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TbMgNi_{4-x}Co_x-(H,D)₂ System: I. Synthesis, Hydrogenation properties, Crystal and Electronic structures

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Abstract

Series of cubic TbMgNi_{4-x}Co_x ($x = 0-4$) pseudo binary compounds have been synthesized either by solid state reaction or mechanical alloying with further annealing treatment. Their hydrogenation properties have been studied by Pressure-Composition-Temperature (*PCT*) measurements, showing the formation of α -, β - and γ -hydrides. The Co for Ni substitution yields a lowering of the equilibrium pressure and an increase of hydrogen capacity. An improvement of the kinetic of hydrogen absorption was observed for increasing Co content. The β -TbMgNi_{4-x}Co_xH₄ ($x = 0-3$) hydrides show an orthorhombic distortion (*Pmn*2₁ space group) whereas β -TbMgCo₄H_{3.3} hydride crystallizes in a monoclinic structure (*Pm* space group) derived from the orthorhombic structure. Sensitivity of the formation of the β -TbMgCo₄H_{3.3} hydride to the temperature has been observed in *PCT* curves: it exists below 50 °C. γ -TbMgNi_{4-x}Co_xH_y ($x = 2-4$, $y > 5$) hydrides preserve the parent cubic structure (*F*-43*m* space group) with an hydrogen induced volume expansion of 17.9–22.3 %. The deuterium for hydrogen substitution in TbMgNiCo₃-(H,D)₂ system prevents fast desorption at room temperature and ambient pressure. The positions of deuterium atoms in the γ -TbMgCo₄D₆ deuteride were determined by neutron powder diffraction. Two types of interstitial sites were found occupied: 87 % of deuterium atoms (D1 site) are located inside Tb₂MgCo₂ octahedra and the remaining 13 % (D2 site) are inside Co₄ tetrahedra. The increase of Co content allows to improve the thermodynamic stability of TbMgNi_{4-x}Co_x hydrides as demonstrated by the lowering of the desorption plateau pressure, the increase of the desorption temperature and of the enthalpy of formation versus Co content. This last experimental result is confirmed by first principles calculations where electronic structures of intermetallic compounds and their cubic TbMgNi_{4-x}Co_xH₆ hydrides are compared for $x = 0, 2$ and 4 .

1. Introduction

Magnesium metal is one of the most attractive material for hydrogen storage with high hydrogen capacity (7.6 wt.%). However, due to some drawbacks as low kinetic and high hydride stability, its use as a medium for energy storage and transportation is limited. To improve both thermodynamic and kinetic properties, Mg-based binary and ternary intermetallic compounds have been extensively investigated¹⁻⁴. Considerable research has been made on magnesium based composite materials, which have improved sorption-desorption characteristics⁵⁻⁸.

The R -Mg- T (R = rare earth, T = Ni, Co, Cu) ternary alloys have attracted interest as hydrogen absorbing materials and particularly as effective negative electrodes for Ni-MH batteries. Mg-rich ternary compounds are of practical interest because their hydrogen capacity can reach 5.5 wt.%^{2,4}. Moreover, Mg-rich alloys, containing more than 50 wt.% of Mg, decompose under hydrogenation into MgH₂, binary rare-earth hydrides (e.g., RH_x) and ternary magnesium transition-metal hydrides (e.g., Mg₂NiH₄)⁴. Nevertheless, these alloys have very interesting hydrolysis properties useful for hydrogen gas recovery⁹. At the same time, R -rich compounds can absorb hydrogen up to 2 wt.% and form crystalline or partially amorphous hydrides, but they decompose during desorption¹⁰⁻¹³. Finally, ternary or pseudo-binary Mg-containing compounds from the T -rich region can reversibly absorb hydrogen from the gas phase or electrochemically (~1.6 wt.%)². For example, it is shown that the partial R substitution by Mg enhances hydrogen absorption properties of the binary RNi₂, RNi₃, R₂Ni₇ and R₅Ni₁₉ compounds¹. Compared to binary R_xNi_y phases, Mg-containing alloys (R_{x-z}Mg_zNi_y) have higher resistance against hydrogenation induced amorphization and thus form crystalline hydrides¹⁴⁻¹⁶. Rare earth-magnesium-based alloys played increasing roles in the solid-state hydrogen storage field.

Since Oesterreicher *et al.*¹⁷ firstly studied LaMgNi₄ compound with MgCu₂/SnMgCu₄ structure type, many studies have been performed on the hydrogenation properties of the RMgNi₄ compounds (preferably with R = light rare earth)^{1,4,18}. Our group has systematically investigated RMgNi_{4-x}Co_x compounds for R = Ce¹⁹, Y²⁰, Nd²¹, La²² and Pr²³], where a 50 % increase of the hydrogen capacity was found upon Co for Ni substitution.

In this work, we have synthesized TbMgNi_{4-x}Co_x alloys to show the influence of Tb as a heavy rare earth on the hydrogenation properties and crystal structure of the hydrides. The results obtained for these compounds are compared with those obtained for light rare earth.

In addition, first principles calculations were performed in the frame of electronic density functional theory (DFT) to analyze the modification of the electronic structures of TbMgNi_{4-x}Co_x compounds upon hydrogen insertion and compare their phase stability with the experimental results.

