Journal of Alloys and Compounds 495 (2010) 541–544

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Study of annealing effects on structural and sorption properties of low energy mechanically alloyed AB_5's

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ARTICLE INFO

Article history:
Received 10 July 2008
Received in revised form 27 October 2009
Accepted 28 October 2009
Available online 5 November 2009

Keywords:
Hydrogen storage materials
Intermetallics
Mechanical alloying
X-ray diffraction

ABSTRACT

In this work, various AB_5's were mechanically alloyed using a low energy mill until *final* or *completion* milling stages were reached. This process leaves micro- and nano-structured materials with highly distorted microstructures. Then, further annealing is needed to obtain an intermetallic suitable for hydrogen thermal compression process. After milling, the samples were annealed and analyzed by X-ray diffraction and Differential Scanning Calorimetry. Hydriding properties were studied using volumetric methods. After annealing at 200 °C for 24 h no changes occur in neither structural nor hydriding properties. For samples annealed at 400 °C, relaxation effects of the structure were observed. It occurs due to the release of strain produced by annealing on the microstructure. It leads to the improvements in both structural and hydriding properties. Strong recrystallization effect was present between 400 and 600 °C. At 600 °C, the main improvements were larger crystallite size, lower strain values and pressure-composition isotherms with well-defined plateaus. Despite this behavior, no evidence of crystallization was observed by Differential Scanning Calorimetry measurements from room temperature up to 500 °C. These topics, the amount of energy supplied during mechanical alloying and the correlation between the structural and sorption properties are discussed according to the governing mechanisms of recrystallization observed in each temperature range. From these results, an improved synthesis-thermal treatment method is outlined.

1. Introduction

AB_5-based intermetallics are successfully synthesized by mechanical alloying [1,2]. Depending on the amount of energy impinged during the process, high, intermediate and low energy mills are used [1–3]. The differences in the starting aggregation state of powders, controlling regimes and condition of mills lead to different final microstructures. Despite the conditions used during the synthesis method, a further annealing treatment is needed to obtain an intermetallic suitable for hydrogen-based applications [1]. Short time periods and low temperature are preferred for annealing. These parameters should assure that the sample exhibits appropriate sorption properties, i.e. flat plateaus, low hysteresis and hydrogen sorption capacities close to the theoretical ones [4]. Equilibrium pressure between a compound and its hydride is affected by the material microstructure such as the presence of residual strain or inhomogeneities. Intermetallics obtained by this combined mechanical alloying/low temperature heating could probably show higher equilibrium pressures than those obtained by full equilibrium methods. Provided the equilibrium pressure values showed by the sample are repeatable during cycling, this material would be adequate for hydrogen thermal compression devices [5].

In this work, as-milled AB_5-based intermetallics were annealed at different conditions to find out the influence of both time and temperature of annealing. Microstructural properties measured by X-ray diffraction, and Differential Scanning Calorimetry are correlated with hydrogen sorption properties analyzed by volumetric methods.

The aim of this paper is the application of these results in a research program focused on the evaluation of materials used in multistage hydrogen compression systems.

2. Experimental

$LaNi_5$ and $La_{0.67}Ce_{0.19}Nd_{0.08}Pr_{0.06}Ni_5$ were synthesized by low energy mechanical alloying (MA). A Uni-Ball-Mill II apparatus (Australian Scientific Instruments) was used [6]. Experimental set-up and sample handling were described elsewhere [3]. Room temperature X-ray diffractograms (XRD) were obtained by means of a Philips PW 1710/01 Instrument. Diffraction patterns were analyzed by the Rietveld

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doi:10.1016/j.jallcom.2009.10.248

