, rather than amorphisation. Annealing the 20 h milled sample at  $500^\circ\text{C}$  for 30 min is found to bring back the absorption capacity to almost the same value as that of the un-milled sample (Fig. 1). However, there is a significant increase in the plateau pressure. Unlike the bulk sample, the plateau region is found to be rather sloppy. Interestingly, for this sample, the



**Fig. 2** – DSC plots for as received (solid line) and cycled (open and filled circles)  $\text{LaNi}_5$  samples. Open circles represent the first run, while filled circles represent the second run (which was done after an isotherm at  $500^\circ\text{C}$  for 10 min).



**Fig. 3** – DSC plots for 10 h milled LaNi<sub>5</sub> sample for first (open circles), second (filled circles) and third (solid line) DSC runs.

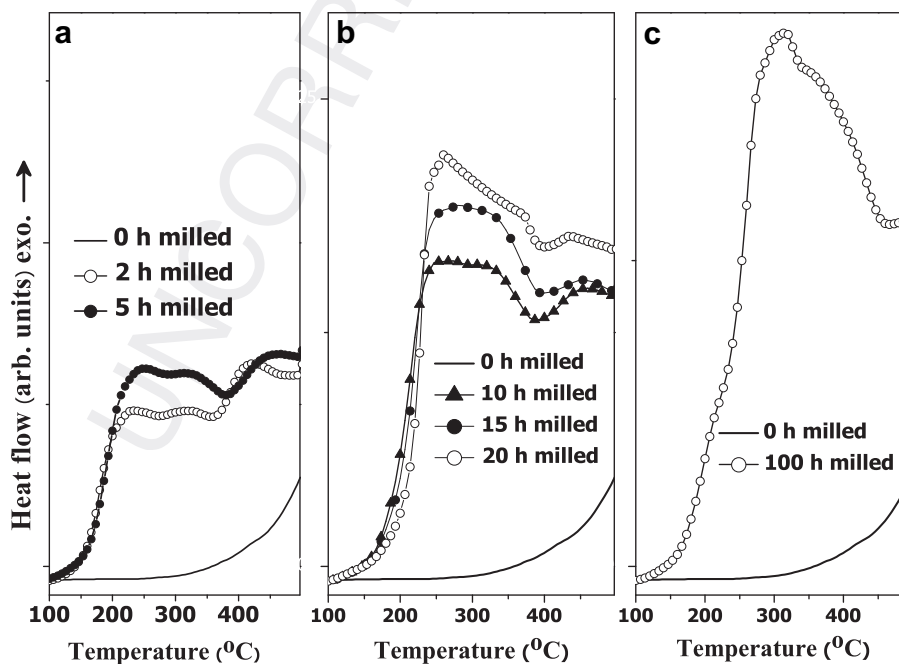
dehydrogenation plateau was found to be similar to the bulk counter-part. Similar results were also observed for the 20 and 100 h milled samples after the annealing treatment at 730 °C [12]. The fact that the absorption capacity is almost regained after annealing at 500 °C, prompted us to analyse the samples using DSC, results of which are presented below.

### 3.2. DSC studies

Upon several absorption–desorption cycles the bulk LaNi<sub>5</sub> is found to contain particles with a reduced grain size together with many defects and dislocations [15–17]. Thermal analysis by DSC is one of the effective methods to study the annealing

behaviour of lattice defects in LaNi<sub>5</sub>, because an excess energy of lattice defects can be detected directly as exothermic features in the heating run of DSC [18]. Fig. 2 shows the DSC curves of an as-received and a well activated LaNi<sub>5</sub> (a sample which has undergone several absorption–desorption cycles) samples. There is hardly any feature in the DSC plot of the as-received sample (solid line in Fig. 2). In contrast, for the activated LaNi<sub>5</sub> sample, the DSC curve shows an enhanced heat flow from 200 °C onwards (open circles in Fig. 2). DSC studies by Nakamura et al. [18] shows similar results as given in Fig. 2. However, they used a larger temperature window (up to 1200 K). In the present case, the maximum temperature for the DSC analysis was set to 500 °C due to the system limitations. Under this condition, in order to see the annealing effects more clearly, we have added an isotherm of 500 °C 10 min to the DSC measurements of the cycled sample, before performing second DSC run on the same sample. Results of the second DSC run on the cycled sample are also shown in Fig. 2 (filled circles). There is a clear difference between the first run and the second. The DSC plots of the second run on the cycled sample are more similar to that of the as-received sample, a result which is in agreement with the results reported by Nakamura et al. [18].

