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Structural and Hydriding Properties of the LaZr2Mn4Ni5-AB3 Type Based Alloy Prepared by Mechanical Alloying from the LaNi5 and ZrMn2 Binary Compounds

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Abstract

In this study, we report on the synthesis of a new AB_3-type compound $LaZr_2Mn_4Ni_5$ (with a content of 40 wt %) at room temperature during 5h of mechanical alloying. This compound was synthesized from the two binary compounds $LaNi_5$ ($CaCu_5$-type structure, P6/mmm space group) and $ZrMn_2$-Laves phase ($MgZn_2$-type structure, $P6_3$/mmc space group) in order to take advantage of the hydrogen absorption properties of these two types of intermetallic compounds. Structural properties were investigated using X-ray diffraction (XRD). The surface morphology of the cycled electrode was observed by a scanning electron microscope (SEM). The electrochemical properties of the $LaZr_2Mn_4Ni_5$–based alloy were determined using the chrono-potentiometry method. The experimental results indicate that the discharge capacity reaches a maximum value of 300 mAh/g. Solid-gaz reaction shows that this compound is able to form the $LaZr_2Mn_4Ni_5H_{13}$ hydride at room temperature at an absorption plateau pressure of about 7 bar.

Keywords: Intermetallic compound; Mechanical alloying; AB3-type compound; Hydrogen storage properties; Electro-chemical discharge capacity

Introduction

Intermetallic compounds AB_n (A = Y; rare earth, M = transition metal, $1 \leq n \leq 5$) are able to store reversibly large amount of hydrogen and are therefore potential materials for energy storage. The H_2 absorption-desorption reaction can be performed either by solid-gas or electrochemical routes [1]. Much research have been performed in order to improve the overall properties of the hydrogen storage alloys and to develop new types of hydrogen storage alloys, used as negative electrode materials for the Ni-MH battery. Applications of Ni-MH batteries require continuously an increase in the energy density [2,3]; weight capacities are still low for practical applications and many efforts are conducted worldwide to develop materials with improved performances regarding energy density [4]. It is well known that element substitution is one of the effective methods for improving the overall properties of the hydrogen storage alloys [5], by the replacement of part of the rare earths or the transition metals of the intermetallic compounds by lighter atoms [3].

Kadir [6] have presented a new series of ternary alloys, AMg_2Ni_9 (where A = La, Ce, Pr, Nd, Sm and Gd), whose structures are built up from alternating $MgNi_2$ Laves-type phases and rare-earth based AB_5 layers. They found that these compounds crystallize in an ordered variant of the $PuNi_3$-type rhombohedral structure (R-3 m space group) [1]. Moreover, it is reported that some of the A-Mg-Ni-based AB_3-type alloys also exhibited promising electrode properties. For example, the La-Mg-Ni-Co system AB_x (x = 3.0-3.5) type quaternary alloys were found to have large discharge capacities of 387-410 mAh/g, higher than those of the commercially used AB_5-type alloys [7].