2. Experimental methods

Starting materials for preparation of TbMgNi_{4-x}Co_x (x = 0–4) intermetallic compounds (IMC) were ingots of Tb, Ni and Co (all with purity ≥ 99.9 %), and Mg powder (325 mesh, 99.8 %). In the first step, TbNi_{4-x}Co_x (x = 0–4) alloy precursors were prepared by arc melting in purified argon atmosphere. The as-cast TbNi_{4-x}Co_x buttons were ground in an agate mortar and then mixed with Mg powder in certain proportions. Mg was added with 3 wt.% excess in order to compensate for its evaporation loss at high temperatures. The powder mixtures were pressed into pellets, placed into tantalum containers, which were further loaded into a stainless-steel autoclave and sealed under Ar atmosphere. Alloys further denoted as No. 7 and No. 9 have been ball milled for 8 h in Ar atmosphere and placed into tantalum container without compressing. Then, several attempts have been made to prepare single phase alloys. All aspects of the heat treatment are summarized in Table 1. Structural analysis of the samples was carried out by X-ray powder diffraction (XRD) using Bruker D8 diffractometer (Cu-K α radiation).

Electron Probe Micro Analysis (EPMA) has been performed for selected samples using SX 100 CAMECA with dispersion analysis of wavelength (WDS) to study the microstructures and elemental

compositions of the alloys. Pieces of the samples were placed in an aluminum holder, filled by Wood's alloys and then optically polished for analysis. The experimentally observed compositions were all within ± 0.1 at. %.

Table 1. Conditions of synthesis and results of XRD analysis of TbMgNi_{4-x}Co_x ($x = 0-4$) alloys.

No.	Alloy	Heat treatment	Cell parameter a (Å)	Composition according to Rietveld refinements	Phase analysis
1	TbMgNi ₄	Slowly heated to 800 °C, then cooled to 500 °C and annealed at this temperature for ~250 h, quenched in cold water	7.0205(1)	TbMgNi ₄	~99 % TbMgNi ₄ + 1 % Tb ₂ Co ₇
2	TbMgNi ₃ Co		7.0333(1)	TbMgNi ₃ Co	100 % TbMgNi ₃ Co
3	TbMgNi ₂ Co ₂		7.0452(1)	Tb _{0.87} Mg _{1.13} Ni ₂ Co ₂	93 % TbMgNi ₂ Co ₂ + 7 % TbCo ₅
4	TbMgNi ₂ Co ₂		7.0441(3)	Tb _{1.03} Mg _{0.97} Ni ₂ Co ₂	94 % TbMgNi ₂ Co ₂ + 6 % TbCo ₅
5	TbMgNi ₂ Co ₂		7.0440(1)	Tb _{1.03} Mg _{0.97} Ni ₂ Co ₂	91 % TbMgNi ₂ Co ₂ + 6 % TbCo ₅ +3 % Tb ₂ Ni ₇
6	TbMgNiCo ₃		7.0500(1)	Tb _{1.02} Mg _{0.98} NiCo ₃	91 % TbMgNiCo ₃ + 2 % Tb ₂ Ni ₇ +6 % Tb ₂ Co ₇
7	TbMgCo ₄	8 h at 800 °C, then quenched in cold water	7.0741(1)* 7.0778(1)	Tb _{1.07} Mg _{0.93} Co ₄	100 % TbMgCo ₄
8	TbMgCo ₄	12 h at 550 °C, then 1 h at 980 °C, 2 h at 1000 °C, 20 h 900 °C and 10 h at 750 °C	7.0755(2)	Tb _{1.04} Mg _{0.96} Co ₄	~99 % TbMgCo ₄ + 1 % Mg
9	TbMgCo ₄	50 h at 700 °C	7.0723(2)	Tb _{0.92} Mg _{1.08} Co ₄	82 % TbMgCo ₄ + 17 % Tb ₂ Co ₇ + 1 % TbCo ₅
10	TbMgCo ₄	18 h at 800 °C, then 48 h at 600 °C	7.0763(1)	Tb _{0.91} Mg _{1.09} Co ₄	96 % TbMgCo ₄ + 4 % MgO

* – data from SRXRD (Synchrotron Radiation X-Ray Diffraction).

Hydrogen absorption-desorption properties of the alloys were characterized using a Sieverts type apparatus. The samples were activated by heating up to 200 °C in dynamic vacuum, cooled to room temperature and then hydrogenated with high purity hydrogen gas (99.999%). Pressure–Composition–Temperature (*PCT*) curves were measured under H₂ pressures from 0.01 to 100 bar at temperatures between 25 and 50 °C. The hydride sample holder was put into liquid nitrogen (77 K) for 30 minutes at a final internal pressure. Then the pressure in the sample-holder was gradually reduced to 1 bar and the hydrogenated samples exposed to air, heated to room temperature and removed from the sample holder. This procedure allows to passivate the surface by a thin oxide layer and to avoid fast hydrogen desorption at ambient pressure and temperature. Then the samples were transferred into small containers and placed in liquid N₂ or fridge to keep them for further different investigations. 6 g of TbMgCo₄ deuteride has been prepared from sample No. 10 (Table 1) for the investigation by neutron powder diffraction (NPD).

The XRD patterns of the hydrides were repeatedly measured on air to follow the partial decomposition with time into initial compounds.

Synchrotron radiation X-ray diffraction experiments (SRXRD) have been performed at room temperature on CRISTAL beam line of synchrotron SOLEIL for selected hydrides and deuterides. The powders were placed in

glass capillaries (0.2-0.3 mm). The wavelength of the monochromatic beam, refined with a LaB₆ reference, was $\lambda = 0.6713 \text{ \AA}$. A Mythen multidetector has been used to obtain a good statistic on a large Q range (1-12.7 \AA^{-1}).