Fig. 3 shows the results of the first, second and third DSC runs on a 10 h milled sample. Like earlier, after each run, we have added an isotherm of 500 °C 10 min. The 10 h milled sample also showed an enhanced heat flow in the DSC curves. Second and third DSC runs on the 10 h milled samples show similar annealing behaviour as that of the cycled sample. These results clearly show that the ball-milling introduce defects in the LaNi<sub>5</sub>, in addition to the particle size reduction. Fig. 4 shows the results of the DSC measurements for different time ball-milled samples. For clarity, the results are presented



**Fig. 4** – DSC plots for ball-milled samples. Results are presented in three frames for clarity. Legends indicate the ball-milling time. Y-scale is identical for the three frames. In all the frames, the data corresponding to the as-received sample (0 h milled) is also included for comparison.

in three frames with identical y-scale. In each frame, the results of the as-received sample are also included for the comparison. In all samples one can observe the effect of defects similar to that of the cycled sample (see Fig. 2). In addition, the heat flow is found to increase with increasing the milling time indicating an increase in the defects density. Local structural studies using Ni K- and La L<sub>3</sub>- edge extended x-ray absorption fine structure (EXAFS) measurements [13,14] clearly showed enhancement of the atomic disorder with increasing ball-milling time, in line with the DSC results. The annealing effects as shown in the case of the 10 h milled sample were also observed for all the milled samples (data not shown). In particular, the second DSC runs of the short-time ball-milled samples were more similar to the bulk data, indicating a better defect-annealing in those cases. Results from the local structural studies using the Ni K- and the La L<sub>3</sub>-edge EXAFS [13,14] showed that the annealing is capable of restoring the atomic order in samples milled up to 20 h. However, these studies showed that the 100 h milled samples retain most of the disorder even after the high temperature annealing. Annealing in this case is found to result only in a random local order rather than a global atomic ordering. Although, the local structural studies using EXAFS show an enhancement in the atomic disorder [13,14], the type and the relative weights of disorder/defects cannot be extracted from those studies. Thus the possibility of the formation of non-stoichiometric compounds, such as La<sub>1-x</sub>Ni<sub>5-y</sub> upon long-time ball-milling cannot be ruled out.

### 3.3. XPS studies

Fig. 5(a) shows the Ni 2p<sub>3/2</sub> and the La 3d<sub>3/2</sub> core-levels for the bulk and the 100 h ball-milled LaNi<sub>5</sub>. There is hardly any difference between the core-level spectra of the bulk and the 100 h ball-milled LaNi<sub>5</sub> (labelled as nano). In Fig. 5(b), we show the core-level spectra corresponding to the Ni 2s. In this case, the 100 h milled sample shows an additional feature in the spectrum, mostly indicating the presence of the oxidized Ni. Earlier photoemission studies showed that the La segregates to the surface of the LaNi<sub>5</sub> in the presence of O<sub>2</sub> or H<sub>2</sub>O, and the Ni precipitations are formed during hydrogenation [19]. This represents a self-restoring mechanism of the active surface, since the highly reactive La removes the oxygen and keeps the Ni in a metallic state. Dissociative adsorption of H<sub>2</sub> may then occur at the Ni atoms present in the surface [19]. It seems such a mechanism is absent in the 100 h milled LaNi<sub>5</sub> samples, leaving Ni oxides on the surface and thus making the hydrogen absorption reactions unfavourable.

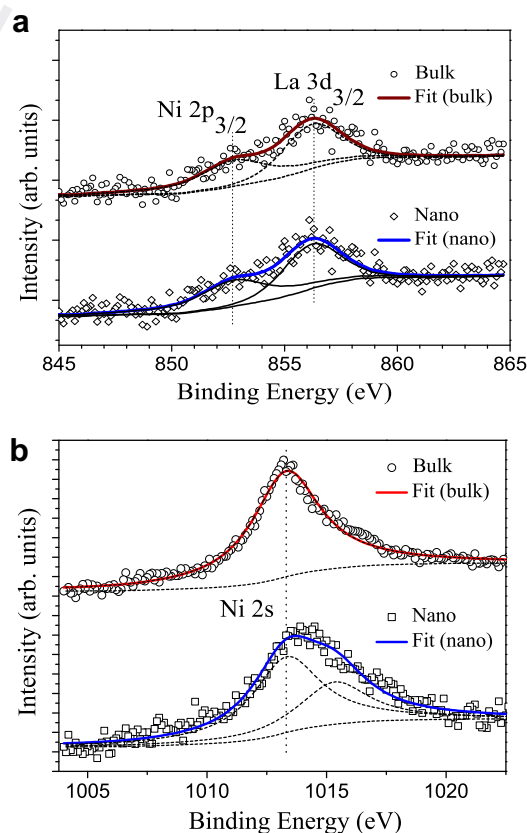
### 3.4. Impurity analysis

Impurity analysis of the milled samples are important due to the fact that the surface-impurities have more pronounced effects in nano-particles owing to the enhanced surface effects at nano-scale. Earlier studies on LaNi<sub>4.2</sub>Al<sub>0.8</sub> system prepared by mechanical-alloying [10] showed similar hydrogenation results as the present case, but the authors attribute it to the presence of the Fe impurities, which were detected using the Auger electron spectroscopy (AES). But as the AES technique is extremely surface sensitive, and as there is a high