In this work we will try to synthesize a new quaternary AB_3-type compound $LaZr_2Mn_4Ni_5$ starting from $ZrMn_2$ Laves phase and $LaNi_5$ assuming the reaction $LaNi_5 + 2\ ZrMn_2 \rightarrow LaZr_2Mn_4Ni_5$, La (A atom type) and Ni (B atom type) are then partially substituted respectively by Zr and Mn. According to thermodynamic properties reported for the binary compounds, the intergrowth between $LaNi_5$ and $ZrMn_2$ should lead to a compound having intermediate properties between those of the two starting binary compounds. The compound $LaNi_5$, which crystallizes in the hexagonal $CaCu_5$-type structure (Haucke phase), exhibits exceptional thermodynamical properties toward hydrogen absorption storing up to 6.6 H per formula unit (f.u.) [8]. However, its equilibrium pressure (P = 1.7 bar at room temperature) is too high for practical applications and the molecular mass of La implies a weight capacity limited to 370 mAh/g [1]. In another hand, the use of Zr-based AB_2 alloys as electrodes in nickel-metal hydride batteries has been intensively studied in recent years. This is due to their large hydrogen reversible capacity compared with AB_5-type compounds presently used in commercial devices [9]. Furthermore, it has been found that the Mn element is beneficial in many respects for the rare earth-based hydrogen storage alloys [10-12]. In this work, as it is not possible to obtain the $LaZr_2Mn_4Ni_5$ compound by high-temperature melting synthesis due to the non-miscibility of the two elements La and Zr [3], this compound will be elaborated by mechanical alloying (MA) since it is a process suitable for alloying non-miscible materials and producing powders having a fine microstructural scale [3,13-17]. In this paper, the structure and the hydrogen storage properties of the mechanically alloyed compound $LaZr_2Mn_4Ni_5$ will be investigated.

Experimental Details

The MA process was carried out using a Fritsch 'Pulverisette 7'

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planetary ball mill, starting from a mixture of two binary compounds $LaNi_5$ and $ZrMn_2$ crushed into powder. These two alloys were prepared by Ultra High Frequency (UHF) induction melting of the pure elements La, Ni and Zr, Mn respectively. The purities of those starting metallic elements were 99.9%, 99.98%, 99.8% and 99.8% respectively. The ingots were melted five times to ensure good homogeneity. For the $LaNi_5$ compound, the synthesis was carried out under secondary vacuum in a water-cooled copper crucible from a stoichiometric mixture of La and Ni elements with atomic composition 1:5. The synthesis of the $ZrMn_2$ compound was made under vacuum and then under argon atmosphere when some losses of Mn by sublimation were observed. Binary compounds were analyzed by electron probe microanalysis (EPMA) using a CAMECA SX-100 to ensure their compositions and homogeneity. A mixture of 2 g of these two alloys was then placed in a cylindrical container which was tightly closed under argon atmosphere in a glove box filled with purified argon. The container made by tungsten carbide was loaded with 5 balls (Ø = 12 mm, m = 6.7851 g) with a balls to powder weight ratio equal to 17:1.

The MA conditions correspond to $0.6645.10^{-1}$ J/Hit kinetic shock energy, 93.35 Hz shock frequency and 3.1025 W/g injected shock power [17,18]. The alloy was milled for 5 hours at a disc rotation speed of 450 rpm. The sample obtained was named as S5.

The structural properties of this sample was obtained by X-ray powder diffraction (XRD) that was performed using Cu; Kα radiation at room temperature on a (θ-2θ) Panalytical X'Pert Pro MPD diffractometer. Diffracted intensities were measured in the range 10°-100° with a two-theta step of 0.04° and the diffractogram were fitted using the Rietveld method with the Fullprof software [19-21]. The Rietveld method was used to refine the lattice parameters, the atomic parameters (site occupancy and atomic coordinates) and to calculate the weight contents of the existing phases.

Electrochemical properties were tested using a composite negative electrode made of the intermetallic compound as active material, carbon black as electronic conductor and poly-tetra-fluoro-ethylene (PTFE) as a binder. The "latex" technology has been used for the electrode preparation; ninety percent of the alloy powder is mixed with 5% of the black carbon and 5% of the polytetrafluoroethylen (PTFE). Two 0.5 cm^2 pieces of this latex are pressed on each side of a nickel grid current collector to prevent the electrode plate from breaking into pieces during the charge-discharge cycling [22]. This grouping forms the negative electrode of Ni-MH accumulator. The counter electrode was formed by the Ni-oxyhydroxide/dihydroxide ($NiOOH/Ni(OH)_2$), whereas the reference electrode was the Hg/ HgO (1 M KOH). The electrolyte was 1 M KOH solution, prepared with deionised water. All electrochemical measurements were conducted at 25°C in a conventional three-electrode open-air cell using VMP system. The discharge capacity of the electrode was determined by a galvanostatical charging–discharging for 30 cycles at C/3 and D/6 regime, respectively between -0.6V and -1.3 V versus Hg/HgO. Every cycle was carried out by charging fully at 150 mA/g for 3 h (this time was majored by 50% due to efficiency of the charging reaction) and discharging at 75 mA/g.