In situ Synchrotron Radiation XRD study was carried out on the BM01B line at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on high-resolution diffractometer using monochromatic X-ray beam ($\lambda = 0.5012 \pm 0.0002 \text{ \AA}$). Thin quartz capillary (diameter 0.5 mm, wall thickness 0.01 mm) was filled by the investigated alloy powder (2–5 mg, sample No.7) and placed in a special quartz cell mounted on a goniometer head and connected to the gas system through a flexible plastic tube. The heating and cooling of the sample was performed using a programmable cryofluidic system with working temperature range -196–230 °C. Initially the sample was heated in a dynamic vacuum to 150 °C and when one reaches this temperature, the hydrogen gas (99.999% purity) was introduced into a quartz cell. Under these conditions, "activation" of the alloy was done and a solid solution of hydrogen in IMC was formed. Further, the sample was slowly cooled (5 K/min) to room temperature to achieve the hydride formation.

Neutron powder diffraction (NPD) data for TbMgCo₄D₆ deuteride has been collected at room temperature using the high resolution 3T2 powder diffractometer at the Laboratoire Léon Brillouin (LLB, CEA, Saclay, France) with $\lambda = 1.225 \text{ \AA}$ (angular range $4.5^\circ \leq 2\theta \leq 121^\circ$ and a step of 0.05°). Deuteride has been transported to the neutron reactor in a cooled reservoir and transferred into vanadium container. Rietveld refinements of the X-ray and neutron data were done with FullProf suite software²⁴.

DSC experiments were performed using Discovery DSC 25 of TA instrument. The heating rate was 5 or 10 K/min.

3. Results and discussion

3.1. Synthesis and crystal structure refinement of TbMgNi_{4-x}Co_x

TbMgNi_{4-x}Co_x ($x = 0-4$) alloys with stoichiometric compositions 1:1:4 have been synthesized (Table 1). Such RMgT₄ ternary IMC crystallize in the SnMgCu₄ structure type, which is an ordered variant of the AuBe₅ type (space group $F\bar{4}3m$). They can be considered also as derivatives of the cubic MgCu₂ type structure (space group $Fd\bar{3}m$). Cell parameter of TbMgNi₄ compound synthesized in this work, $7.02047(6) \text{ \AA}$, is in good agreement with literature data, $7.0365(4) \text{ \AA}$ ²⁵. The unit cell volume V of TbMgNi_{4-x}Co_x IMC increases almost linearly versus Co content (Fig. 1), with a deviation for $x = 3$. However, the chemical composition of this IMC measured by WDS is Tb_{0.96(1)}Mg_{1.05(2)}Ni_{1.03(3)}Co_{2.96(4)} in agreement with the nominal composition and cannot explain this deviation. Previous studies reported partial disordering of rare earth and magnesium atoms between $4a$ and $4c$ sites in the structures of RMgNi_{4-x}Co_x compounds^{19-21,25}. In this work a small deviation from the 1:1:4 stoichiometry has been observed as well. At the beginning, crystal structure refinements have been performed assuming ordered 1:1:4 composition. However, this resulted in a negative B_{iso} parameter for Mg atoms in $4c$ position for TbMgNi_{4-x}Co_x ($x = 2, 3$ and 4). Refinements of site occupancies gave us positive value of B_{iso} and Mg concentration in the range $0.92(1)-0.98(1)$ Mg atoms per formula unit (at./f.u.). Apparently, it is related to the difficulty to prepare stoichiometric Mg-based alloys, as Mg can easily evaporate at synthesis conditions. According to the different

synthesis protocols, undesirable impurity phases still exist in some of the TbMgNi_{4-x}Co_x alloys (TbT₅ and Tb₂T₇). Crystallographic parameters of TbMgNi_{4-x}Co_x ($x = 0-4$) ternary compounds obtained from X-ray diffraction data are given in Tables 1 and S1 (supplementary material). SRXRD pattern of TbMgCo₄ is presented in Fig. S1 for comparison with XRD patterns of the selected hydrides.

The formation of ordered RMgCo₄ compounds was also found for $R = \text{Ce}^{19}$ and Y^{20} , but not for $R = \text{La}^{22}$, Pr^{23} , Nd^{21} . It is explained by the small solubility of Mg in RCo₂ as only 6 at. % of Mg is found for $R = \text{Nd}^{12}$, while it reaches 16–20 at. % for $R = \text{Y}^{26}$ and Tb^{27} . Co-containing alloys can be synthesized by Co for Ni substitution in the RMgNi_{4-x}Co_x IMC, but are limited to $x = 3$ Co at./f.u. for light $R = \text{La}^{22}$, Pr^{23} , Nd^{21} . The formation of NdMgNi_{4-x}Co_x compounds ($x = 0-3$) with cubic structure has been found, whereas NdMgCo₄ does not form²¹.

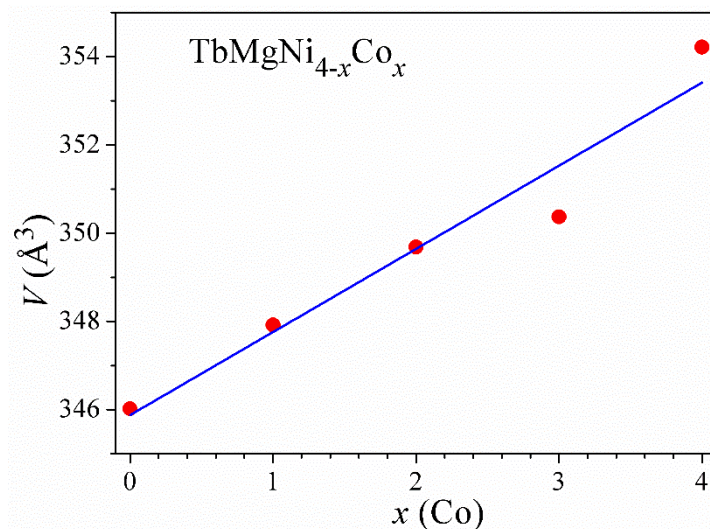


Fig. 1. Change of the unit cell volume with Co content for TbMgNi_{4-x}Co_x ($x = 0-4$) compounds.

