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-type compound LaZr₂Mn₄Ni₅ (with a content of 40 wt %) at room temperature during 5h of mechanical alloying. This compound was synthesized from the two binary compounds LaNi₅ (CaCu₅-type structure, P6/mmm space group) and ZrMn₂ Laves phase (MgZn₂-type structure, P6/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 LaZr₂Mn₄Ni₅-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 LaZr₂Mn₄Ni₅H₁₃ 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 ABₓ (A = Y; rare earth, M = transition metal, 1 ≤ n ≤ 5) are able to store reversibly large amount of hydrogen and are therefore potential materials for energy storage. The H₂ 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, AMg₉Niₓ (where A = La, Ce, Pr, Nd, Sm and Gd), whose structures are built up from alternating MgNi₂ Laves-type phases and rare-earth based AB layers. They found that these compounds crystallize in an ordered variant of the PuNi₃-type rhombohedral structure (R-3 m space group) [1]. Moreover, it is reported that some of the A-Mg-Ni-based ABₓ-type alloys also exhibited promising electrode properties. For example, the La-Mg-Ni-Co system ABₓ (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 ABₓ-type alloys [7].

In this work we will try to synthesize a new quaternary ABₓ-type compound LaZr₂Mn₄Ni₅, starting from ZrMn₂ Laves phase and LaNi₅, assuming the reaction LaNi₅ + 2 ZrMn₂ → LaZr₂Mn₄Ni₅. 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 LaNi₅ and ZrMn₂ should lead to a compound having intermediate properties between those of the two starting binary compounds. The compound LaNi₅, which crystallizes in the hexagonal CaCu₅-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 ABₓ 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 ABₓ-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 LaZr₂Mn₄Ni₅ 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 LaZr₂Mn₄Ni₅ will be investigated.

Experimental Details
The MA process was carried out using a Fritsch ‘Pulverisette 7’
planetary ball mill, starting from a mixture of two binary compounds LaNi5 and ZrMn2 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. 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 LaZr2Mn4Ni5

The results of the structural characterization of the two starting compounds LaNi5 and ZrMn2 shows that LaNi5 compound is single phase with the composition LaNi5(100), and crystallizes in the hexagonal CaCu5-type (P6/mmm space group) with a = 5.0115(1) Å and c = 3.9850(1) Å. For the ZrMn2 compound, the corresponding XRD pattern can be indexed in the P6/mmc space parameters with a = 5.0425(1) Å and c = 8.2835(3) Å, more details are given in our previous work [24].

MA starting from LaNi5 and ZrMn2 leads to the formation of a nanocrystalline AB2-type phase with the hexagonal PuNi3-type structure (S.G: R-3m) [6,25]. This phase is formed in coexistence with ZrMn2 phase (MgZn2-type structure, P63/mmc space group) and a cubic nanocrystalline AB2-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 LaNi5 compound totally disappear after 5 h of MA whereas those of ZrMn2 phase are still present. For the formed AB2 phase with PuNi3-type structure, the results show that La atoms are located not only at the 3a site of the PuNi3-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 AMg2Ni9 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 the particles produced by MA of LaNi5 and ZrMn2 formed a quaternary compound with AB2 composition.

Electrochemical measurements

Figure 2a presents a typical discharge curve of the LaZr2Mn4Ni5 alloy electrode at 25°C after being activated. Obviously, this curve has
Figure 2: Rietveld refinement of the X-ray diffraction pattern of S5 sample mechanically alloyed during 5 h [24].

(a) Discharge capacity (mAh/g) vs. Potential (V)
(b) Electrochemical capacity (mAh/g) vs. number of cycles

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.

