Journal of Alloys and Compounds 480 (2009) 912–916

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of ball-milling on the hydrogen sorption properties of $LaNi_5$

B. Joseph*, B. Schiavo

Istituto Tecnologie Avanzate, C/o Base di ASI “Luigi Broglio”, SS 113, Trapani 91100, Italy

ARTICLE INFO

Article history:
Received 14 November 2008
Received in revised form 17 February 2009
Accepted 18 February 2009
Available online 4 March 2009

Keywords:
Hydrogen absorbing materials
Intermetallics
Mechanical alloying

ABSTRACT

Pressure–composition isotherms of $LaNi_5$ alloys were studied as function of ball-milling time. Results indicate that ball-milling convert a part of the $LaNi_5$ to a non-absorbing state—a state which does not absorb hydrogen under conditions where un-milled $LaNi_5$ powders absorb and transform to $LaNi_5H_6$, in addition to particle size reduction and creation of defects. The non-absorbing fraction in the milled sample is found to grow with increase in the ball-milling time. The resistance to the hydride formation of the long-time ball-milled $LaNi_5$ samples is found to continue even after a 1-h high vacuum annealing at around 1000 K. This indicates that the hydrogen-absorption-resist-anomalous state formed during the long-time ball-milling is rather stable.

1. Introduction

Storage of large quantities of hydrogen at safe pressures is a key requirement in establishing a hydrogen-based economy [1]. The most feasible hydrogen storage technique seems to be the solid state storage of hydrogen [2]. In this regard, the inter-metallic compound $LaNi_5$ is one of the most widely studied material. The hydrogen storage properties of $LaNi_5$ were recognised a few decades ago [3]. Compared to some other possible hydrogen storage materials, the gravimetric capacity of this material is relatively low (~1.4 wt%). However, this compound continues to attract much interest due to its excellent room temperature hydrogen storage capabilities. $LaNi_5$-based compounds are also finding increasing applications in storage batteries replacing nickel–cadmium based ones [4,5]. In some of the earlier studies, partial substitution of La or Ni has been attempted to increase the performance of this compound. For example, ‘*A*’ site substitution by Ce [6] or ‘*B*’ site substitution by Al, Fe, Sn, Co, Mn, or a combination of few of these elements [4,5,7–14], were found to have positive results in many cases. Although there are several studies reported on this system, a systematic study on the ball-milling effects of the parent compound, $LaNi_5$, seems to be absent. Zaluka et al. had reported improved hydrogen absorption kinetics for “nanocrystalline” $LaNi_5$ particles with Pd catalyst [15]. In yet another study, Aoyagi et al. carried out ball-milling of $LaNi_5$ particles up to 1 min and found that such a ball-milling can improve the hydrogen sorption kinetics [16]. However, in these studies, there were no attempts to measure the pressure–composition isotherms (PCIs) of the ball-milled samples. A later study on mechanical grinding of $LaNi_5$ powders for 2 h, using a planetary mill at 250 rotations per minute (RPM), showed the average size of the milled particles to be around 1.2 μm [17]. The above study also showed that the absorption properties of the milled samples were almost similar to that of the un-milled samples. However, the first hydrogenation cycle of the milled powders showed a strong slope which was ascribed to the presence of several hydride phases in the milled sample [17]. In a later study, mechanical alloying of La and Ni was used to form $LaNi_5$ nanoparticles, where the as-alloyed particles were found to be amorphous with very little hydrogen absorption [18]. However, annealing is found to result in grain growth, release of microstrain, and increase in storage capacity. Similar results were also found for a 5 h ball-milled $LaNi_5$ sample [18]. In an earlier study, Anani et al. showed that mechanically milled and annealed $LaNi_5$ samples have similar hydrogen absorption behaviour as that of the samples prepared by arc-melting [4]. In a recent study, Jurczyk et al. reported the preparation of nanocrystalline $LaNi_5$ using mechanical alloying of La and Ni in appropriate ratio [7]. Their results show that by mechanical alloying one can produce nanoparticles of $LaNi_5$, but in amorphous form with little hydrogen absorption properties. An annealing at 700 °C for 30 min lead to recrystallization of the amorphous nanoparticles and the annealed powders show hydrogen absorption similar to the bulk $LaNi_5$. However, none of the above studies addressed the effect of long-time ball-milling on the hydrogen sorption properties of $LaNi_5$. It is known from some of the above studies that ball-milling up to 2 h is not capable of producing nanocrystalline $LaNi_5$ particles [17]. Ball-milling studies on Mg show that long-time ball-milling has a pronounced effect on the hydrogen sorption properties [19,20]. This report presents a systematic study about the hydrogen sorption properties of long-time ball-milled $LaNi_5$ powders, with and without high temperature annealing. Our results indicate that similar to mechanical alloying,

