The structure and thermal stability of mechanically alloyed Mg_{1.8}Al_{0.2}Ni alloys

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Abstract: Mg_{1.8}Al_{0.2}Ni alloys were synthesized by mechanical alloying (MA) with different ball-milling duration. The structure and thermal behavior were determined by X-ray diffraction and differential scanning calorimetry. The lattice parameters as well as the lattice volumes, the weight contents and the crystallite sizes of the existing phases were determined by XRD patterns refinement based on the Rietveld method. The results show that Mg_{2}Ni phase was obtained after 8 h of milling. The variation of the ball-milling duration from 8 to 48 h leads to the formation of nanomaterials with an average grain size of 9 nm. Thermal stability study revealed three exothermic peaks for the alloys obtained after 6 and 7 h of milling and four exothermic peaks for higher duration of milling. The first, second and third crystallization reactions for Mg_{1.8}Al_{0.2}Ni obtained after 6 and 7 h of milling take place at 100-200°C, 200-300°C and 400-500°C for heating rate of 20°C.min^{-1}. So, by optimizing the milling and annealing conditions, we were able to obtain the Mg_{1.8}Al_{0.2}Ni nanocrystalline phase after 8 h of mechanical alloying at 250 rpm, 6 h of mechanical alloying at 250 rpm and annealing at 500°C or 7 h of mechanical alloying at 250 rpm and annealing at 225°C.

Keywords: Hydrogen-storage materials; Nanostructured materials; Mechanical alloying; Differential scanning calorimetry (DSC); X-ray diffraction (XRD).

INTRODUCTION

The hydrogen storage in the transportable reservoirs in the form of gas or liquid presents a big problem of flammability and explosion. To reduce these risks, the intermetallics hydrides represent good candidates for this handling. The storage in the hydride form presents a reduced specific volume as well as a good safety due to the low hydrogen pressure. In this context, the researches revealed that the Mg_{2}Ni alloy is considered as most promising compound used for the hydrogen storage but its low kinetic of hydrogen absorption and desorption and its low corrosion resistance in an alkaline aqueous solution limited its use. It is reported [1] that the substitution of Mg by a more electronegative element can decrease significantly the hydrogen absorption temperature. Aluminum has been chosen as the substitution element due to its good accessibility and relatively high electronegativity. Regarding material processing, Mg_{2}Ni has been traditionally produced by melting, and hence it is difficult to obtain high Mg_{2}Ni quality because of the large differences in melting points and vapor pressures between Mg and Ni [2]. However, it is now possible to avoid the inherent difficulties of the melting technique by using mechanical alloying [3,4-6]. In this work, the structural properties of the Mg_{1.8}Al_{0.2}Ni alloys were investigated. The effects of subsequent annealing on the crystal structure of the MA alloys were also studied.

EXPERIMENTALS DETAILS

To prepare Mg_{1.8}Al_{0.2}Ni alloys by mechanical alloying (MA), 1g amount of powder mixture of Mg (98%), Ni (99.9%) and Al (99%) was milled in Retsh PM 400 planetary ball mill. The powder mixture of Mg, Al and Ni was prepared according to the respective atomic stoichiometry 1.8: 0.2: 1 and was introduced in a cylindrical steel container of 50 cm³. The container was loaded with 5 stainless steel balls (Φ=15 mm, m=13.6 g) with a
balls to powder weight ratio equal to 68:1. The container was sealed with elastomer Taurus ring under argon atmosphere in a glove box. The alloying duration was varied from zero until 48 h. The milling speed was equal to 250 rpm. The mechanical alloying (MA) conditions corresponding to 250 rpm disc rotation speed are 0.63 J hit$^{-1}$ kinetic shock energy, 45.6 Hz shock frequency and 5.745 W g$^{-1}$ injected shock power [7,8]. Structural characterization was carried out by X-ray powder diffraction (XRD) with Cu Ka radiation at room temperature on a Panalytical X'Pert Pro MPD diffractometer. The patterns were recorded for two-theta angular position ranging from 10 to 100 degree with a two-theta step of 0.04. The identification of the existing phases in the alloyed alloys was realized by the high score plus software. The Rietveld method [9-10], with the Fullproof software [11], was used to refine the lattice parameters, the atomic parameters and to determine the weight contents of the different phases. The thermal behavior of MA alloys was examined with a SETARAM DSC131 differential scanning calorimeter operating under nitrogen atmosphere at a heating rate of 20°C min$^{-1}$ in a temperature range of 25-500°C.