The surface morphology of the cycled electrode was observed by a scanning electron microscope (SEM). The pressure-composition-temperature curve (P-C-T) was measured using a volumetric Sievert's method for pressure between 0.1 and 1 MPa at room temperature [23]. The sample was first activated by 3 hydriding-dehydriding cycles to reduce the grain size and to increase the kinetic (absorption at 25°C under 9 bar and desorption under primary vacuum at 35°C). In addition, the hydride formation is confirmed by X-ray diffraction measurements carried out after the hydrogen absorption.

Result and Discussions

Structural characterization of the mechanically alloyed compound $LaZr_2Mn_4Ni_5$

The results of the structural characterization of the two starting compounds $LaNi_5$ and $ZrMn_2$ shows that $LaNi_5$ compound is single phase with the composition $LaNi_{4.98(3)}$ and crystallizes in the hexagonal $CaCu_5$-type structure (P6/mmm space group) with a = 5.0115(1) Å and c = 3.9850(1) Å. For the $ZrMn_2$ compound, the corresponding XRD pattern can be indexed in the $P6_3/mmc$ structure with parameters a = 5.0425(1) Å and c = 8.2835(3) Å, more details are given in our previous work [24].

MA starting from $LaNi_5$ and $ZrMn_2$ leads to the formation of a nanocrystalline AB_3-type phase with the hexagonal $PuNi_3$-type structure (S.G: R-3m) (Z = 3) [6,25]. This phase is formed in coexistence with $ZrMn_2$ phase ($MgZn_2$-type structure, $P6_3/mmc$ space group) and a cubic nanocrystalline AB_2-type phase Zr-Mn-Ni (C15-type) (S.G: Fd-3 m) [26].

Figure 1 shows the XRD pattern refinement of S5 sample for which Rietveld structural parameters are reported in Table 1. As can be seen in Figure 1, the peaks of $LaNi_5$ compound totally disappear after 5 h of MA whereas those of $ZrMn_2$ phase are still present. For the formed AB_3 phase with $PuNi_3$-type structure, the results show that La atoms are located not only at the 3a site of the $PuNi_3$-type structure, but also at the 6c site [24]. Both 3a and 6c sites are then occupied by both La and Zr elements indicating that the alloy is not a fully ordered compound having the same structure as previously reported for AMg_2Ni_9 compounds [6,25,27-29].

In our previous work, we have showed by transmission electron microscopy (TEM) examinations that the particles size of the mechanically alloyed sample during 5 h is rather inhomogeneous, ranging from 0.5 to 5 µm and the La + Zr/ Mn + Ni ratio have an average about 3 [24]. These results confirm the XRD analysis and show that that the particles produced by MA of $LaNi_5$ and $ZrMn_2$ formed a quaternary compound with AB_3 composition.

Electrochemical measurements

Figure 2a presents a typical discharge curve of the $LaZr_2Mn_4Ni_5$ alloy electrode at 25°C after being activated. Obviously, this curve has