probability for the Fe to diffuse to surface in presence of oxygen [20], the presence of Fe impurities in that case, cannot be taken as an indication that the surface of all the crystallites formed upon ball-milling contain Fe impurities. Proton induced X-ray emission (PIXE) using 3 MeV H<sup>+</sup> ions, is a powerful quantitative technique for the impurity analysis [21]. The information this technique provides is in the range of few microns and hence the results do not get influenced by the surface segregation effects. PIXE results from the milled samples indicated that no heavy element impurities like Fe are present above the ppm-levels (the detection limit of PIXE) in the 100 h milled samples. The most probable impurity candidate in the present case is iron (due to the possible erosion of the milling media), presence of which is checked by comparing the PIXE spectra of the milled samples with a standard sample containing 10 ppm Fe. These studies showed that if Fe is present in the milled sample, the contamination level is below 10 ppm.

## 4. Summary

Long-time ball-milling of the bulk LaNi<sub>5</sub> results in the formation of nano-particles which are resistant to hydrogen



**Fig. 5 – (color-online) XPS spectra showing (a) Ni 2p<sub>3/2</sub> and La 3d<sub>3/2</sub> and (b) Ni 2s of the bulk (open circles) and the 100 h ball-milled (open boxes) LaNi<sub>5</sub> samples together with peak deconvolution. A Shirley background is assumed for the deconvolution. The peak positions are shown with dotted lines.**

sorption reactions. DSC studies indicate a partial elimination of defects at 500 °C in a more efficient way for the short-time ball-milled powders compared to the long-time ball-milled ones. XPS results show no significant changes in the core-level electronic structure for the La and the Ni of LaNi<sub>5</sub> in the bulk and the nano-structured forms. However, the presence of an oxide-component in Ni, gives an indication that the self-restoring mechanism of the active surface observed in the bulk sample [19], may not be occurring in the nano-powders. X-ray diffraction together with local structural studies using Ni K-edge and La L<sub>3</sub> EXAFS showed that the long-time ball-milled samples have large atomic disorder [13,14]. Annealing is found to be effective in restoring the atomic order only for samples milled up to 20 h [13,14]. From the present studies, it may be concluded that the reduced unit-cell volume together with large atomic disorder is causing a higher energy barrier for the hydride phase formation in the nano-structured LaNi<sub>5</sub> samples prepared by ball-milling.

## Acknowledgements

One of the authors (BJ) wishes to thank Institute of Physics, Bhubaneswar for a three month visiting position November 2008. He also wishes to thank Prof. N.L. Saini for support and encouragement. Authors acknowledge the help of Dr. Dinesh and Eng. A.K. Behera in PIXE in measurements.