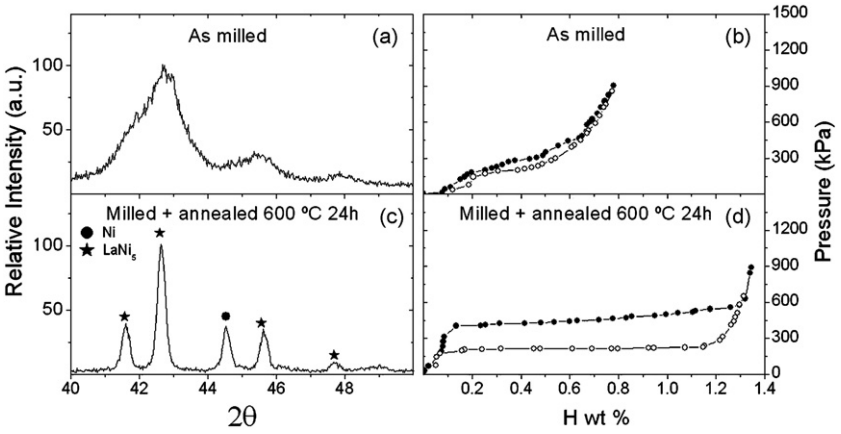

Fig. 1. (a and c) Diffraction patterns of $LaNi_5$ as-milled and milled + annealed. (b and d) PCI at 25 °C of as-milled and milled + annealed $LaNi_5$. Full and hollow symbols correspond to absorption and desorption, respectively.

method [7] using DBWS software [8]. Strain and crystallite size effects were estimated from diffraction peaks by assuming empirically a Gauss distribution and a Cauchy (Lorentz) component, respectively. Neutron Activation Analysis (NAA) and Energy Dispersive Spectroscopy (EDS) were used to verify the chemical composition [6]. Differential Scanning Calorimetry (DSC) measurements were done using a DSC 2910 TA Instruments calorimeter. Heating rates varied from 5 to 25 °C/min under 122 ml min^{-1} Ar flow rate.

Fully automatic Sieverts' type equipment was used to measure hydrogen sorption properties. Details of this experimental set-up device are published in Ref. [9].

3. Results and discussion

3.1. Correlation between the properties of as-milled and annealed samples

The diffraction pattern of as-milled $LaNi_5$ is shown in Fig. 1(a). Broad peaks, typical of materials obtained by milling, are observed [10]. The profile shape is caused by two main contributions: cell parameter deformation due to strain and reduction in the size of crystallites [1–3,6]. Milling process leaves the material with strain, vacancies and other microstructural inhomogeneities. These material features generate different chemical potentials for the intermetallic–hydrogen interaction in each particle. As a result, pressure-composition isotherms (PCI) show steeped plateau and low storage capacity as observed in Fig. 1(b). Under these conditions, the intermetallic is not suitable for hydrogen compression applications because an unstable and low efficient thermal hydrogen compression stage would be obtained.

A thermal treatment after milling is needed in order to improve the structural properties. The annealing produces an increment in the size of crystallites and a decrement of strain. After the treatment, thinner and multiple peaks evolve from a broad one. A better defined diffraction pattern is obtained as shown in Fig. 1(c). These structural changes are correlated with hydrogen sorption properties as observed in Fig. 1(d). The PCI shows low plateau slope and storage capacity near the theoretical value. These conditions were found for $LaNi_5$ samples annealed at 600 °C for 24 h.

The intermetallics of the (La,Ce,Nd,Pr)Ni_5 family share the same crystalline structure and space group (*P*6/*mmm*). Therefore, the effect of an annealing process on hydrogen sorption properties should be analogous. Then, the results obtained for $LaNi_5$ can be applied to any other intermetallic of the same family.

3.2. Thermal behavior

The thermal behavior of a $LaNi_5$ sample was analyzed by DSC. The results are shown in Fig. 2(a). Unlike samples of the same compound synthesized using high-energy mills, no recrystallization peak is observed in the range 50–500 °C [1]. Diffraction patterns of $LaNi_5$ after annealing at 200, 400 and 600 °C are shown in Fig. 2(b). Almost no difference is observed between the XRD of the as-milled sample (Fig. 1(a)) and the one of the sample annealed at 200 °C for 24 h (Fig. 2(b)). Negligible crystallization is concluded. Slight change on the diffraction pattern is observed as annealing temperature is increased from 200 to 400 °C (Fig. 2(b)). Significant changes can be observed in the diffraction pattern of the sample annealed at 600 °C for 24 h (Figs. 1(c) and 2(b)). It is evident that the main recrystallization processes occur within the 400–600 °C range. Since adequate hydrogen sorption properties are obtained at 600 °C, it is selected for the thermal treatments. This temperature value of annealing was reported previously for $LaNi_5$ obtained by MA in a high-energy mill [1].