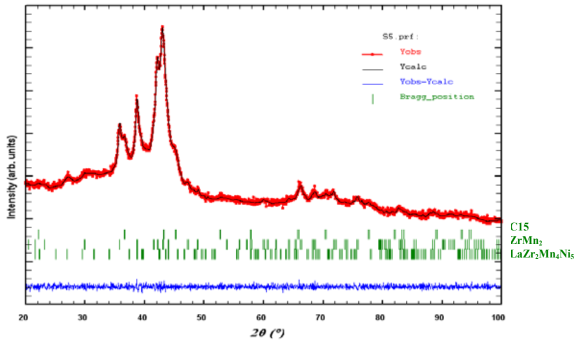
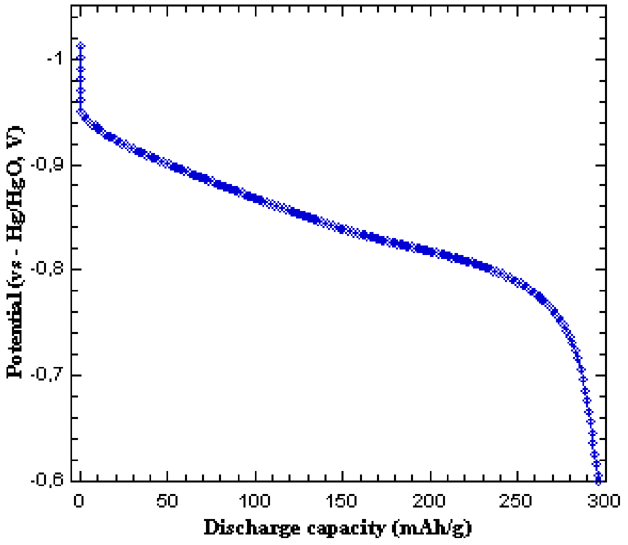


Figure 1: Rietveld refinement of the X-ray diffraction pattern of S5 sample mechanically alloyed during 5 h [24].



(a)

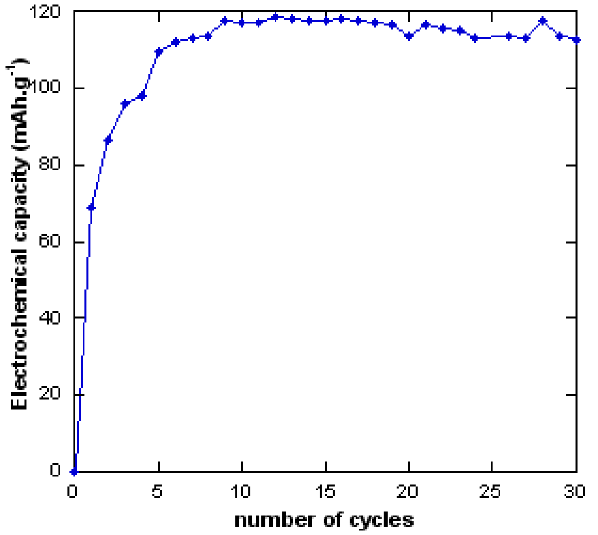
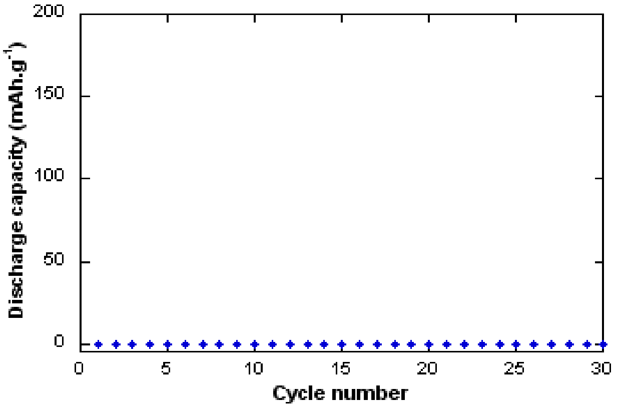


Figure 2: Rietveld refinement of the X-ray diffraction pattern of S5 sample mechanically alloyed during 5 h [24].

