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# Effects of mechanical alloying on the hydrogen storage properties of the $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x = 4, 8$) materials

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ABSTRACT

A recent method to obtain hydrogen storage materials based on magnesium is mechanical alloying. This method offers some advantages by enhancing surface properties of material and alloying by intimately mixing the constitutive elements, at the atomic scale, in the same time with the required processing temperature and time reducing, which lead to a low cost of delivered materials. The aim of this research is to enhance the hydrogen storage capacity of the magnesium alloys by adding some elements such as Ti, Fe and Ni, by mechanical alloying. The $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x = 4, 8$) alloys were prepared by mechanical alloying for 10, 20 and 60 h in petroleum ether medium, followed by a subsequent thermal treatment at 450 °C for 3 h, in argon atmosphere. The milling time influence on the hydrogen storage properties of the obtained materials is presented. Increasing of milling time generates single-phase materials having enhanced homogeneity. The $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x = 4$) material has a hydrogen storage capacity of 5.33 wt% hydrogen, which is totally reversible. These materials can be used for the high temperature hydrogen storage applications.



## 1. Introduction

If hydrogen is to become a viable energy carrier in the future, there is a clear need for lightweight, safe and affordable hydrogen storage media. This has led in recent years, to the well-documented search for potential hydrogen storage materials. A number of recent review articles give good overviews of this work and there is a large amount of published research in the field [1–3].

Magnesium and magnesium rich alloys have attracted attention in recent years for their high hydrogen storage capacity, abundance and low cost. However, the high temperature required for the hydrogen absorption and desorption processes and poor kinetic characteristics hinder the applications of Mg-based alloys. In order to improve their thermodynamic and electrochemical performances many efforts have been done [4–10]. On the other hand, titanium based alloys are also among the most promising materials for electrodes due to their relatively good kinetics. Based on the high hydrogen capacity for both Mg and some Ti-based alloys, new compounds of Mg–Ti–Ni–Fe alloys, are developed [11–14].

So, for instance, Guo et al. [15], reported about the influence of milling time on the hydrogen storage properties of $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$, ($x = 0, 4, 8, 12$) alloys. They have shown that increasing milling time until 80 h, the amount of Mg amorphous phase increases, influencing the hydrogen storage properties of the obtained materials. Comparing the hydrogen storage properties of these alloys after 40 h of milling, they have shown that the alloys which contain both Ni and Fe elements exhibit much higher hydrogen storage capacity than those without these elements, e.g. $Mg_{76}Ti_{12}Fe_{12}$ and $Mg_{76}Ti_{12}Ni_{12}$. The maximum hydrogen storage capacity of 3.31 wt% was reached for the $Mg_{76}Ti_{12}Fe_8Ni_4$ material. Also, the hydrogen absorption plateau pressure for $Mg_{76}Ti_{12}Fe_8Ni_4$ and $Mg_{76}Ti_{12}Fe_4Ni_8$ was decreased. The authors explain this behaviour due to the both $Mg_2Ni$ and NiTi phase formation during mechanical milling. They also observed that the hysteresis between hydrogen absorption and desorption decreases gradually with increasing the amount of substitution Ni for Fe. They have shown that increasing milling time and, implicitly, the amorphous phase proportion, are unfavourable for improving hydrogen storage capacity. The present research continues the investigation realized by Jin Guo et al. and, in addition, proposes a post heat treatment step in order to remove the mechanical tensions induced by milling and to replace the amorphous phase.

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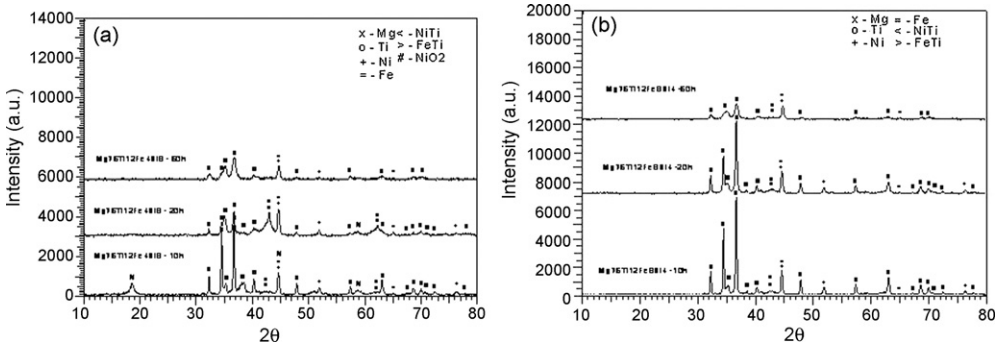



**Fig. 1.** (a, b) X-ray diffraction patterns for the $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x$ = 4, 8) alloys, after 10, 20 and 60 h of mechanical alloying (a) $x$ = 4; (b) $x$ = 8.