RESULTS AND DISCUSSION

1. Structural characterization of Mg$_{1.8}$Al$_{0.2}$Ni compound

1.1. Influence of milling duration on Mg$_{1.8}$Al$_{0.2}$Ni formation

Figure 1 shows XRD patterns of the MA alloys obtained after different milling times with rotation speed of 250 rpm.

As milling time increased, the diffraction peaks becomes broad and their intensities are reduced. For duration equal to 6 h, peaks of Al disappeared and only those of elemental Mg and Ni are remaining. After 7 h of MA, residual Ni and Mg peaks persist with the appearance of AlNi peaks. An amorphous halo located at the intense magnesium peak (30° ≤ 2θ ≤ 37°) appeared. After 8 h, we note the formation of Mg$_{1.8}$Al$_{0.2}$Ni phase and the disappearance of the residual Mg. Amorphous and AlNi phases continue to exist. Above 10 h of MA, Ni peaks disappeared and only Mg$_{1.8}$Al$_{0.2}$Ni, AlNi and amorphous phases exist. Results of the Rietveld refinement of the XRD patterns are reported in table I.

According to table I, Mg$_{1.8}$Al$_{0.2}$Ni phase appears from 8 h of milling with a content of 69%. This content increases to reach a maximum of 72 % after 14 h of MA and decreases for higher alloying duration until 46.7 % after 48 h of alloying. Instead, the content of AlNi phase decreases from 37% after 7 h to reach 28 % after 14 h of MA and then increases to 53 % after 48 h. In fact, the AlNi formation is favoured by the large domain of solubility of Al and Ni in the AlNi lattice (45-60 Ni at % domain) as shown by figure 2.

Figure 3 gives the variation of the weight content of the different formed phases as function of alloying duration. The Mg$_{1.8}$Al$_{0.2}$Ni phase has a hexagonal crystalline structure for all durations. Several studies [12-16] reported that the substitution of the Mg by Al in the Mg$_{2.4}$AlNi keep the same hexagonal crystalline structure of Mg$_3$Ni for a substitution rate x<0.5 but turns to a cubic phase for x≥0.5 [12,15-16].

With increasing alloying duration from 8 to 48 h, grain size of Mg$_{1.8}$Al$_{0.2}$Ni phase remains stable (about 9 nm) whereas that of the AlNi phase increases from 8 to 14 nm. This size increase can be due to the conversion of cumulated kinetic shock energy ($E_{\text{cum}} = P_{\text{inj}} \cdot \Delta t$) to the injected shock power and $\Delta t$ the alloying duration) to a heat energy.

Figure 1: XRD patterns of the milled Mg$_{1.8}$Al$_{0.2}$Ni alloys as a function of milling time with a rotation speed of 250 rpm.
Table 1: Results of the Rietveld refinement of XRD patterns of Mg$_{1.8}$Al$_{0.2}$Ni alloys obtained after various alloying durations.

<table>
<thead>
<tr>
<th>Alloying duration (h)</th>
<th>Phase</th>
<th>Content (wt%)</th>
<th>Lattice parameters</th>
<th>V (Å³)</th>
<th>Grain size (nm)</th>
<th>Rw (%)</th>
<th>R$_{Bragg}$ (%)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6h</td>
<td>Mg (P 63/M M C) Ni (F m -3 m)</td>
<td>43.73(0.68)</td>
<td>5.1959(6)</td>
<td>3.1959(6)</td>
<td>10</td>
<td>0.131</td>
<td>0.242</td>
<td>3.66</td>
</tr>
<tr>
<td>7h</td>
<td>Mg (P 63/M M C) Ni (F m -3 m) AlNi (Pm-3m)</td>
<td>34.52(0.67)</td>
<td>5.082(3)</td>
<td>3.1812(9)</td>
<td>8</td>
<td>0.208</td>
<td>0.289</td>
<td>0.919</td>
</tr>
<tr>
<td>8h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>68.79(0.89)</td>
<td>13.442</td>
<td>5.2656(9)</td>
<td>3.66</td>
<td>0.242</td>
<td>0.212</td>
<td>0.796</td>
</tr>
<tr>
<td>10h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>69.99(0.86)</td>
<td>13.274</td>
<td>5.2251(7)</td>
<td>25.025(4)</td>
<td>0.848</td>
<td>0.703</td>
<td>0.927</td>
</tr>
<tr>
<td>14h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>68.36(0.84)</td>
<td>13.252</td>
<td>5.215(1)</td>
<td>13.274</td>
<td>313.8(1)</td>
<td>25.025(4)</td>
<td>0.848</td>
</tr>
<tr>
<td>16h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>66.33(0.69)</td>
<td>13.266</td>
<td>5.231(1)</td>
<td>29.239(5)</td>
<td>0.152</td>
<td>0.177</td>
<td>0.893</td>
</tr>
<tr>
<td>19h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>60.78(0.86)</td>
<td>13.270</td>
<td>5.215(1)</td>
<td>13.274</td>
<td>314.4(1)</td>
<td>25.025(4)</td>
<td>0.848</td>
</tr>
<tr>
<td>30h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>46.67(0.35)</td>
<td>13.3159</td>
<td>5.2253(5)</td>
<td>314.86(7)</td>
<td>0.210</td>
<td>0.207</td>
<td>0.817</td>
</tr>
<tr>
<td>48h</td>
<td>Mg$<em>{1.8}$Al$</em>{0.2}$Ni (P 62 2 2) AlNi (Pm-3m)</td>
<td>53.33(0.33)</td>
<td>13.3159</td>
<td>5.2253(5)</td>
<td>314.86(7)</td>
<td>0.210</td>
<td>0.207</td>
<td>0.817</td>
</tr>
</tbody>
</table>