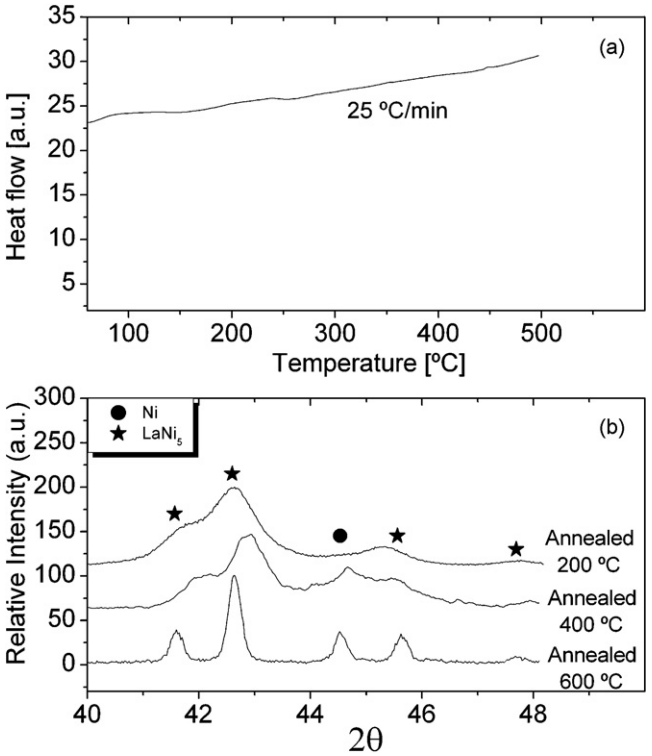

Fig. 2. (a) DSC curve of $LaNi_5$. (b) Diffraction patterns of mechanically alloyed $LaNi_5$ after annealing at various temperatures.