The present paper reports the influence of mechanical alloying followed by annealing on the hydrogen storage capacity of $Mg_{76}Ti_{12}Fe_8Ni_4$ and $Mg_{76}Ti_{12}Fe_4Ni_8$ alloys.

## 2. Experimental

The starting materials for mechanical alloying were Mg (<100 μm), Ni (<10 μm), Fe (<100 μm) and Ti (<100 μm) and the purity were above 99.9% for all elements. The selected composition of metallic powders were mixed and were mechanical alloyed in a planetary ball mill with a rotation speed of 300 rpm, in petroleum ether medium for 10, 20, 30 and 60 h. The powders were placed in stainless steel vials together with stainless steel balls of 5, 10 and 12 mm in diameter. The ball-to powder ratio was 10:1. The 60 h mechanical alloyed material has been subsequently annealed at 450 °C for 3 h in argon atmosphere, in order to crystallize the amorphous phases.

Special attention was given to powders handling during the entire technological process in order to avoid, as much as possible, the powder-air contact. A great deal of attention was given to the dosing, mixing and filling the vials of the mill, as well as to the samples analysis. Also, the samples were extracted from the vials in an inert atmosphere, into a glove-box.

The crystal structures of the $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x$ = 4, 8) type alloys were determined by X-ray diffraction, with Cu Kα radiation and Ni Kα filter operated at 40 kV and 100 mA. The PDF file diffractions were used to determine the phase formation.

The microstructural aspects were evidenced using a scanning electron microscope of JSM 5600 LV type and the quantitative chemical microanalysis was done using an energy dispersive X-ray spectrometer of Oxford Instrument type.

To prevent oxidation of samples for microscopic and X-ray diffraction analyses, the powders were soaked in a special solution.

Hydrogen absorption–desorption isotherm curves for the studied alloys were obtained by the volumetric method using a Sievert-type apparatus, which was presented previously [16].

Previous to this process, the samples were activated by vacuuming them at 400 °C for 3 h, followed by a reduction in temperature to 300 °C. Once the temperature stabilized, the hydrogen was introduced over the sample into the reactor at pressure of 60 bars and was kept overnight. The vacuuming process was repeated until the absorption capacity remained constant.

This activation was necessary because it is well known that FeTi [1] and $Mg_2Ni$ [2] type alloys need an activation treatment before testing due to their superficial oxide layer, gasses and humidity absorbed by their surfaces, that inhibit hydrogen absorption. Finally, the pressure–composition isotherms were collected at the following temperatures: 300, 330 and 360 °C.

## 3. Results

### 3.1. Crystal structures

Fig. 1a and b shows the X-ray diffraction patterns for $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x$ = 4, 8) alloys, mechanically alloyed for 10, 20 and 60 h, respectively.

As Guo et al. have shown [15], and in concordance with the phase diagram, the main phases of the $Mg_{76}Ti_{12}Fe_{12}$ and $Mg_{76}Ni_{12}Ti_{12}$ alloys are $Fe_2Ti$ and $Mg_2Ni$, respectively, and as a consequence, these phases should be also found in the $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x$ = 4 and 8) type alloys, together with the secondary NiTi phase.

By indexing the X-ray patterns of the interested materials after 10, 20 and 60 h of milling, it is clear that the mechanically milled mixtures are partially reacted. The pure constituent can be observed together with the new formed NiTi and FeTi phases. The increasing of mechanical alloying time leads to the substantially increasing of new formed phases amounts.

Regarding the Ni content influence on the new phases formation in the system, it is shown that by increasing of Ni content from 4 to 8 wt%, the Mg peak intensity diminishes, owing to the Ni and Mg alloying, Fig. 2. A big amount of Ni content favours the development of the $Mg_2Ni$ synthesis reaction. With increasing the milling time, the Mg peak gradually decreases and the diffraction profile become broadened, meaning that amorphisation degree is increasing.