Figure 2: The binary phase Al-Ni diagram [17]

Figure 3: Evolution of the weight content of the different obtained phases as function of milling time
1.2. Influence of the annealing treatment on the Mg$_{1.8}$Al$_{0.2}$Ni formation

The thermal behavior of the Mg$_{1.8}$Al$_{0.2}$Ni samples, alloyed at different durations, was studied by DSC. Figure 4a shows the DSC curves, recorded at a heating rate of 20°C min$^{-1}$, of Mg$_{1.8}$Al$_{0.2}$Ni alloys obtained after 6, 7, 8, 10, 14, 16, 19, 30 and 48 h of mechanical alloying.

The DSC curves show a similar thermal behavior of the different samples except those of the alloys obtained after 6 and 7 h of milling for which the Mg$_{1.8}$Al$_{0.2}$Ni phase is not formed yet. For Mg$_{1.8}$Al$_{0.2}$Ni samples milled for 6 and 7 h, the DSC curves exhibit three exothermic peaks located at 160, 220 and 310°C. For higher alloying duration, the DSC curves show four exothermic peaks located approximately at 130, 200, 310 and 400°C. For higher alloying duration, the DSC curves show four exothermic peaks located approximately at 130, 200, 310 and 400°C. For higher alloying duration, the DSC curves show four exothermic peaks located approximately at 130, 200, 310 and 400°C. For higher alloying duration, the DSC curves show four exothermic peaks located approximately at 130, 200, 310 and 400°C. For higher alloying duration, the DSC curves show four exothermic peaks located approximately at 130, 200, 310 and 400°C.

It is observed in these curves that as the milling duration increases, the peak temperature of the first peak shifts toward lower temperatures. This peak, which appears at about 100-200°C (Figure 4a-zone a), is well defined for samples milled at 6 and 7 h and more intense for sample milled at 7 h. The intensity increase of this peak is probably due to the highest quantity of the amorphous phase after 7 h of milling. For alloying duration higher than 8 h, the DSC curves show a remarkable change of the behavior and the first peak becomes very broad and with low intensity. This last duration corresponds to the formation of Mg$_{1.8}$Al$_{0.2}$Ni phase with weight content (69%) according to the XRD results (Table I). Furthermore, the first peak tends to overlap with the second. This last is broad and takes place between 200 and 300°C (Figure 4a-zone b). The third peak is located between 400 and 500°C (Figure 4a, zone c). This peak shifts toward higher temperatures and its intensity increases as the alloying duration increases. The fourth exothermic peak is a low intensity peak.

XRD was carried out to understand the structural changes which take place in each sample after each heat treatment. Figure 4b shows the XRD patterns of alloyed samples after DSC heat treatment until 500°C. XRD patterns showed a good crystallinity of all samples with the disappearance of the amorphous phase. So, after heat treatment of the as alloyed Mg$_{1.8}$Al$_{0.2}$Ni samples, a highly crystalline Mg$_2$Ni and Mg$_2$AlNi$_2$ phases were obtained for all durations. This result is in agreement with the results reported by Chen et al [18] who obtained...
the crystalline Mg$_2$Ni and Mg$_2$AlNi$_2$ phases during the synthesis of Mg$_{2-x}$Al$_x$Ni$_2$ alloys with $0.1 \leq x < 0.5$ by combustion synthesis. Whereas, Wang et al [19] obtained a multiphase alloy containing Mg$_{1.75}$Al$_{0.25}$Ni, Mg$_2$Ni, AlNi, MgO and Mg phases after a mechanical alloying during 5 h followed by a calcination at 500°C during 5 h of the Mg$_{1.75}$Al$_{0.25}$Ni sample.