3.2. Hydrogen absorption properties of the TbMgNi_{4-x}Co_x

After an activation pretreatment at 200 °C under primary vacuum, all the pseudo-binary TbMgNi_{4-x}Co_x ($x = 0-4$) alloys readily absorb hydrogen at room temperature. Hydrogen storage capacity reaches 3.3 to 6 H at./f.u. depending on the Co content. The absorption isotherms at 25 °C are shown in Fig. 2a. All the compounds present a plateau corresponding to $\alpha \rightarrow \beta$ phase transformation with equilibrium pressure decreasing from 10.9 to 1 bar of H₂ for TbMgNi₄ to TbMgCo₄ compounds respectively (Fig. 2b). It was not possible to observe second plateaus in *PCT* curves of TbMgNi₄ and TbMgNi₃Co because the maximum pressure of the setup was limited to 100 bar H₂ while higher plateau pressures are expected. A second plateau corresponding to $\beta \rightarrow \gamma$ phase transformation was nevertheless observed for the TbMgNi_{4-x}Co_x compounds with larger Co content ($x = 2, 3$ and 4). It is clearly visible that with increasing Co content and therefore cell volume of the alloys, the equilibrium pressure of the first plateaus decreases as expected from the inverse relationship between equilibrium pressure and cell volume. The same trend has been observed for the second plateau. In addition, the pressure difference between first and second plateaus decreases as a function of Co content. Dependences of the equilibrium pressure versus the Co content are presented in Fig. 2b. The pressure of the first plateau changes sharply for $x = 0$ to 2 and with a smaller slope for $x = 2$ to 4. The equilibrium pressure of the second plateaus decreases sharply as x increases from 2 to 4.

An interesting finding has been observed for TbMgCo₄-H₂ system. At T = 25 °C two plateaus exist, while at T = 50 °C only one prolonged plateau has been observed (Fig. 2c). However a change of slope is seen in the absorption and desorption curve at 50 °C for ~3.6 H at./f.u. It shows the sensitivity of the formation of this β -hydride to the temperature which critical temperature of formation should be between 25 and 50 °C.

First hydrogenation curves of selected alloys are presented in Fig. 2d. An improvement of the kinetics of hydrogen absorption was observed for increasing Co content. The difference in the hydrogenation curves at different Co-content primarily resulted from the difference of rate in the short initial period of reaction.

Reaction kinetic curves were analyzed with Johnson–Mehl–Avrami (JMA) equation²⁸:

$$\ln(-\ln(1 - \xi)) = \ln(k) + n \cdot \ln(t) \text{ or } y = 1 - \exp(-(k \cdot x)^n)$$

ξ stands for the reaction fraction after a certain period of reaction time t ; k is the reaction rate constant; and n is the Avrami exponent, related to the system geometry.

The values of the reaction rate constant k and the Avrami exponent have been calculated for different compounds from JMA equation from the best fits of the kinetic data under isothermal conditions (Table 2). For all compounds, hydrogenation region at 10 bar H₂ was taken into account. It is noticeable that both k and n increase with the Co content. The obtained data shows that the hydrogenation rate increases with Co content. Similar results were obtained for Pr- and Pr_{0.5}La_{0.5}-containing alloys²³.