---

* Corresponding author. Tel.: +39 0923550115; fax: +39 0923538493.
E-mail addresses: boby.joseph@gmail.com, boby@iopb.res.in (B. Joseph).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.02.062

ball-milling of the bulk $LaNi_5$ has an adverse effect on the hydrogen sorption properties. However, unlike mechanically alloyed samples, in which amorphisation is the reason for the reduced hydrogen sorption properties, ball-milling seems to result in the formation of an anomalous state which is not absorbing hydrogen under usual plateau pressures.

2. Experimental details

Hydrogen storage grade $LaNi_5$ samples from Sigma–Aldrich were used for the present study. Milling of these samples were carried out using a *FRITSCH* miller, with a stainless steel vial and stainless steel balls, at 240 RPM with a ball-to-powder ratio around 10. Ball-milling was carried out in cycles of 20 min mill-time and 20 min pause-time to avoid over-heating of the sample during the milling process. Samples were prepared with milling times 2, 20 and 100 h. PCIs of the as-received and the ball-milled samples were measured using Sievert's method [21] using an automated PCT apparatus from HyEnergy. All the sample handlings were carried out in an argon filled glove box (MBRAUN) to prevent possible contact with air. After the completion of few PCI measurements on all the ball-milled and the as-received samples, all these samples were annealed at 730 °C for 1 h under high vacuum ($\sim 5 \times 10^{-6}$ mbar). Following annealing, the PCI measurements were again carried out on all the annealed samples.

3. Results and discussions

Fig. 1 shows the PCI absorption curves (rehydrogenation) at 35 °C for an as-received and ball-milled (2, 20 and 100 h) $LaNi_5$ samples. PCIs of the ball-milled samples are quite different compared to the PCI of the as-received sample. Maximum hydrogen storage capacity of $LaNi_5$ seems to be gradually decreasing with increasing ball-milling time. There is also a noticeable increase in the plateau pressure for the 2 h and the 20 h milled samples. For the 100 h milled sample, there is almost no plateau region in the PCI curve [Fig. 1(d)]. Some earlier studies on $LaNi_5$, where the samples are prepared by ball-milling of the elemental components in the appropriate ratio [4,7], show a similar pressure–composition data as that of the present 100 h ball-milled sample. The X-ray diffraction (XRD) studies of Jurczyk et al. show that such a pressure–composition behaviour is due to amorphised $LaNi_5$ particles [7]. During the ball-milling process, the powder particles which are trapped between the colliding balls are subjected to compressive impact forces. The powder particles are deformed, fractured and cold-welded, leading to defects in the system and also an average particle size reduction [22]. Following the studies on mechanical alloying of $LaNi_5$ [4,7], one would be tempted to attribute the observed reduction in the storage capacity to the formation of an amorphous phase in the ball-milled samples. As the amorphous phase will not contribute to the hydride phase formation, there will be a decrease in the hydrogen storage capacity with increase in the amorphisation. It is interesting to note that the ball-milling process result in average particle size reduction and creation of defects, both contribute to the faster hydrogen absorption kinetics. Mg is a classical example showing this effect [19,20]. Ball-milling is a non-equilibrium process, and there are chances for the creation of anomalous phases during such non-equilibrium processes, which are otherwise difficult to form [22]. The reduction in the storage capacity observed in the ball-milled sample can be either due to the creation of such an anomalous state, which is not absorbing hydrogen at usual plateau pressure of $LaNi_5$ at room temperature, or, as mentioned, can be due to the formation of an amorphous phase. In the present case, it looks like the former is the cause; some justification for such an argument is given in the next paragraph.