To understand the chemical reaction or the physical phenomena related to each one of the three exothermic peaks, the 7 h as milled Mg$_{1.8}$Al$_{0.2}$Ni sample was submitted to DSC treatments up to the temperatures above each peak. Then, XRD analysis was carried out after each DSC treatment. According to DSC curves (Figure 5a), three temperatures were chosen for DSC/XRD measurements.

After 225°C (temperature above the first peak), we noticed the presence of the remaining elemental crystalline Ni, Mg and the MA formed AlNi and the starting of formation of crystalline crystallization of Mg$_{1.8}$Al$_{0.2}$Ni phase. So, we assume that the first exothermic peak is related to the crystallization of the amorphous phase which chemical composition is close to Mg$_{1.8}$Al$_{0.2}$Ni phase. After treatment at 320°C (temperature above the second peak), the Mg$_{1.8}$Al$_{0.2}$Ni phase crystallized better, peaks of residual Mg and Ni disappears whereas AlNi peaks persist. At this temperature, the ternary crystalline Mg$_3$AlNi$_2$ phase starts to form. The formation of this ternary compound could be attributed to excessive loss of Mg element as compared to Al one during milling to reach the composition of Mg$_{1.8}$Al$_{0.2}$Ni which is close to that of Mg$_{1.5}$Al$_{0.5}$Ni. This ternary compound was also obtained by Guanglie et al. [20] after calcination at 540-550°C and by Xiujuan et al [21] by combustion synthesis. This behavior was also seen for substitution of Mg by Ti (Mg$_3$TiNi$_2$) [15].

This is thermodynamically favorable when the overall energy is increased by a thermal activation. So, the second exothermic reaction is attributed to the formation of Mg$_3$AlNi$_2$ crystalline phase. After 410°C (temperature above the third peak), the AlNi crystalline peaks disappeared and the peak intensities of Mg$_{1.8}$Al$_{0.2}$Ni decreased considerably whereas, the Mg$_3$AlNi$_2$ phase crystallized better and better. So, the third peak is attributed to more formation of Mg$_3$AlNi$_2$ crystalline phase from AlNi phase and remaining Ni and Mg in the amorphous phase. After 500°C, XRD pattern analysis revealed that the alloy contained only two phases: the well crystallized Mg$_3$AlNi$_2$ phase and the Mg$_{1.8}$Al$_{0.2}$Ni phase.

So, by optimizing the milling and annealing conditions, we were able to obtain the Mg$_{1.8}$Al$_{0.2}$Ni crystalline phase after 8 h of mechanical alloying at 250 rpm, 6 h of mechanical alloying and annealing at 500°C or 7 h of mechanical alloying and annealing at 225°C.
CONCLUSION

Mg$_{1.8}$Al$_{0.2}$Ni nanocrystalline compounds were synthesized from pure magnesium, nickel and aluminum powders using mechanical alloying. The structural and thermal properties of the MA samples were analyzed. The Mg$_{1.8}$Al$_{0.2}$Ni alloys obtained after mechanical alloying duration ranging from 8 to 48 h are constituted of Mg$_{1.8}$Al$_{0.2}$Ni phase with hexagonal Mg$_2$Ni-type structure coexisting with AlNi phase. Thermal stability study revealed three exothermic peaks for the alloys obtained after 6 and 7 h of milling and four exothermic peaks for higher MA durations. For Mg$_{1.8}$Al$_{0.2}$Ni-7h alloys, the 1st exothermic peak is attributed to the crystallization of the amorphous phase in Mg$_{1.8}$Al$_{0.2}$Ni phase. The 2nd exothermic peak is attributed to the formation of nanocrystalline Mg$_3$AlNi$_2$ due to excessive loss of Mg element as compared to Al one during milling to reach the composition of Mg$_{1.5}$Al$_{0.5}$Ni. The third exothermic peak is related to more formation of Mg$_3$AlNi$_2$ crystalline phase from AlNi phase and remaining Ni and Mg in the amorphous phase.

REFERENCES