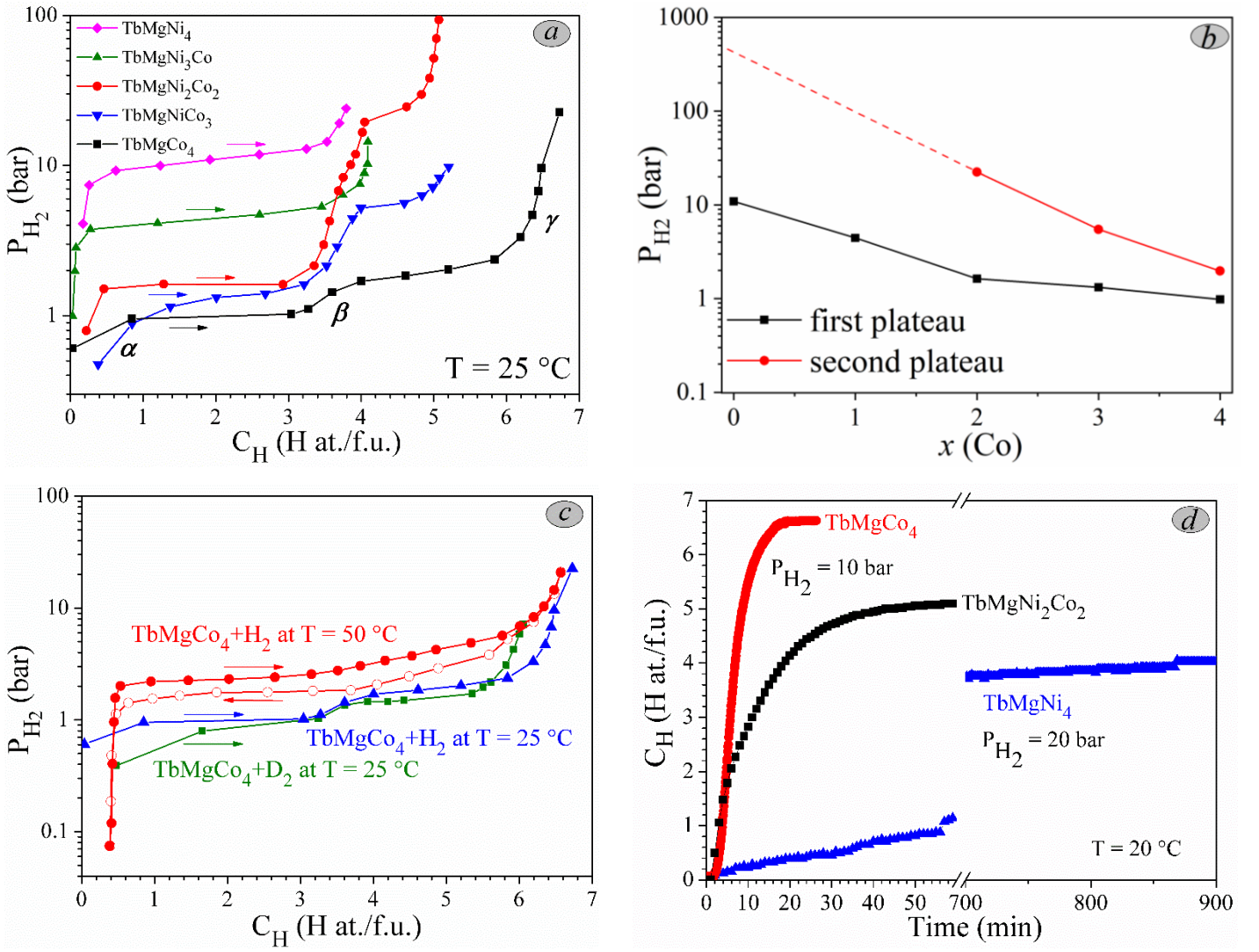


Fig. 2. Hydrogenation properties of the $\text{TbMgNi}_{4-x}\text{Co}_x$ alloys: hydrogen absorption isotherms at 25 °C (a); evolution of the equilibrium pressure with $x(\text{Co})$ (b), comparison of PCT curves for the $\text{TbMgCo}_4\text{-H}_2$ system at 25 and 50 °C (c), and first hydrogenation curves for the $\text{TbMgNi}_{4-x}\text{Co}_x$ (d).

Table 2. JMA kinetic parameters of the formation of $\text{TbMgNi}_{4-x}\text{Co}_x$ hydrides.

Compound	$\ln(k)$	k	n	R^2
TbMgNi_4	-9.3763	$8.47 \cdot 10^{-5}$	0.87(1)	0.9855
$\text{TbMgNi}_2\text{Co}_2$	-6.6003	$1.36 \cdot 10^{-3}$	1.04(1)	0.9983
TbMgCo_4	-6.1193	$2.1 \cdot 10^{-3}$	2.16(3)	0.9947

In all $\text{RMgNi}_{4-x}\text{Co}_x\text{-H}_2$ systems, the hydrogen capacity and kinetics of the hydride formation is improved by introduction of Co ^{20-23,29,30}. PCT curves with two plateaus for the $\text{TbMgNi}_{4-x}\text{Co}_x$ compounds ($x \geq 2$) resemble those obtained for isostructural LaMgNi_4 ³¹ and CeMgCo_4 ¹⁹ compounds, where formation of the α -, β -, γ -hydrides have been also observed. For $\text{RMgNi}_{4-x}\text{Co}_x$ compounds^{19-23,29,30} only one plateau has been observed. Moreover, for the $(\text{Nd,Pr})_{1-y}\text{La}_y\text{MgNi}_{4-x}\text{Co}_x$ alloys, La and Co substitution initiates an easiest way to observe the $\beta \rightarrow \gamma$ transformation at 10 bar H_2 ^{22,23}. For YMgCo_4 compound, an extended plateau was observed in the temperature range 20–60 °C²⁰ like at 50 °C for TbMgCo_4 in this work.

According to the variation of the equilibrium pressures (Fig. 2b), the second plateau pressures of TbMgNi_{4-x}Co_x could be near 400 and 110 bar for $x = 0$ and 1 respectively. To confirm this assumption experiment at higher hydrogen pressure should be done and results of first principles calculations are presented in section 3.5. Interesting, that theoretical calculations suggested that RMgNi₄H₄ can transform into RMgNi₄H₆ at 2.64 and 85 kbar H₂ for $R = \text{Sm}$ and Gd respectively³². On the other hand, CeMgCo₄ displays a second plateau below 100 bar H₂¹⁹, whereas hydrogenation of the CeMgNi₄ alloy leads to an alloy decomposition³³.