## REFERENCES

- [1] Crabtree GW, Dresselhaus MS, Buchanan MV. The hydrogen economy. *Physics Today* 2004;57:39–45, <http://dx.doi.org/10.1063/1.1878333>.
- [2] (a) van den Berg AWC, Areàn CO. Materials for hydrogen storage: current research trends and perspectives. *Chemical Communications*:668–81, <http://dx.doi.org/10.1039/b712576n>; 2008; (b) Vincent B, Gregg R, Mildred D, Gang C. Size effects on the hydrogen storage properties of nanostructured metal hydrides: a review. *International Journal of Energy Research* 2007;31:637–63, <http://dx.doi.org/10.1002/er.1284>.
- [3] Fichtner M. Nanotechnological aspects in materials for hydrogen storage. *Advanced Engineering Materials* 2005;7(6):443–55, <http://dx.doi.org/10.1002/adem.200590011>.
- [4] Zaluska A, Zaluski L, Strom-Olsen JO. Nanocrystalline magnesium for hydrogen storage. *Journal of Alloys and Compounds* 1999;288(1–2):217, [http://dx.doi.org/10.1016/S0925-8388\(99\)00073](http://dx.doi.org/10.1016/S0925-8388(99)00073).
- [5] (a) Dornheim M, Doppiu S, Barkhordarian G, Boesenberg U, Klassen T, Gutfleisch O, et al. Hydrogen storage in Mg-based hydrides and hydride composites. *Scripta Materialia* 2007;56:841–6, <http://dx.doi.org/10.1016/j.scriptamat.2007.01.003>; (b) Zhang S, Gross AF, Van Atta SL, Lopez M, Liu P, Ahn CC, et al. The synthesis and hydrogen storage properties of a MgH<sub>2</sub> incorporated carbon aerogel scaffold. *Nanotechnology* 2009;20:204027, <http://dx.doi.org/10.1088/0957-4484/20/20/204027>; (c) Peng B, Liang J, Tao Z, Chen J. Magnesium nanostructures for energy storage and conversion. *Journal of Materials Chemistry* 2009;19, <http://dx.doi.org/10.1039/B816478A>. 2877–2833.
- [6] (a) Dornheim M, Eigen N, Barkhordarian G, Klassen T, Bormann R. Tailoring hydrogen storage materials towards application. *Advanced Engineering Materials* 2006;8(5):377–85, <http://dx.doi.org/10.1002/adem.200600018>; (b) Lotosky MV, Denys RV, Yartys VA. Combustion-type hydrogenation of nanostructured Mg-based composites for hydrogen storage. *International Journal of Energy Research* 2009;113:1114, <http://dx.doi.org/10.1002/er.1604>.
- [7] Suryanarayana C. Mechanical alloying and milling. *Progress in Material Science* 2001;46:1–184, [http://dx.doi.org/10.1016/S0079-6425\(99\)00010-9](http://dx.doi.org/10.1016/S0079-6425(99)00010-9).
- [8] Khandelwal A, Agresti F, Capurso G, Lo Russo S, Maddalena A, Gialanella S, et al. Pellets of MgH<sub>2</sub>-based composites as practical material for solid state hydrogen storage. *International Journal of Hydrogen Energy* 2010;35(8):3565, <http://dx.doi.org/10.1016/j.ijhydene.2010.01.076>.
- [9] (a) Tan Z, Yang Y, Li Y, Shao H. The performances of La<sub>1-x</sub>Ce<sub>x</sub>Ni<sub>5</sub> (0=x=1) hydrogen storage alloys studied by powder microelectrode. *Journal of Alloys and Compounds* 2008;453(1–2):79–86, <http://dx.doi.org/10.1016/j.jallcom.2006.11.063>; (b) Adzic GD, Johnson JR, Reilly JJ, McBreen J, Mukerjee S. Cerium content and cycle life of multicomponent AB<sub>5</sub> hydride electrodes. *Journal of Electrochemical Society* 1995;142(10):3429–33, <http://dx.doi.org/10.1149/1.2049999>.
- [10] Smardz L, Smardz K, Jurczyk M, Jakubowicz J. Surface analysis of polycrystalline and nanocrystalline LaNi<sub>5</sub>-type alloys. *Journal of Alloys and Compounds* 2000;313(1–2):192–200, [http://dx.doi.org/10.1016/S0925-8388\(00\)01194-4](http://dx.doi.org/10.1016/S0925-8388(00)01194-4).
- [11] (a) Pandey SK, Srivastava A, Srivastava ON. Improvement in hydrogen storage capacity in LaNi<sub>5</sub> through substitution of Ni by Fe. *International Journal of Hydrogen Energy* 2007;32(13):2461–5, <http://dx.doi.org/10.1016/j.ijhydene.2006.12.003>; (b) Meli F, Zuttel A, Schlapbach L. Electrochemical and surface properties of iron-containing AB<sub>5</sub>-type alloys. *Journal of Alloys and Compounds* 1995;231(1–2):639–44, [http://dx.doi.org/10.1016/0925-8388\(95\)01744-5](http://dx.doi.org/10.1016/0925-8388(95)01744-5); (c) Lambert SW, Chandra D, Cathey WN, Lynch FE, Bowman Jr RC. Investigation of hydriding properties of LaNi<sub>4</sub>.8Sn<sub>0.2</sub>, LaNi<sub>4</sub>.27Sn<sub>0.24</sub> and La<sub>0.9</sub>Gd<sub>0.1</sub>Ni<sub>5</sub> after thermal cycling and aging. *Journal of Alloys and Compounds* 1992;187(1):113–35, [http://dx.doi.org/10.1016/0925-8388\(92\)90527-G](http://dx.doi.org/10.1016/0925-8388(92)90527-G).
- [12] Joseph B, Schiavo B. Effects of ball-milling on the hydrogen sorption properties of LaNi<sub>5</sub>. *Journal of Alloys and Compounds* 2009;480(2):912–6, <http://dx.doi.org/10.1016/j.jallcom.2009.02.062>.
- [13] Joseph B, Iadecola A, Schiavo B, Cognigni A, Olivi L, D'Ali Staiti G, et al. Local structure of ball-milled LaNi<sub>5</sub> hydrogen storage material by Ni K-edge EXAFS. *Journal of Solid State Chemistry* 2010;183(7):1550–4, <http://dx.doi.org/10.1016/j.jssc.2010.04.034>.
- [14] Joseph B, Iadecola A, Schiavo B, Cognigni A, Olivi L, D'Ali Staiti G, et al. Large atomic disorder in nanostructured LaNi<sub>5</sub> alloys: a La L<sub>3</sub> extended X-ray absorption fine structure study. *Journal of Physics and Chemistry of Solids* 2010;71(2010):1069–72, <http://dx.doi.org/10.1016/j.jpcs.2010.03.008>.
- [15] (a) Inui H, Yamamoto T, Hirota M, Yamaguchi M. Lattice defects introduced during hydrogen absorption-desorption cycles and their effects on PCT characteristics in some intermetallic compounds. *Journal of Alloys and Compounds* 2002;330–332:117–24, [http://dx.doi.org/10.1016/S0925-8388\(01\)01489-X](http://dx.doi.org/10.1016/S0925-8388(01)01489-X); (b) Yamamoto T, Inui H, Yamaguchi M. Effects of lattice defects on hydrogen absorption-desorption pressures in LaNi<sub>5</sub>. *Material Science and Engineering A* 2002;329:367–71, [http://dx.doi.org/10.1016/S0921-5093\(01\)01604-5](http://dx.doi.org/10.1016/S0921-5093(01)01604-5); (c) Kim G-H, Lee S-G, Lee K-Y, Chun C-H, Lee J-Y. Observation of the defects induced by hydrogen absorption and