After 60 h of mechanical milling, the intensity of diffraction peaks is strongly weakened. This shows that with milling time increasing, both the amount of the new formed phases and the amorphisation degree of material are increasing. After the post heat treatment step, the 60 h mechanical alloyed $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x$ = 4, 8) materials perform a phase change by thermal activation, from the amorphous to the crystalline phase (Fig. 3). Increasing of crystalline phase is contributing to the change of crystal lattice parameters by the reorganization of atoms.

The heat treatment assures the reducing of crystal lattice parameters. The nickel oxide formation after the annealing treatment might be the effect of a poor handling of powders or the effect of too long deposition time, in the case of the $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x$ = 8) material.

### 3.2. Microstructural aspects

In this paper, microstructural aspects were evidenced only for the $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x$ = 4) material. The analysis has shown the powder morphology, the surface shape, the microstructural and the chemical homogeneity degree. After 60 h of mechanical alloying, the general view reveals the obtaining of some relatively homogeneous mechano-composite conglomerates, having a stratificate structure with very fine elemental powders (Fig. 4a). Also, the same aspect is evidenced for the annealed materials (Fig. 4b), but in this case, the boundaries between the small elemental powders of the mechano-composite powders, are less evidenced (Fig. 4c and d).

The mechano-composite powders are different in size and shape, being close to the polygonal shape having rounded planes, for both processing variants.

The quantitative chemical analysis (Fig. 5) reveals the fact that the processed materials have the chemical composition very close to that of the starting mixture.

In the particles, the constitutive elements are well dispersed, some small clusters of nickel and iron being also present. The low amount of magnesium might be the reason for the amorphisation effect after 60 h of milling.

### 3.3. Hydrogen storage properties

Fig. 6a and b shows the hydrogen sorption/desorption isotherms for the $Mg_{76}Ti_{12}Fe_4Ni_8$ alloy, after 60 h of mechanical milling and

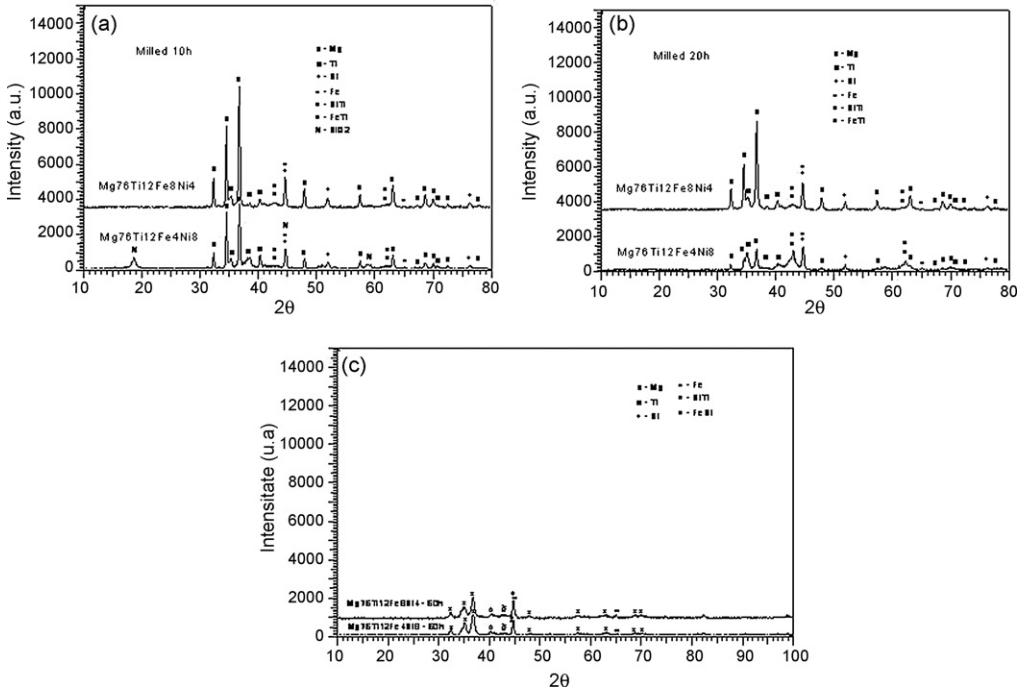



**Fig. 2.** (a, b) X-ray diffraction patterns for the $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x = 4, 8$) alloys, after 10, 20 and 60 h of mechanical alloying.