3.3. Crystal structures of the TbMgNi_{4-x}Co_x-based hydrides

Hydrides of the TbMgNi_{4-x}Co_x compounds with $x = 0, 1, 2, 3$ and 4 were exposed to air to passivate the surface and characterized by XRD and SRXRD. Rietveld refinements of the different XRD patterns of selected TbMgNi_{4-x}Co_x hydrides and deuterides are shown in Figures S1 and S2. The structures of different β - and γ -hydrides are presented in Table 3. First, it was found that the hydrogenation of TbMgNi_{4-x}Co_x with $x = 0, 1, 2$ and 3 leads to an orthorhombic deformation (space group $Pmn2_1$) of the original cubic structure (space group $F\bar{4}3m$) with a cell volume expansion of 12.6–14.7 % (Table 3 and Fig. 3a). However, it was observed that TbMgCo₄H_{3.3} crystallizes in a monoclinic structure (space group Pm , $a = 5.4091(8)$ Å, $b = 5.0035(6)$ Å, $c = 7.3606(9)$ Å, $\beta = 96.18(1)^\circ$) (Figure S1). This monoclinic structure corresponds to a distortion of the orthorhombic cell and can be obtained by a lowering of the crystal symmetry from $Pmn2_1$ (No. 31) to Pm (No. 6). Full resolution of this new structure with D-atom location, will be done later by NPD measurement. The variation of β -hydride cell parameters versus Co content is presented in Fig. 3b. a and b cell parameters decrease monotonously, while c sharply increases up to $x = 2$ and saturates at 3 Co at/f.u. Further hydrogenation of the TbMgNi_{4-x}Co_x alloys yields cubic γ -hydrides for $x = 2, 3$ and 4. These hydrides retain initial cubic symmetry of the parent compound with isotropic expansion of the unit cell of 17.9–22.3 % (Table 3). Synthesis of γ -hydrides with cubic structure for the TbMgNi_{4-x}Co_x compounds with $x = 0$ and 1 would require higher hydrogen pressure as previously discussed.

Subsequently, isotope influence on phase structure and stability has been observed in the TbMgNiCo₃–(H,D)₂ system. TbMgNiCo₃H_{5.2} hydride is unstable versus time and decomposes very fast into orthorhombic phase with $y = 3.7$ H/f.u. On the other hand, TbMgNiCo₃D_{5.4} deuteride remains stable and keep a cubic structure. XRD patterns for hydrides and deuterides are compared in Fig. 3c. TbMgCo₄ absorbs 6.6 H at./f.u. at 9.5 bar H₂, but desorb hydrogen down to 5.2 H at./f.u. at 1 bar H₂. Cell parameter for the cubic hydride TbMgCo₄H_{5.2} has been determined by SRXRD ($a = 7.5035(2)$ Å³) and it is in agreement with our previous result for TbMgCo₄H_{5.3}²⁷ from XRD ($a = 7.5212(9)$ Å³). TbMgCo₄D₆ deuteride ($a = 7.5663(2)$ Å) is also more stable than its corresponding hydride. The cubic structure of TbMgNi₂Co₂H₅ hydride was observed after very fast scan.

Cell volume (V) variations versus Co content are presented in Fig. 3d. The cell volume of TbMgNi_{4-x}Co_x β -hydrides increases from $x = 0$ to 2, decreases abruptly for $x = 3$ and increases again for monoclinic hydride with $x = 4$. This discontinuous cell volume variation is mainly related to the variation of the c parameter with $x(\text{Co})$. This anomalous variation for $x = 3$ can be related to the small deviation from linearity of the initial compound cell volume (Fig. 1). The γ -deuteride (hydride) cell volume V increases continuously (volume of the TbMgNi₂Co₂H₅ hydride has been used instead of deuteride).

Table 3. Crystal structure data for the TbMgNi_{4-x}Co_xH_y hydrides/deuterides (synthesized at room temperature) from Rietveld refinements of X-ray diffraction data.

Hydride	P _{final} H ₂ , bar	Space Group	Unit cell parameters (Å)			V(Å ³)	ΔV/ V, %	ΔV/n _H , Å ³ /at.H	
			a	b	c				
β-TbMgNi ₄ H _{3.8}	24.0	<i>Pmn</i> 2 ₁	5.0182(6)	5.4178(6)	7.2834(8)	198.02(4)	14.7	3.2	
β-TbMgNi ₃ CoH _{4.1}	10.3	<i>Pmn</i> 2 ₁	5.0074(2)	5.4060(3)	7.3225(3)	198.22(2)	14.3	3.0	
β-TbMgNi ₂ Co ₂ H _{3.7}	6.8	<i>Pmn</i> 2 ₁	4.9957(5)	5.4084(6)	7.3588(7)	198.83(3)	13.7	3.0	
γ-TbMgNi ₂ Co ₂ H _{~5}	52.0	<i>F</i> 43 <i>m</i>	7.4419(7)			412.15(7)	17.9	3.1	
β-TbMgNiCo ₃ H _{3.7}	2.4	<i>Pmn</i> 2 ₁	4.981(1)	5.390(2)	7.350(2)	197.3(1)	12.6	3.0	
γ-TbMgNiCo ₃ H _{5.2}	9.8	<i>fast decomposition into β-TbMgNiCo₃H_{3.7}</i>							
γ-TbMgNiCo ₃ D _{5.4}	7.3	<i>F</i> 43 <i>m</i>	7.4785(3)			418.26(3)	19.4	3.1	
β-TbMgCo ₄ H _{3.3}	1.5	<i>Pm</i>	5.4091(8)	5.0035(6)	7.3606(9)	198.05(5)	11.8	3.2	
			β=96.18(1)°						
γ-TbMgCo ₄ H _{5.2}	2.3	<i>F</i> 43 <i>m</i>	7.5035(2)			422.47(2)	19.3	3.3	
γ-TbMgCo ₄ D ₆	7.1	<i>F</i> 43 <i>m</i>	7.5663(2)			433.15(2)	22.2	3.3	

Statistical mixture of Mg/Tb were taken as it was calculated for IMC and fixed for hydrides.