- 651 desorption in LaNi<sub>5</sub>. *Acta Metallurgica et Materialia* 1995;43  
652 (6):2233–40, [http://dx.doi.org/10.1016/0956-7151\(94\)00441-2](http://dx.doi.org/10.1016/0956-7151(94)00441-2).
- 653 [16] Nakamura Y, Akiba E. In-situ X-ray diffraction study on LaNi<sub>5</sub>  
654 and LaNi<sub>4.75</sub>Al<sub>0.25</sub> in the initial activation process. *Journal*  
655 *of Alloys and Compounds* 2000;308(1–2):309–18.
- 656 [17] Nakamura Y, Oguro K, Uehara I, Akiba E. X-ray diffraction  
657 peak broadening and degradation in LaNi<sub>5</sub>-based alloys.  
658 *International Journal of Hydrogen Energy* 2000;25(6):531–7,  
659 [http://dx.doi.org/10.1016/S0360-3199\(99\)00066-X](http://dx.doi.org/10.1016/S0360-3199(99)00066-X).
- 660 [18] Nakamura R, Asano K, Yoshimi K, Iijima Y. Thermal analysis of  
661 lattice defects in LaNi<sub>5</sub>. *Journal of Alloys and Compounds* 2006;  
662 413(1–2):211–3, <http://dx.doi.org/10.1016/j.jallcom.2005.03.112>.
- 663 [19] Siegmann HC, Schlapbach L, Brundle CR. Self-restoring of  
664 the active surface in the hydrogen sponge LaNi<sub>5</sub>. *Physical*  
*Review Letters* 1978;40:972, <http://dx.doi.org/10.1103/PhysRevLett.40.972>.
- 665 [20] (a) Burton JJ, Polizzotti RS. Surface segregation in alloys,  
666 dilute solutions of Cr, Fe and Ni in Pt. *Surface Science* 1977;66  
667 (1):1–13, [http://dx.doi.org/10.1016/0039-6028\(77\)90395-8](http://dx.doi.org/10.1016/0039-6028(77)90395-8);  
668 (b) Bera S, Bhattacharjee K, Kuri G, Dev BN. Probing atomic  
669 migration in nanostructured multilayers, application of  
670 X-ray standing wave fileds. *Physical Review Letters* 2007;98  
671 (19):196103, <http://dx.doi.org/10.1103/PhysRevLett.98.196103>.
- 672 [21] Mathew S, Satpati B, Joseph B, Dev BN, Nirmala R, Malik SK,  
673 et al. Magnetism in C<sub>60</sub> films induced by proton irradiation.  
674 *Physical Review B* 2007;75:075426, <http://dx.doi.org/10.1103/PhysRevB.75.075426>.
- 675  
676  
677  
678

UNCORRECTED PROOF