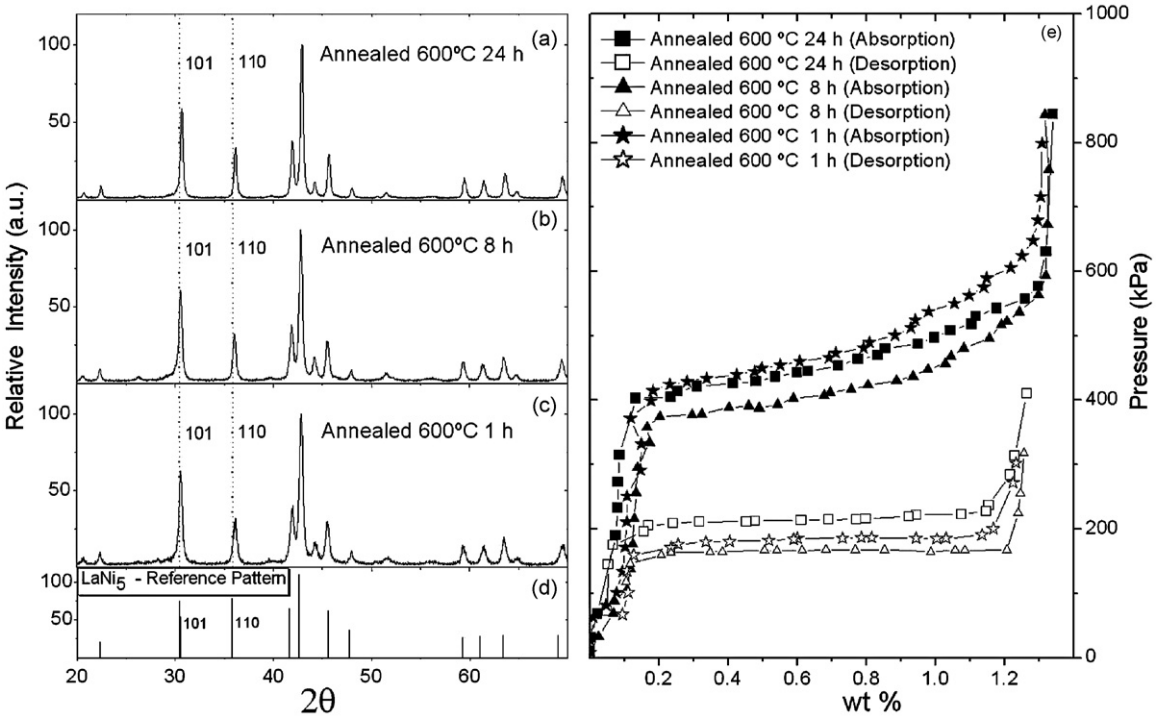

Fig. 3. (a–c) Diffraction patterns of mechanically alloyed $La_{0.67}Ce_{0.19}Nd_{0.08}Pr_{0.06}Ni_5$. Samples were heated during different periods of time at 600 °C. (d) Reference pattern of $LaNi_5$. (e) PCI's of $LaNi_5$ at 25 °C after annealing during various periods of time at 600 °C.

3.3. Optimization of the synthesis-pretreatment process

In order to optimize the process, samples of a multi-substituted AB_5 ($La_{0.67}Ce_{0.19}Nd_{0.08}Pr_{0.06}Ni_5$) were annealed at 600 °C for 24, 8 and 1 h. The diffraction patterns of these samples are shown in Fig. 3(a, b and c), respectively. As a guide to the eye, the (1 0 1) and (1 1 0) *h k l* planes are indicated in dashed lines. For comparison, reference pattern of $LaNi_5$ is also depicted in Fig. 3(d). Since the diffraction patterns are similar, a quantification of the microstructural properties is done. In each case, Rietveld refinements [7] showed that the mixture maintains $La_{0.67}Ce_{0.19}Nd_{0.08}Pr_{0.06}Ni_5$(87 wt%)–Ni(13 wt%) ratio with R_{wp} values close to 10%. In these refinements, R_{wp} stands for the goodness of the fit [7,8]. A summary of the microstructural results is shown in Table 1. As observed, at annealing temperature of 600 °C, crystallite size and strain values do not change significantly as annealing time decreases. Then, it is concluded that a thermal treatment at this temperature for 1 h is appropriate for obtaining AB_5 intermetallics with satisfactory structural properties. The correlation between AB_5 crystallization and sorption properties of mechanically alloyed $LaNi_5$ is shown in Fig. 3 and summarized in Table 1. Almost no effect of thermal treatment duration on the equilibrium pressure is observed. Similar values of equilibrium pressure, hydrogen storage capacity and hysteresis are obtained.

From these results, it is concluded that multi-substituted AB_5's obtained by low energy MA should be processed in a two-step procedure:

(1) Synthesis by MA up to *final* or *completion* stage.
(2) Annealing at 600 °C for 1 h in order to improve structural and hydrogen sorption properties.

In AB_5 synthesis by MA, final composition is reached after *final* stage [3]. Further milling only leads to particle refinement [3]. Depending on the initial aggregation state of the reactants and the amount of energy supplied during milling, the integrated milling time (t_i) needed to reach *completion* stage would vary among 40 and 350 h in a low energy mill [3,6,11]. These values are higher to those obtained using high/intermediate energy mills [12]. Since composition does not change after *final* stage, milling time is optimized if the synthesis is stopped at the start of this stage. Then, t_i value can be shortened by 50% reaching values similar to those used in high-energy milling [12]. This combined process is an opti-

Table 1
Comparison of the microstructural properties of $La_{0.67}Ce_{0.19}Nd_{0.08}Pr_{0.06}Ni_5$ and hydrogen sorption properties of $LaNi_5$ after various thermal treatments.