**Table 1**
The heat of reaction and the entropy variation in the $Mg_{76}Ti_{12}Fe_4Ni_8$–$H_2$ system.

| Process type | $\Delta H$ (kJ/mol $H_2$) | $\Delta S$ (J/mol $H_2$) |
|---|---|---|
| Sorption | 73.6 | 132.4 |
| Desorption | 73.1 | 129.6 |

**Table 2**
The values of the reaction enthalpy ($\Delta H$) and of the entropy variation ($\Delta S$), as obtained from the van't Hoff representations for the hydrogen absorption and desorption process for the $Mg_{76}Ti_{18}Fe_8Ni_4$(TT)–$H_2$ system.

| Process | $\Delta H$ (kJ/mol $H_2$) | $\Delta S$ (J/mol $H_2$) |
|---|---|---|
| Absorption | 71.79 | 128.37 |
| Desorption | 69.58 | 123.6 |

annealing at 450 °C for 3 h, at the following temperatures: 300, 330 and 360 °C. This material has a maximum hydrogen storage capacity of 4.75 wt%, which is basically completely desorbed at the temperatures that were investigated.

The presence of only one plateau is clear evidence that this alloy has hydrogen behaviour of a single phase. It can also be noticed that this alloy has a close to zero hysteresis, as is shown in Fig. 7, which presents the hydrogen absorption and desorption isotherms for the thermal treated $Mg_{76}Ti_{12}Fe_4Ni_8$ alloy at 300 °C.

In Table 1, the heat of reaction and the entropy variation in the $Mg_{76}Ti_{12}Fe_4Ni_8$–$H_2$ system determined by using the van't Hoff ($\ln P_H = f(1/T)$) representation, are presented.

The $Mg_{76}Ti_{12}Fe_8Ni_4$ materials have a maximum hydrogen storage capacity of 5.33 wt% which is better than the value proper to the $Mg_{76}Ti_{12}Fe_4Ni_8$ materials (Fig. 8).

This hydrogen amount can be completely desorbed over the temperature domain that was studied.

The existence of a single plateau pressure is a clear evidence that the alloy has a single phase behaviour (Fig. 9).

From the van't Hoff representation, $\ln P_{H_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$ there were calculated the values for the variation of the enthalpy ($\Delta H$) and entropy ($\Delta S$) energies, characteristic to the hydrogen reaction process with the $Mg_{76}Ti_{12}Fe_8Ni_4$ alloy. The values of the plateau pressures used in this representation are those corresponding the middle of the plateau (~2.5 wt% H), both for absorption and desorption.

The values of the thermodynamic energies ($\Delta H$ and $\Delta S$) characteristic to the absorption/desorption process for the $Mg_{76}Ti_{12}Fe_8Ni_4$–$H_2$ system at 300 °C are shown in Table 2.

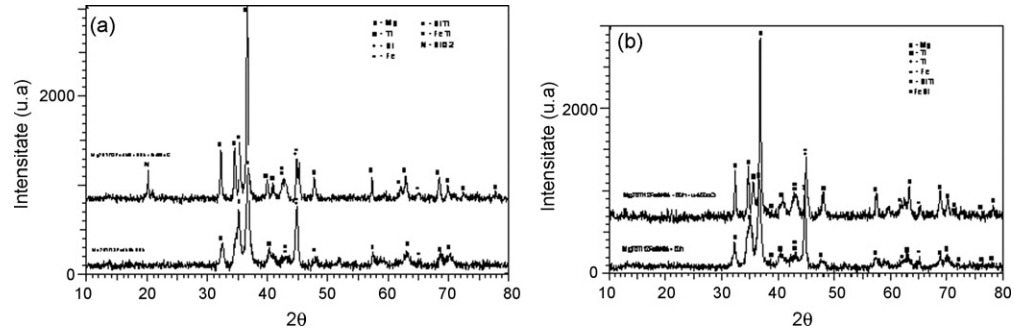



**Fig. 3.** (a, b) Heat treatment influence on the amorphisation degree and on the phase transformation in the 60 h mechanical milled $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ materials—(a) $x = 4$; (b) $x = 8$.