Although, the results shown in Fig. 1 show that the hydrogen storage capacity decrease with increase in ball-milling time, an independent kinetic measurements with a high starting pressure (around 100 bar) showed that the 100 h milled sample absorbs hydrogen up to the expected maximum capacity. Fig. 2 shows the absorption kinetics of the 100 h milled sample and an as-received sample at 35 °C under an applied pressure of 100 bar. The 100 h milled sample shows quite slow absorption kinetics as compared to the as-received sample. Under identical conditions with an applied pressure of 20 bar, the 100 h milled sample hardly absorbs any hydrogen. This is also evident from the PCI curve shown in Fig. 1(d). These results support the idea that the ball-milling of $LaNi_5$ lead to the formation of some anomalous state which is resistant to the hydrogen absorption rather than the formation of an amorphous phase. If ball-milling might have lead to the formation of an amorphous phase, there is no chance that such an amorphous phase absorbs hydrogen to the expected maximum capacity of the crystalline $LaNi_5$. In absence of this anomalous state formation, as in the present case, one would have expected the ball-milled $LaNi_5$ powder to be a better hydrogen storage media with faster kinetics. However, possibly due to the formation of an anomalous state which is very resistant to hydrogen absorption at low pressures, the ball-milled $LaNi_5$ powders show rather poor hydrogen storage properties compared to the un-milled samples.

It is interesting to note that some of the earlier studies [15,16] showed an improvement in the kinetics of the ball-milled $LaNi_5$ samples, where the milling times were significantly lower than the present case. As shown in one such similar study [17], such short time ball-milling only leads to particle size reduction up to few microns. Scanning electron microscopy studies on the cycled samples show that after a couple of absorption–desorption cycles, average particle size of $LaNi_5$ get reduced and become of the order of few microns [23]. Thus ball-milling for times less than 1 h, essentially leads to somewhat similar effects as that of the hydrogen absorption–desorption cycling. Thus short-time ball-milling can lead to an improvement in the kinetics of $LaNi_5$ samples compared to un-activated powders. The slow kinetics of the un-activated powders is obvious from the higher plateau pressures observed in the first cycle [23].

A careful look at the data presented in Fig. 1 reveals that, for the milled samples there is a significant absorption at very low pressures (initial part of the PCIs), whereas for the un-milled sample [Fig. 1(a)], there is almost no absorption until the applied pressure reaches a value close to the plateau pressure. As mentioned earlier, milling causes defects and particles size reduction. The enhanced absorption observed for the milled samples at very low pressures is mostly due to the hydrogen adsorption at the defect-states in the surface. If one considers only the low pressure hydrogen sorption process, clearly the ball-milled samples have a faster kinetics. Annealing can lead to the removal of such surface defect-states, and hence the enhanced absorption observed at low pressures for the milled samples are not expected for the ball-milled-and-annealed samples. Indeed this is found to be true for the annealed samples (shown later).