(a) Discharge capacity (mAh/g) vs. Cycle number
(b) Discharge capacity (mAh/g) vs. Cycle number

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 AB₃-based alloy (S5) as function of the number of cycles. However, as this alloy contains additionally to the AB₃ phase, the ZrMn₂ 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 ZrMn₂ compound measured for 30 cycles of charging/discharging by galvanostatic cycling at room temperature and atmospheric pressure to deduce the discharge capacity of the AB₃-type compound. Therefore ZrMn₂ compound, in these conditions does not contribute to the total discharge capacity determined in Figure 2b for S5 sample based on LaZr₂Mn₄Ni₅ compound. According to the literature, the electrochemical discharge capacity of the ZrMn₂ 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 ZrMn₂ compound, the Zr-Mn-Ni Laves phase does not absorb hydrogen and thus does not contribute to the total discharge capacity of the synthesized AB₃-type based alloy (S5). Thus, the discharge capacity of the prepared alloy depends only of the mass proportion of the LaZr₂Mn₄Ni₅, AB₃-type compound. The corresponding capacity obtained can be therefore expressed in AB₃-type phase weight (mAh/g AB₃), its variation versus the cycle number is given in Figure 5.

According to Figure 5, the LaZr,Mn,Ni, 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
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 Mn₃O₄ 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].

**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 AₓBᵧHₓ and A’ₓB’ᵧH’ₓ. 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, ZrMn₂...
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 ZrMn2 compound and the first one to the LaZr2Mn4Ni5 compound. Therefore, by converting the absorption weight capacities to H/f.u capacities, the hydride A B H₆ is LaZr₂Mn₄Ni₅H₁₃. We can then conclude that the LaZr₂Mn₄Ni₅ compound absorbs hydrogen at room temperature; its absorption capacity in these conditions is in the range of 13 H/f.u.

The hydride formation as a result of the solid-gas 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 PuNi₃-type structure, is preserved for the LaZr₂Mn₄Ni₅ compound like in some RMg₂Ni₉ type alloys [25,27,28].

The lattice parameters and the cell volumes, determined by 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 LaZr₂Mn₄Ni₅ compound. Some other AB₃-type compounds exhibit plateau pressures greater than 1 atm; the LaMg₂Ni₉ 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 is about -22.5 KJ (molH₂)⁻¹ at 293 K, this proves that the studied LaMg₂Ni₉-AB₃ 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 LaZr₂Mn₄Ni₅ compound reported in this work.

Conclusion

The hydrogen storage alloy LaZr₂Mn₄Ni₅ was successfully synthesized at room temperature, for only 5 h of mechanical alloying, from the mixture of the two binary compounds LaNi₅, and ZrMn₂, at 40 wt.%. The following conclusions can be drawn concerning structural characterization and the hydrogen absorption properties of the mechanically alloyed compound LaZr₂Mn₄Ni₅ which is either solid-gas or electrochemical routes:

- XRD analysis show the formation of a composite that is mainly consist of LaZr₂Mn₄Ni₅ compound with hexagonal PuNi₃-type structure coexisting with the ZrMn₂ binary compound (MgZn₂-type structure C14, P6₃/mmc space group) and a cubic AB₃-type phase Zr-Mn-Ni (Cu₃Mn-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 LaMg₂Ni₉ compound.
- Rietveld analysis proves that LaZr₂Mn₄Ni₅ 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 LaMg₂Ni₉ 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 LaZr₂Mn₄Ni₅ compound. The corresponding capacity obtained can be therefore expressed in AB₃-type phase weight (mAh/g AB₃), it is of about 300 mAh/g AB₃.
- The LaZr₂Mn₄Ni₅ compound can absorb hydrogen at room temperature; its absorption capacity in these conditions is in the range of 13 H/f.u at a plateau pressure of about 7 bar.

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Table 2: Lattice parameters determined for the hydrided LaZr₂Mn₄Ni₅-based alloy after hydrogenation at room temperature.

| Phase       | a (Å)     | c (Å)    |
|-------------|-----------|----------|
| ZrMn₂       | 4.821(3)  | 27.29(3) |
| LaZr₂Mn₄Ni₅| 5.0297(7) | 8.216(1) |

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