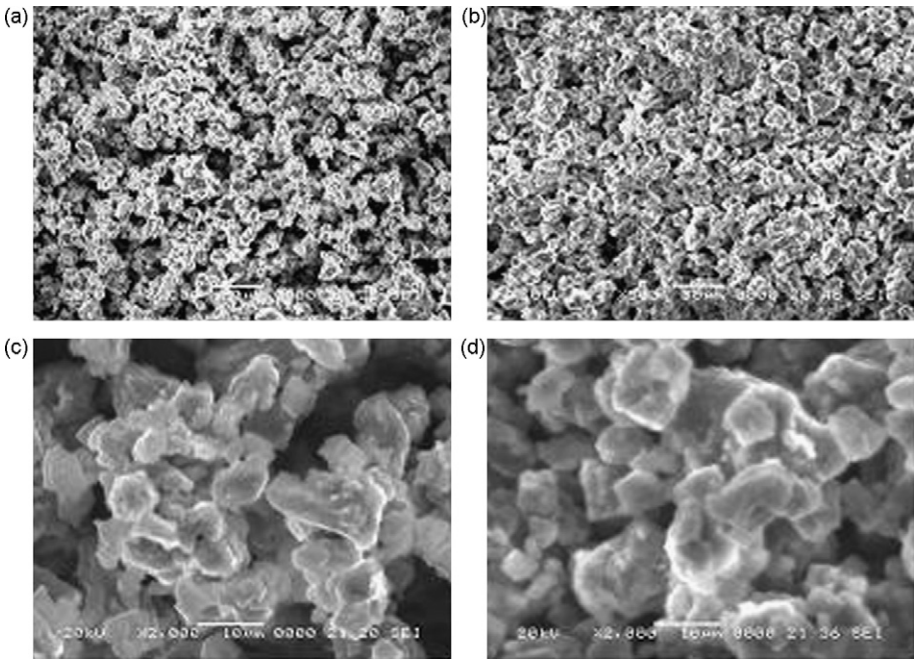
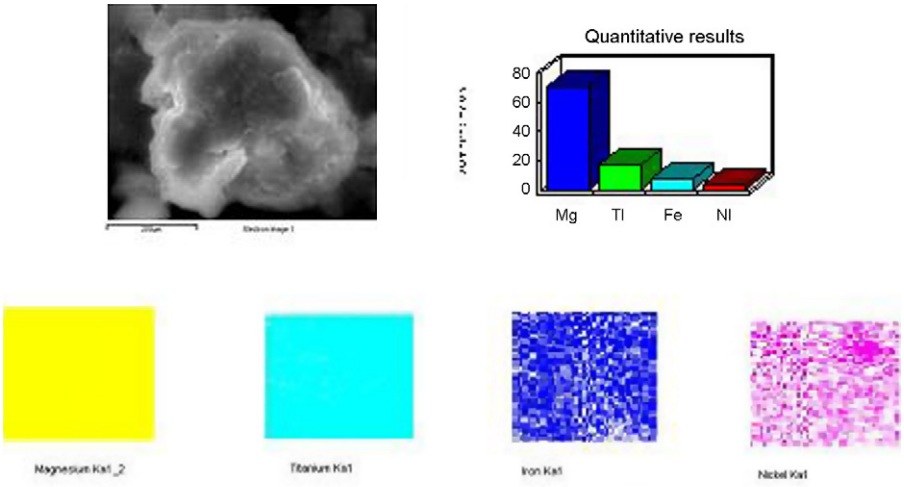



**Fig. 4.** (a, b, c, and d) The mechano-composite powders morphology of the $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x = 4$) materials.

## 4. Discussions

The activation of the samples was done at 400 °C, which is below the thermal treatment value, in order to avoid structural modifications which were observed at 450 °C. In Fig. 10 it is represented the variation of the hydrogen absorption capacity as a function of the number of activation cycles.

The analysis of the figure indicates the need for five activation cycles until the maximum hydrogen absorption capacity was obtained. This behaviour can be explained by the formation of Fe-




| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|
| Mg K | 61.54 | 0.8756 | 71.33 | 0.20 | 83.92 |
| Ti K | 14.85 | 0.8598 | 17.52 | 0.13 | 10.46 |
| Fe K | 6.27 | 0.8651 | 7.36 | 0.15 | 3.77 |
| Ni K | 3.25 | 0.8718 | 3.79 | 0.16 | 1.85 |
| Totals | | | 100.00 | | |