As mentioned in the experimental section, all the ball-milled samples were further studied by annealing these samples under high vacuum at 730 °C for 1 h. The PCI curves of the ball-milled-and-annealed samples at 35 °C corresponding to the rehydrogenation (after activation, second PCI run) are shown in Fig. 3(a–c). For comparison, the rehydrogenation data corresponding to the as-received sample is also included in the figures. This comparison shows that there is a clear increase in the plateau pressures of the ball-milled-and-annealed samples. The plateau pressure is found to increase with increase in the milling time. A comparison of Figs. 1 and 3 clearly shows the difference in the low-pressure–absorption behaviour of the as-milled and the milled-and-annealed samples

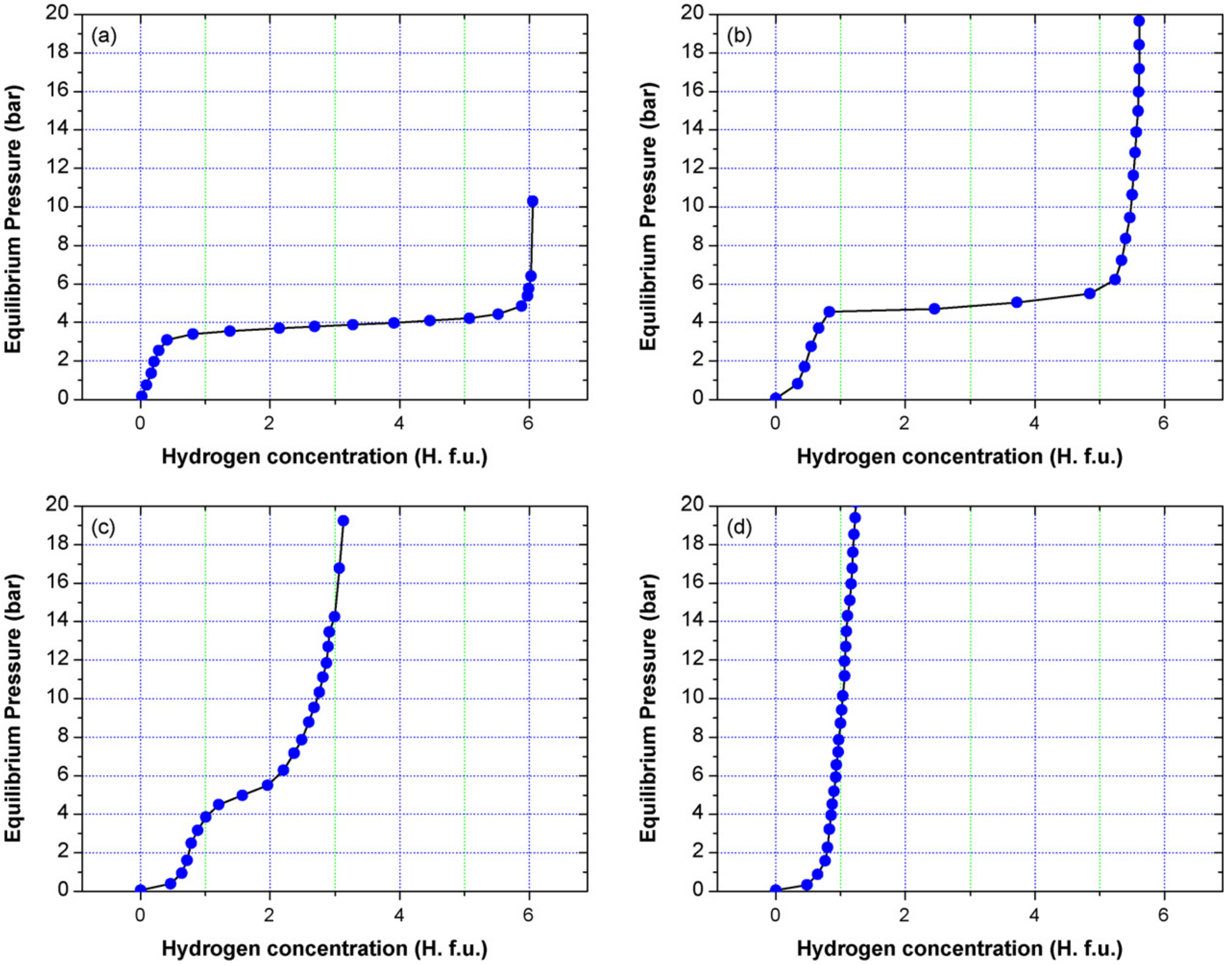

Fig. 1. Rehydrogenation PCIs at 35 °C for (a) as-received, (b) 2 h milled, (c) 20 h milled and (d) 100 h milled $LaNi_5$ samples.