Treatment	Sample						
	$La_{0.67}Ce_{0.19}Nd_{0.08}Pr_{0.06}Ni_5$			$LaNi_5$			
	h k l	Crystallite size (Å) ± 10	Strain (%) ± 0.05	Pa range (kPa)	Pd range (kPa)	Capacity (wt%)	Hysteresis log(Pa/Pd)
Milled + 600 °C 24 h	1 0 1	750	0.45	390	235	1.1	0.37
	1 1 0	830	0.35	–575	–175		
Milled + 600 °C 8 h	1 0 1	610	0.50	375	165	1.1	0.46
	1 1 0	660	0.40	–535	–145		
Milled + 600 °C 1 h	1 0 1	580	0.55	415	200	1.1	0.45
	1 1 0	530	0.50	–605	–160		

mization over traditional high temperature ($T > 900\,^{\circ}C$)—long time annealing ($t > 24\,h$) equilibrium methods. This is the main goal of our frame scientific program.

4. Conclusions

The optimization of an integral process including synthesis and pretreatment for ready to use AB_5's for hydrogen compression devices should include:

(a) Mechanical alloying up to *final* or *completion* milling stages. The lowest milling time is achieved by stopping the milling at the starting of the final stage. At this point, integrated milling times can be shortened up to 50% approaching to those of high-energy mills.
(b) Annealing at 600 °C. This temperature cannot be deduced from DSC measurements of samples obtained by low energy MA because no recrystallization peak is observed. For thermal treatments performed at 200 °C for 24 h, recrystallization is not evidenced, this is shown in Fig. 2(b). Between 200 and 400 °C, this process is enhanced as depicted in Fig. 2(b). Structural properties are sensibly improved after thermal treatments at 600 °C, this is presented in Fig. 2(b). At this temperature, annealing time can be shortened up to 1 h. The improvement on structural and hydrogen sorption properties is shown in Fig. 3. These annealing parameters values: 600 °C for 1 h, led to appropriate AB_5 materials suitable for hydrogen thermal compression applications.

Acknowledgements

The authors wish to thank to the Agencia Nacional de Promoción Científica y Tecnológica of Argentina (Projects N° PICT 2005-33473 and PAE-PICT-2007-00158) and to the Universidad Nacional de Cuyo of Argentina (Project: Síntesis, mejora y aplicación de materiales para compresión térmica de hidrógeno) for partial financial support.

References

[1] G. Liang, J. Huot, R. Schultz, J. Alloys Compd. 320 (2001) 133–139.
[2] M. Jurczyk, K. Smardz, W. Rajewski, L. Smardsz, Mater. Sci. Eng. A 303 (1–2) (2001) 70–76.
[3] M.R. Esquivel, G. Meyer, J. Alloys Compd. 446–447 (2007) 212–217.
[4] L.O. Valøen, A. Zaluska, L. Zaluski, H. Tanaka, N. Kuriyama, J.O. Ström-Olsen, R. Turnold, J. Alloys Compd. 306 (1–2) (2000) 235–244.
[5] P. Dantzer, Mater. Sci. Eng. A 329–331 (2002) 313–320.
[6] B.A. Talagañis, M.R. Esquivel, G. Meyer, 7° Congreso de Metalurgia y Materiales SAM/CoNaMet 2007, ISBN: 978-950-42-0094-9.
[7] R.A. Young, The Rietveld Method International Union of Crystallography, Oxford University Press, 1993.
[8] R.A. Young, A.C. Larson, C.O. Paiva Santos, J. Appl. Crystallogr. 28 (1995) 366–367.
[9] G. Meyer, D. Rodriguez, F. Castro, G. Fernández, Hydrogen energy process, in: Proceedings of the 11th World Hydrogen Energy Conference, vol. 2, 1996, pp. 1293–1298.
[10] R. Jenkins, R. Snyder, Introduction to X-ray Powder Diffractometry, John Wiley & Sons Inc., New York, 1996, pp. 89–95.
[11] M.R. Esquivel, J.J. Andrade Gamboa, F.C. Gennari, G. Meyer, Sohn International Symposium Advanced Processing of metals and materials, vol. 4, 2006, pp. 517–526.
[12] M. Jurcyzk, J. Alloys Compd. 307 (2000) 279–282.