**Fig. 5.** The chemical quantitative analysis for a 60 h mechanical alloyed mechano-composite powders.

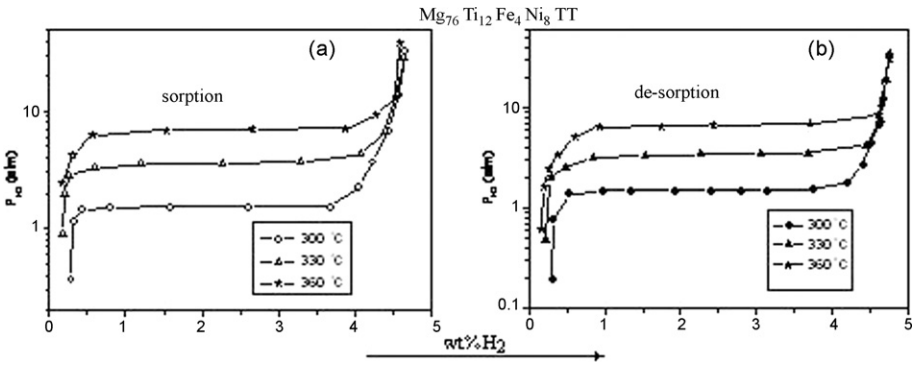



**Fig. 6.** The absorption/desorption isotherms for $Mg_{76}Ti_{12}Fe_4Ni_8$ alloy, after 60 h mechanical milling and annealing at 450 °C for 3 h.

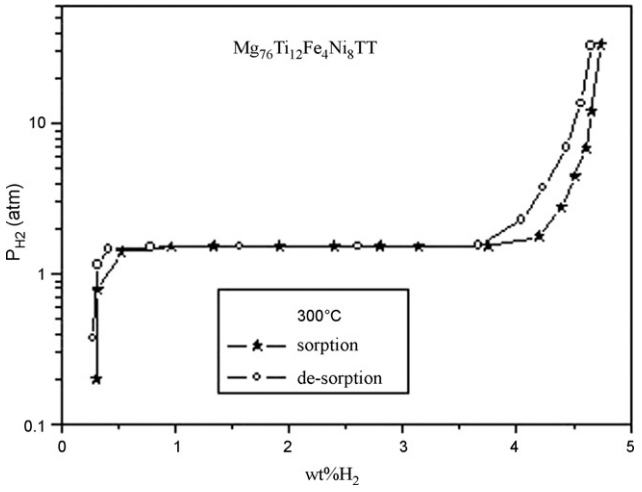



**Fig. 7.** The absorption/desorption isotherms for the heat treated $Mg_{76}Ti_{12}Fe_4Ni_8$ alloy at 300 °C.

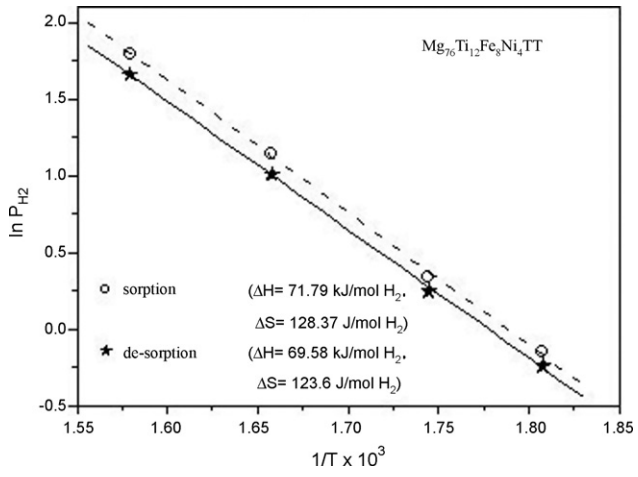



**Fig. 9.** The van't Hoff ($\ln P_H = f(1/T)$) representation for the $Mg_{76}Ti_{12}Fe_8Ni_4$–$H_2$ system.

rich clusters on the alloy surface and which have a catalytic role in the dissociation of the hydrogen molecule [3] and the need for the formation of clean surfaces through the process of breaking up of the powder particles [4]. Presence of iron clusters identified by SEM-EDS show that the activation treatment of materials before the beginning of hydrogen storage measurements can be similar with the activation treatment of FeTi alloy which develops Fe-rich clusters near its surface, with a catalytic role in the hydrogen molecule dissociation reaction [3].

The obtained results are in concordance with those described by Guo et al. [15]. After mechanical alloying the both obtained materials are of multiphase type. As present phases being identified near the residual phases, namely Mg, Ni and Ti, are the new formed phases—NiTi, FeTi, $Mg_2Ni$ and $Fe_2Ti$. Similar with results of Guo et al. [15], the increasing of milling time contributes to the increasing of the amorphous phase proportion. Increase of Ni content from 4% to 8% produces an increase of amorphisation degree.