(initial parts of the PCIs). As mentioned earlier, for the annealed samples there is almost no absorption at very low pressures. This is due to the absence of the surface defects which were causing adsorption in case of the milled samples. The maximum absorption capacity of the ball-milled samples after annealing is almost identical with that of the as-received sample; however there is a difference in the plateau pressure. This change is maximum for the 100 h milled-and-annealed sample.

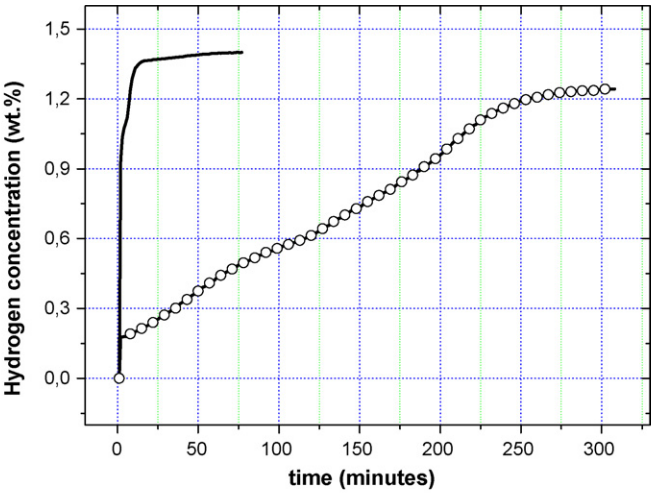

Fig. 2. Absorption kinetics at 35 °C for a 100 h ball-milled $LaNi_5$ sample under 100 bar H_2 pressure (open circles). Absorption kinetics corresponding to an activated $LaNi_5$ sample under identical conditions (solid line) is also included in the figure for comparison.

The PCI curves of the ball-milled-and-annealed samples at 35 °C corresponding to the dehydrogenation are shown in Fig. 4. As expected the dehydrogenation PCI of the as-received sample after annealing have exactly the same behaviour as that of the sample before annealing [Fig. 4(a)]. Interestingly, there is also a good overlap between the dehydrogenation PCI of the 20 h milled-and-annealed sample with that of the as-received sample [Fig. 4(b)]. However, in case of the 100 h milled-and-annealed sample, there is a significant increase in the dehydrogenation plateau as compared to the as-received sample. It is interesting to recall that in the as-milled case, the 100 h milled sample did not show any plateau in the rehydrogenation process (below 20 bar).

Although ball-milling is very effective for the nano-structuring of the powdered samples, there are chances of incorporation of very small amounts of impurities, coming due to the erosion of the milling media. Such an effect is seen in an earlier study involving the ball-milled $LaNi_{4.8}Al_{0.2}$ samples [12], where Auger electron spectroscopy is used to study the effect the surface contamination due to the ball-milling process. Following the above work, in the present case also one may expect a slight contamination in the ball-milled samples, the amount of impurities increasing with increase in milling time. Thus the highest time milled sample is suppose to have the largest contamination. Following such an argument, the observed deviation of the dehydrogenation plateau pressure for the 100 h milled-and-annealed sample compared to the dehydrogena-