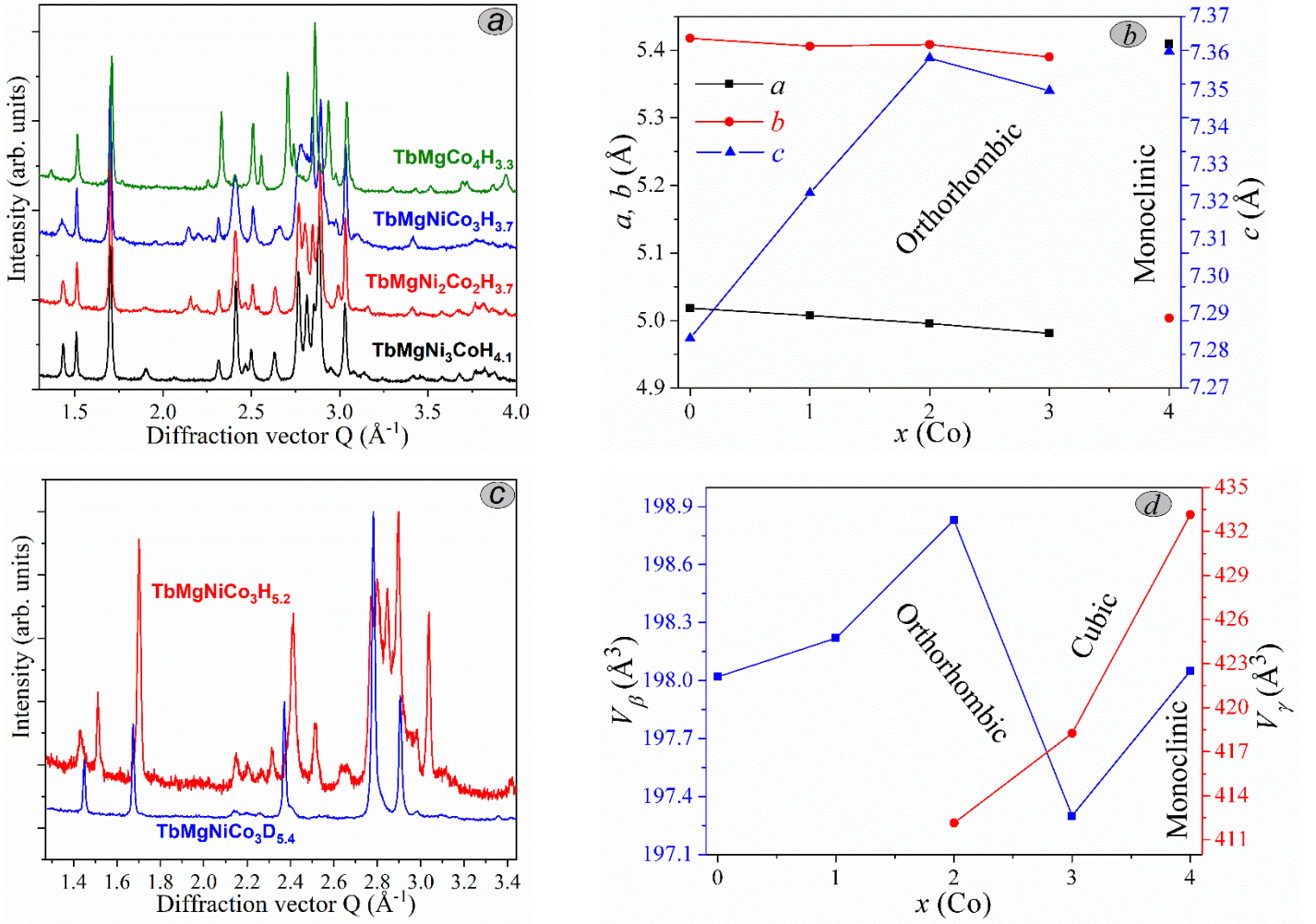


Fig. 3. XRD patterns of the selected TbMgNi_{4-x}Co_x hydrides (a,b) and evolution of the cell parameters versus Co content (c,d).

Crystal structure of TbMgCo₄D₆ deuteride has been studied in more detail by neutron powder diffraction. Saturated TbMgCo₄D_{6.1} deuteride has been obtained at room temperature and 7.1 bar D₂. According to volumetric measurement, the final concentration of the deuterium in the IMC at 1 bar D₂ was 6 D at./f.u. This deuteride keeps the cubic structure of the parent compound with a large cell volume expansion ($\Delta V/V = 22.3\%$). Several XRD and SRXRD measurements have showed that TbMgCo₄D₆ remains stable over several months contrary to hydrides of Ni rich compounds which decompose during storage.

The structural parameters determined from XRD and NPD datasets are reported in Table 4. Fig. 4 shows the refined neutron diffraction pattern at room temperature and unit cell projection of this deuteride. As starting structural model in Rietveld refinements of the deuteride NPD pattern, we used structural parameters of TbMgCo₄D₆ obtained from XRD data. The lattice parameters determined of TbMgCo₄D₆ determined from NPD are close to those determined by XRD. The positions of the deuterium atoms have been found using differential Fourier method. The deuterium atoms partially occupy two types of interstitial sites: 87 % D atoms are located in D1 which form a Tb₂MgCo₂ octahedra and 13 % (D2) are located in Co₄ tetrahedra. Total deuterium content obtained from Rietveld refinements is 5.9(2) D at./f.u. in good agreement with the value of 6.0 D at./f.u. measured from pressure variation. Similar type of R₂MgT₂ and T₄ coordination of D atoms was observed in CeMgCo₄D_{4.21}¹⁹ and LaMgNi₄D_{4.85}²⁹ deuterides.