In view of hydrogen storage capacity, the untreated materials exhibit inadequate properties. These results are not discussed in this paper but they are similar with the results obtained by Guo et al. [15]. The heat treated materials exhibit good hydrogen storage capacity properties. Compared with the results presented in [15], the $Mg_{76}Ti_{12}Fe_8Ni_4$ material exhibits the best hydrogen storage

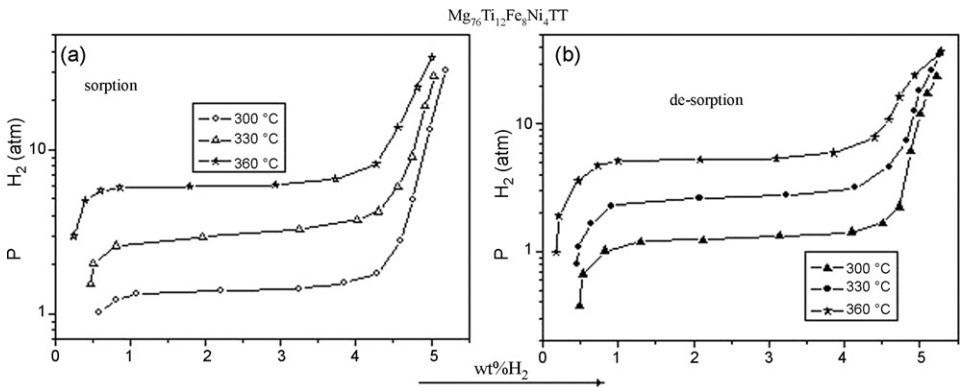



**Fig. 8.** The absorption/desorption isotherms for $Mg_{76}Ti_{12}Fe_8Ni_4$ ($x = 8$) alloy, after 60 h mechanical milling and annealing at 450 °C for 3 h.

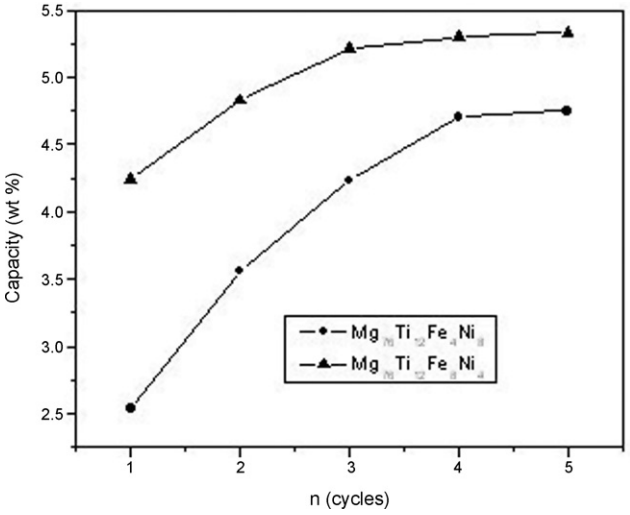



**Fig. 10.** Variation of the hydrogen absorption capacity for the alloy family $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x$ = 4 and 8), as a function of the number of activation cycles.

capacity in mechanical milled state, and kept this advantage after heat treatment. The heat treatment assures increasing of hydrogen storage properties of the materials of approximately 2 times for both compositions.

## 5. Conclusions

- The binary alloy phase structures, namely FeTi, $Mg_2Ni$ and NiTi have been found in the $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ ($x$ = 4, 8) alloys.
- Increase of Ni content from 4 to 8 wt% contributes to the increasing of the amorphisation degree of powders.
- 60 h mechanical alloying allows the obtaining of very homogenous materials.
- The heat treatment of the mechanically alloyed materials for 60 h, have conducted to the obtaining of very homogeneous materials.
- With Ni content increasing, the hydrogen storage capacity is decreasing.
- The applied post thermal treatment assures increasing of hydrogen storage capacity of approximately 2 times, for both compositions, when compare it with the mechanical milled state.
- The $Mg_{76}Ti_{12}Fe_8Ni_4$ materials have high hydrogen storage capacity (5.33 wt%) and high reversibility degree and can be used for the high temperature hydrogen storage applications.

## Acknowledgement

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