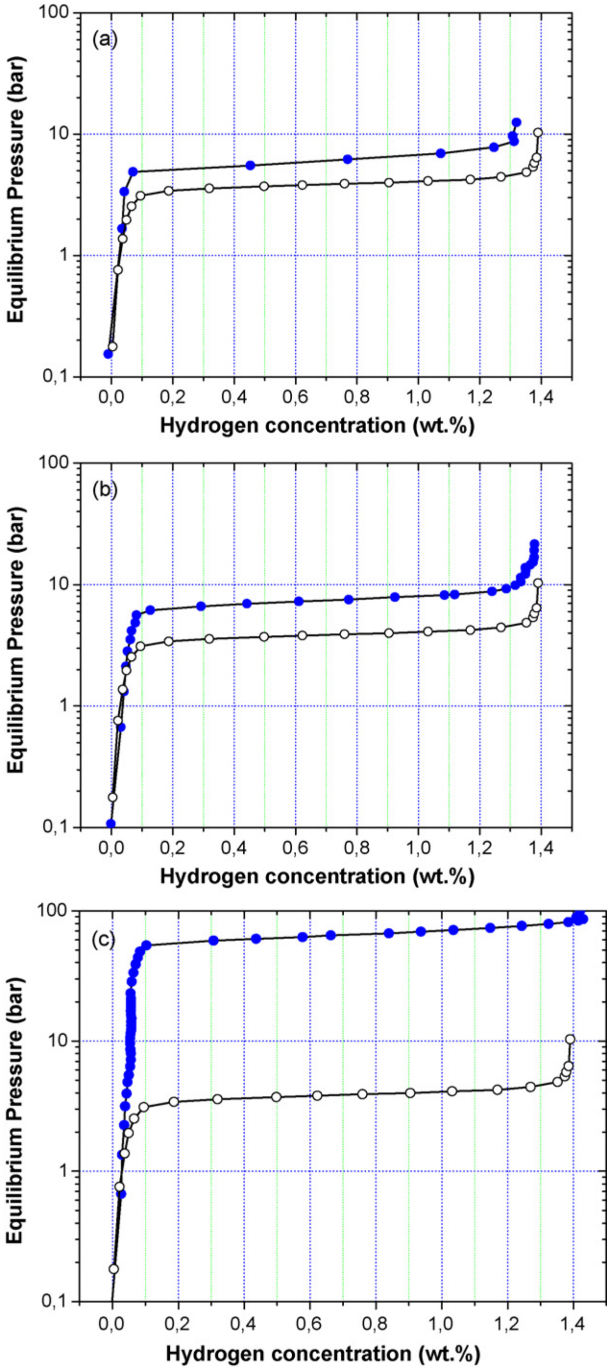

Fig. 3. Rehydrogenation PCIs at 35 °C for milled-and-annealed $LaNi_5$ samples (solid circles): (a) 2 h, (b) 20 h and (c) 100 h. In all the cases, rehydrogenation curves corresponding to the as-received sample (open circles) is also included for comparison.