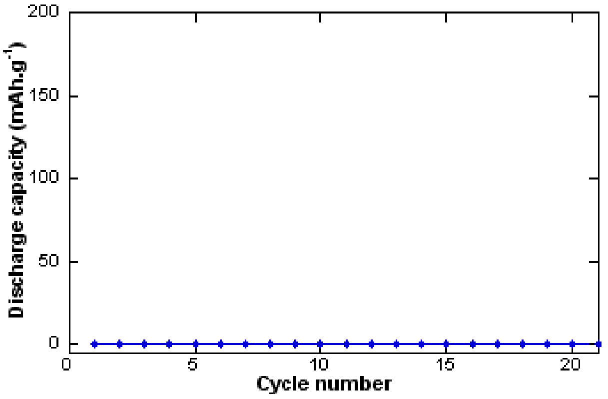
a wide discharge potential plateau based on the oxidation of desorbed hydrogen from the hydride. The mid-discharge potential is about -0.849V.

Figure 2b shows the variation of the electrochemical discharge capacity of the AB_3-based alloy (S5) as function of the number of cycles. However, as this alloy contains additionally to the AB_3 phase, the $ZrMn_2$ compound and the Zr-Ni-Mn Laves phase (C15-type) with significant mass proportions, it was, therefore, necessary to characterize their reactivity with hydrogen and measure their individual electrochemical discharge capacity to determine their contribution to the total discharge capacity.

Figure 3a shows the discharge capacity of the $ZrMn_2$ compound measured for 30 cycles of charging/discharging by galvanostatic cycling at room temperature and atmospheric pressure to deduce the discharge capacity of the AB_3-type compound. Therefore $ZrMn_2$ compound, in these conditions does not contribute to the total discharge capacity determined in Figure 2b for S5 sample based on $LaZr_2Mn_4Ni_5$ compound. According to the literature, the electrochemical discharge capacity of the $ZrMn_2$ compound is practically zero at 30°C and atmospheric pressure [30]. Nevertheless, it absorbs nearly 4 H/f.u, for maximum pressure of 8 bar, at room temperature, by solid-gas reaction [31]. The electrochemical discharge capacity of the C15 Laves phase Zr-Mn-Ni was also measured (Figure 3b) in order to determine its contribution to the discharge capacity of the S5 alloy. This latter compound was synthesized by UHF induction melting and it's a single phase which structure can be described in the cubic Fd-3 m space group (Figure 4). Figure 3b shows that similarly to the $ZrMn_2$ compound, the Zr-Mn-Ni Laves phase does not absorb hydrogen and thus does not contribute to the total discharge capacity of the synthesized AB_3-type based alloy (S5). Thus, the discharge capacity of the prepared alloy depends only of the mass proportion of the $LaZr_2Mn_4Ni_5$ AB_3-type compound. The corresponding capacity obtained can be therefore expressed in AB_3-type phase wheight (mAh/g AB_3), its variation versus the cycle number is given in Figure 5.



(a)



(b)

Figure 3: Variation of the discharge capacity of (a) the ZrMn2 compound and (b) the C15 Laves phase type Zr-Mn-Ni, measured at atmospheric pressure and room temperature as function of the cycle number.

According to Figure 5, the $LaZr_2Mn_4Ni_5$ has a good cycle life since the discharge capacities have approximately stable values even after 30 cycles of charging/discharging. The maximum reversible capacity is

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Phases	Content (wt%)	a (Å)	c (Å)	R_f (%)	R_{Bragg} (%)	χ^2
$ZrMn_2$	38(1)	5.0231(f)	8.2475(f)	0.705	0.508	
AB_2 (C15)	21.5(0.6)	6.955(2)	—	0.229	0.104	
$AB_3(LaZr_2Mn_4Ni_5)$	39.9(0.9)	4.815(2)	27.269(18)	0.482	0.348	1.18

(f) : fixed parameter

Table 1: Structural parameters determined by Rietveld refinement of the XRD pattern of the S5 sample.