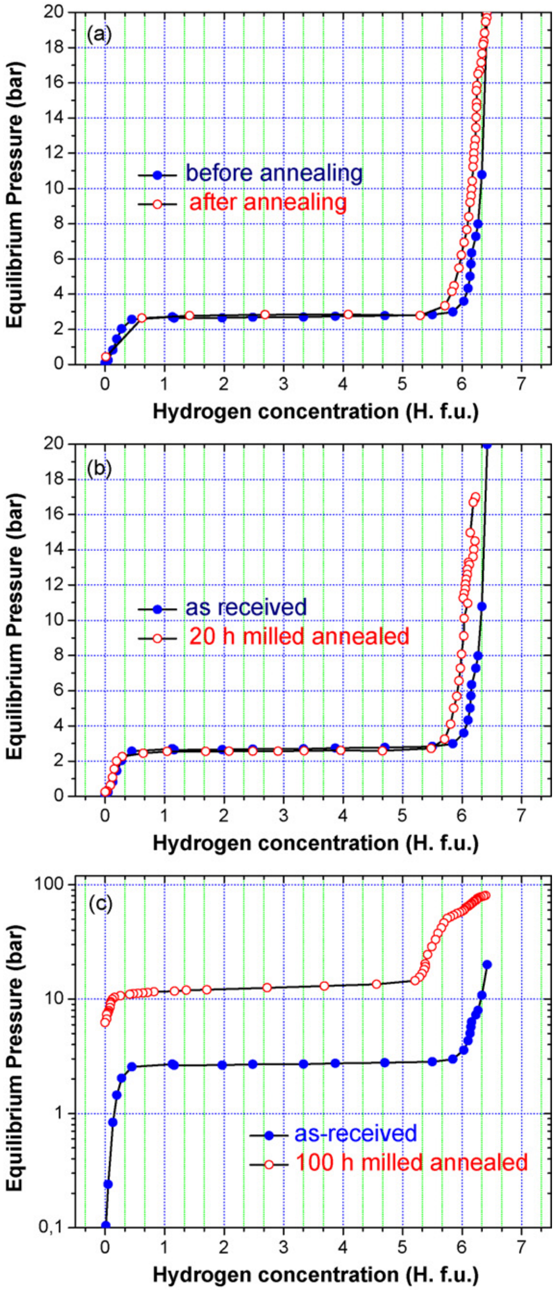

Fig. 4. Dehydrogenation PCIs at 35 °C for the annealed $LaNi_5$ samples (open circles): (a) as-received, (b) 20 h milled and (c) 100 h milled. In all the cases, dehydrogenation curves corresponding to the as-received sample (solid circles) are also included for comparison.

tion plateau pressure of the un-milled $LaNi_5$, can be attributed to the effect of impurities incorporated during the ball-milling. The effect of such impurities will be more prominent when the particle sizes are the smallest, especially in the nanometer regime. However, we do not expect a significant amount of contamination in our samples. Earlier studies on Fe doping of the $LaNi_5$ is found to result only in a decrease of the plateau pressure [8]. Similar is the case with doping Si, Ge, Sn [10], Co [11], Al or Mn [14]. Erosion of the ball-milling media in the present case can at best lead to the addition of some Fe to the $LaNi_5$ powders. If that is the case, one expects a reduction in the plateau pressure for 100 h milled-and-annealed sample. However, for the 100 h milled-and-annealed samples, an enhancement in the plateau pressure is seen to occur. This clearly indicates that the Fe contamination induced effects may not be prominent in the present ball-milled samples. Thus it is most probable that the long-time ball-milling induces the creation of some anomalous state in $LaNi_5$ which is quite resistant to the hydrogen absorption. However, it is important to mention that the present measurements are not capable of directly probing any microscopic changes between the bulk and the long-time-ball-milled samples. Analysis of the long-time-ball-milled samples for the structure, surface states, etc., are quite important in this regard.

4. Conclusions

A systematic hydrogen sorption study of ball-milled $LaNi_5$ hydrogen storage alloys indicate that the long-time ball-milling cause the formation of some anomalous state, which is very resistant against hydrogen absorption, in addition to creation of lattice defects and particle size reduction. This anomalous state is found to cause a reduction in the hydrogen storage capacity of the $LaNi_5$ alloy at pressures under which the un-milled $LaNi_5$ completely transforms to $LaNi_5H_6$. The dehydrogenation plateau pressure of the 100 h milled-and-annealed sample is found to be significantly higher compared to the un-milled samples. This indicates that the anomalous state formed in the long-time ball-milled samples are rather stable. Microscopic characterization of the nanostructures produced in the long-time-ball-milled samples is very important to understand the observed results.

Acknowledgements

Financial support from project *POR-MISURA 3.15-Azione C-Nanomaterials for the energy and ecological sector* is kindly acknowledged. Authors thank Prof. D'Alì for useful suggestions and encouragement. Thanks are also to Ing. Di Via, Lucia and Alfonso for their helps during the experiments.

References

[1] G.W. Crabtree, M.S. Dresselhaus, M.V. Buchanan, Phys. Today 157 (2004) 39–45.
[2] L. Schlapbach, A. Zuttel, Nature 414 (2001) 353.
[3] J.H.N. van Vucht, F.A. Kuijipers, H.C.A.M. Bruning, Philips Res. Rep. 25 (1970) 133.
[4] A. Anani, A. Visintin, K. Petrov, S. Srinivasan, J.J. Reily, J.R. Johnson, R.B. Schwarz, P.B. Desch, J. Power Sources 47 (1994) 261.
[5] M. Jurczyk, L. Smardz, K. Smardz, M. Nowak, J. Solid State Chem. 171 (2003) 30–37.
[6] Zuxian Tan, Yifu Yang, Yan Li, Huixia Shao, J. Alloys Compd. 453 (2008) 79–86;
G.D. Adzic, J.R. Lohnson, J.J. Reilly, J. McBreen, S. Mukerjee, J. Electrochem. Soc. 142 (1995) 3429;
X.X. Yuan, H.S. Liu, Z.F. Ma, N.X. Xu, J. Alloys Compd. 359 (2003) 300.
[7] M. Jurczyk, M. Nowak, E. Jankowska, J. Jakubowicz, J. Alloys Compd. 339 (2002) 339–343.
[8] F. Meli, A. Zuttel, L. Schlapbach, J. Alloys Compd. 231 (1995) 639–644.
[9] S.K. Pandey, A. Srivastava, O.N. Srivastava, Int. J. Hydrogen Energy 32 (2007) 2461.
[10] S. Luo, Ted B. Flanagan, R.C. Bowmann Jr., J. Alloys Compd. 330–332 (2002) 531–5353;
B. Fultz, C.K. Witham, T.J. Udovic, J. Alloys Compd. 335 (2002) 165–175.
[11] Kohta Asano, Yoshiaki Iijima, Masuo Okada, J. Alloys Compd. 389 (2005) 215–219.
[12] L. Smardz, K. Smardz, M. Jurczyk, J. Jakubowicz, J. Alloys Compd. 313 (2000) 192–200.
[13] J. Liu, Y. Yang, H. Shao, J. Alloys Compd. 429 (2007) 285–291.
[14] J.M. Joubert, M. Latroche, R. Cerny, A. Percheron-Guégan, K. Yvon, J. Alloys Compd. 330–332 (2002) 208–214;
M. Latroche, A. Percheron-Guégan, Y. Chabre, J. Bouet, J. Pannetier, E. Ressouche, J. Alloys Compd. 231 (1995) 537–545;
Y. Nakamura, K. Oguro, I. Uehara, E. Akiba, Int. J. Hydrogen Energy 25 (2000) 531–537.
[15] A. Zaluska, L. Zaluski, P. Tessier, J.O. Strom-Olsen, R. Schulz, J. Alloys Compd. 217 (1995) 295–300.
[16] H. Aoyagi, K. Aoki, T. Masumoto, J. Alloys Compd. 231 (1995) 804–809.
[17] S. Corré, M. Bououdina, N. Kuriyama, D. Fruchart, G. Adachi, J. Alloys Compd. 292 (1999) 166–173.
[18] G. Lang, J. Huot, R. Schulz, J. Alloys Compd. 320 (2001) 133–139.
[19] A. Zaluska, L. Zaluski, J.O. Strom-Olsen, J. Alloys Compd. 288 (1999) 217–225.
[20] M. Dornheim, S. Doppiu, G. Barkhordarian, U. Boesenberg, T. Klassen, O. Gutfleisch, R. Bormann, Scripta Mater. 56 (2007) 841–846.
[21] Sieverts, Zeitschrift für Metalkunde 21 (1929) 37–49.
[22] J.S. Benjamin, Sci. Am. 234 (1976) 108–116;
C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1–184.
[23] H. Inui, T. Yamamoto, M. Hirota, M. Yamaguchi, J. Alloys Compd. 330–332 (2002) 117–124.