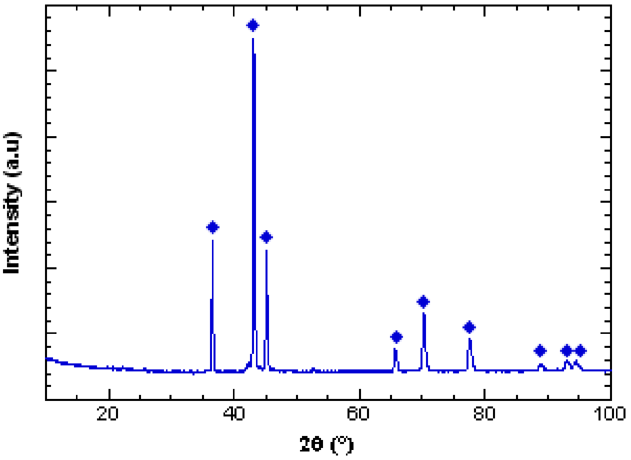

Figure 4: X-ray diffraction pattern of the Zr-Mn-Ni Laves phase (C15 type) synthesized by UHF induction melting, indexed in Fd-3m space group.

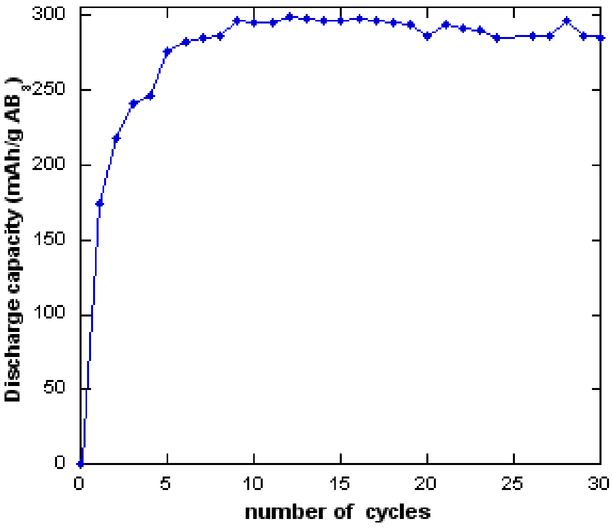

Figure 5: Variation of the electrochemical capacity of LaZr2Mn4Ni5 versus the cycle number.

about 298.56 mAh.g^{-1} equivalent to 9.12 H/f.u. The discharge capacity of the alloy powder increases to reaches 298.56 mAh/g after 12 cycles and then decreases to 293.6 mAh/g after a few charge-discharge cycles.

The capacity decay of the hydrogen storage alloy electrode is mainly due to the pulverization and oxidation of the active material components to form oxides or hydroxides [32,33].

Figure 6 shows the electrode surface morphologies by SEM of the S5 sample before and after 30 charge-discharge cycles. The alloy consists of large particles and clusters of fine particles. In fact the formed oxide or hydroxide layer acts as a barrier to the hydrogen diffusion and leads to the decrease of the number of hydrogen atoms which can be absorbed by the material. In fact, during the cycling, the rare earth elements such as La or the transition metal such as Mn segregate to the grain boundaries, where they were subject to corrosion. The corrosion products are disposed on the surface of grain particles as $La(OH)_3$ or as Mn_3O_4 and act as a barrier to the hydrogen diffusion in the particle volume which in turn decrease the alloy discharge capacity. It was shown that the thickness of the corrosion layer increases generally with the number of charging/discharging cycles [34-36].

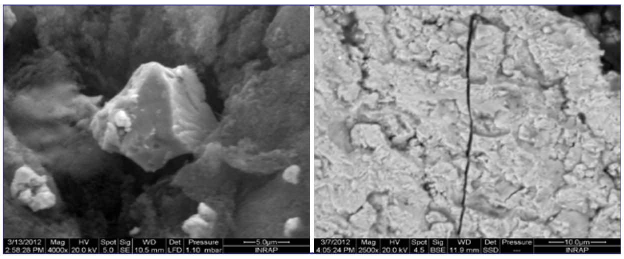

Figure 6: SEM micrographs of electrode surface morphologies of S5 sample (a) before cycling and (b) after 30 cycles of charging discharging.

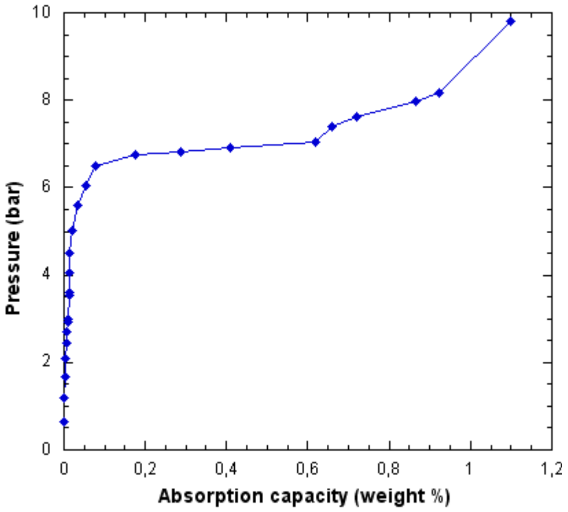

Figure 7: PCT curve measured at 25°C for the sample elaborated by mechanical alloying from the two binary compounds LaNi5 and ZrMn2.

Gas hydrogenation P-C-T isotherm

The pressure-composition-isotherm (P-C-T) measured at 25°C is presented in Figure 7. The PCT curve of this alloy has two absorption plateau pressures, showing the presence of two types of hydrides $A_xB_yH_z$ and $A'_xB'_yH'_z$. The first one is characterized by the formation of the first plateau at a pressure of about 7 bar, corresponding to an absorption capacity of 0.6 wt%, the second is characterized by the second plateau at a maximum pressure of about 8 bar corresponding to an absorption capacity of 0.32 wt%. Indeed, according to the literature, $ZrMn_2$

compound, one of the constituents of the synthesized composite, can absorb nearly 4 H/f.u by solid-gas reaction for maximum pressure of 8 bar, at room temperature [31]. Thus, the second plateau can be attributed to the $ZrMn_2$ compound and the first one to the $LaZr_2Mn_4Ni_5$ compound. Therefore, by converting the absorption weight capacities to H/f.u capacities, the hydride $A_xB_yH_z$ is $LaZr_2Mn_4Ni_5H_{13}$. We can then conclude that the $LaZr_2Mn_4Ni_5$ compound absorbs hydrogen at room temperature; its absorption capacity in these conditions is in the range of 13 H/uf.

The hydride formation as a result of the solid-gaz absorption of hydrogen by the alloy has been ascertained by XRD analysis. Figure 8 presents the XRD diffractogram of the hydrided alloy. This Figure 8 shows no diffraction peaks of other phases and/or none other of pure metals are observed in the XRD diffractogram of the formed hydride and all the initial phases or compounds before hydrogenation are identified. It is also found that all the hydrided phases still preserve their structures. The hexagonal $PuNi_3$-type structure, is preserved for the $LaZr_2Mn_4Ni_5$ compound like in some RMg_2Ni_9 type alloys [25,27,28].

The lattice parameters and the cell volumes, determined by the the Fullprof program are summarized in Table 2. It is seen that the cell volume has not changed significantly. The reason for this observation is associated with a partial desorption of the solid-gas stored hydrogen in the course of the ex-situ XRD measurement.

This unavoidable desorption, in our case, is a result of hydrogen under pressure driven decomposition initiated upon taking the alloy out of the sample holder, clearly proving that the formed hydride is not stable, it should therefore have an equilibrium plateau pressure greater than atmospheric pressure at room temperature which is explaining the value of 7 bar of the absorption plateau pressure measured for the $LaZr_2Mn_4Ni_5$ compound. Some other AB_3-type compounds exhibit plateau pressures greater than 1 atm: the $LaMg_2Ni_9$ compound has a plateau pressure of H absorbing about 22 bar at 80°C [37], this compound according to Liao [7] shows a plateau pressure of 4 bar at 25°C. Denys [38] have determined the enthalpy value of the hydride formation for this latter compound it is about -22.5 KJ $(mol_{H2})^{-1}$ at 293 K, this proves that the studied $LaMg_2Ni_9$-AB_3 type compound is also stable with an absorption equilibrium plateau pressure at 122 bar and a desorption plateau pressure at 18 bar at 20°C. These values are in agreement with that of $LaZr_2Mn_4Ni_5$ compound reported in this work.

Conclusion

The hydrogen storage alloy $LaZr_2Mn_4Ni_5$ was successfully synthesized at room temperature, for only 5 h of mechanical alloying, from the mixture of the two binary compounds $LaNi_5$ and $ZrMn_2$ at 40 wt.%. The following conclusions can be drawn concerning structural characterization and the hydrogen absorption properties of the mechanically alloyed compound $LaZr_2Mn_4Ni_5$ determined either by solid-gas or electrochemical routes:

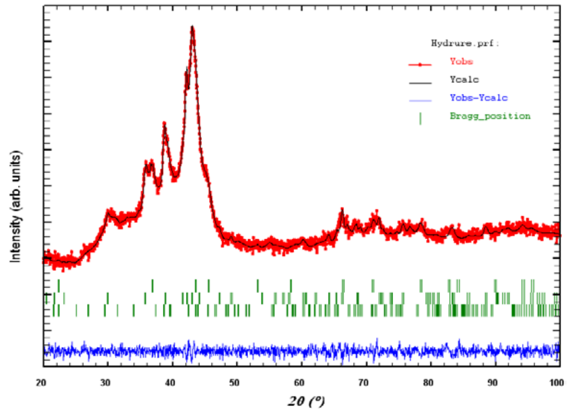

Figure 8: Rietveld refinement of the X-ray diffraction pattern of the hydrided alloy.

Phase	a (Å)	c (Å)
$ZrMn_2$	5.0297(7)	8.216(1)
$LaZr_2Mn_4Ni_5$	4.821(3)	27.29(3)

Table 2: Lattice parameters determined for the hydrided $LaZr_2Mn_4Ni_5$-based alloy after hydrogenation at room temperature.

- XRD analysis show the formation of a composite that is mainly consist of $LaZr_2Mn_4Ni_5$ compound with hexagonal $PuNi_3$-type structure coexisting with the $ZrMn_2$ binary compound ($MgZn_2$-type structure C14, $P6_3/mmc$ space group) and a cubic AB_2-type Laves phase Zr-Mn-Ni ($MgCu_2$-type structure C15, Fd-3 m space group).
- The partial substitution of La and Ni by respectively Zr and Mn does not change the main phase structure but affects the lattice parameters. The overall effect is an increase of the cell volume and of c/a ratio as compared to the $LaMg_2Ni_9$ compound.
- Rietveld analysis proves that $LaZr_2Mn_4Ni_5$ is not fully ordered since both of La and Zr atoms are located simultaneously in the two types of allowed sites 3a and 6c contrarily to the $LaMg_2Ni_9$ compound where La atoms occupy only 3a site and Mg atoms the 6c site.
- The electrochemical measurements show that the discharge capacity of the synthesized alloy depends only of the mass proportion of the $LaZr_2Mn_4Ni_5$ compound. The corresponding capacity obtained can be therefore expressed in AB_3-type phase wheight (mAh/g AB_3), it is of about 300 mAh/g AB_3.
- The $LaZr_2Mn_4Ni_5$ compound can absorb hydrogen at room temperature; its absorption capacity in these conditions is in the range of 13 H/uf at a plateau pressure of about 7 bar.

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