Mg–D and Co–D distances are 1.819(1) Å and 1.614(1)–1.684(2) Å respectively. These value are comparable to those obtained for CeMgCo₄D_{4.21}¹⁹ ($d_{\text{Mg-D}} = 1.835$ Å and $d_{\text{Co-D}} = 1.646$ Å) where one 24g position is filled. Mg–D distances in LaMgNi₄D_{4.85}³¹ and NdMgNi₄D_{3.6}³⁴, PrMgNi₄D₄ and Pr_{0.6}Mg_{1.4}Ni₄D_{3.6}³⁵ are in the range 1.856–2.221 Å.

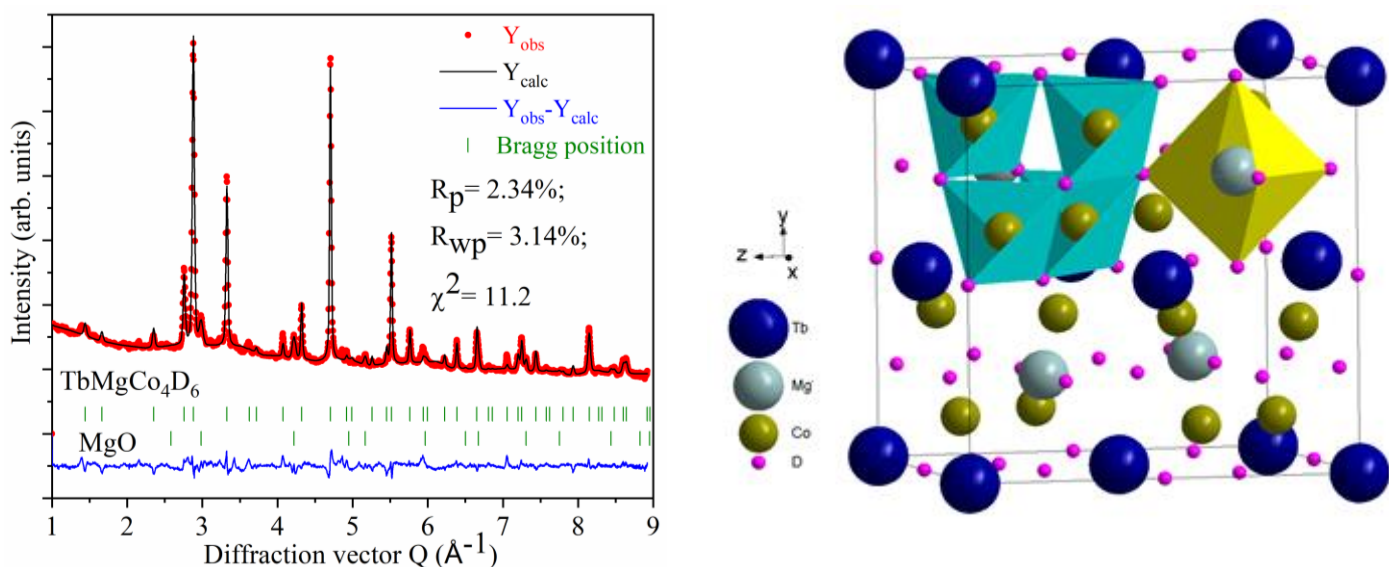


Fig. 4. Refined NPD pattern (1 – 97 wt.% TbMgCo₄D₆, 2 – 3 wt.% MgO) and unit cell projection of the TbMgCo₄D₆ deuteride with an environment of D atoms around Co and Mg.

Table 4. Crystallographical parameters of the TbMgCo₄D₆ deuteride from Rietveld refinements of XRD and NPD data.

Deuteride	TbMgCo ₄ D ₆	
Refinement	XRD	NPD
Space group	<i>F</i> 43 <i>m</i> (No. = 216)	
Unit cell parameters:		
<i>a</i> , Å	7.5663(2)	7.5553(2)
<i>V</i> , Å ³	433.15(2)	431.28(2)
Δ <i>V</i> / <i>V</i> , %	~22.0	
Atomic positions:		
Tb in 4 <i>a</i> (0, 0, 0)		
* <i>n</i> _{Tb} / <i>n</i> _{Mg}	0.84(-)Tb/0.16(-)Mg	
<i>B</i> _{iso} , Å ²	1.58(7)	2.23(11)
Mg in 4 <i>c</i> (1/4, 1/4, 1/4)		
* <i>n</i> _{Mg} / <i>n</i> _{Tb}	0.93(-)Mg/0.07(-)Tb	
<i>B</i> _{iso} , Å ²	3.4(3)	2.16(9)
Co in 16 <i>e</i> (<i>x</i> , <i>x</i> , <i>x</i>)		
<i>x</i>	0.6236(2)	0.6233(3)
<i>B</i> _{iso} , Å ²	1.19(6)	1.91(7)
D1 in 24 <i>g</i> (<i>x</i> , 1/4, 1/4)		
<i>x</i>		0.4904(4)
<i>n</i>		0.86(1)
D2 in 4 <i>b</i> (1/2, 1/2, 1/2)		
<i>n</i>		0.76(1)
<i>B</i> _{iso} , Å ² for all D		3.56(4)
Calculated D content		5.9(2)
Volumetric capacity, D at./f.u.	6.0	
<i>R</i> -factors		
<i>R</i> _p , %	1.21	2.34
<i>R</i> _{wp} , %	1.59	3.14
χ ²	1.72	11.2
Shortest Me–D distances, Å		
Mg–D1		1.819(1)
Co–D2		1.614(1)
Co–D1		1.684(2)

*Statistical mixtures of Mg/Tb were taken as it was calculated for IMC and fixed for deuteride.

3.4. DSC studies of the TbMgNi_{4-x}Co_xH_y hydrides

DSC studies have been performed to determine the enthalpy and temperature of desorption (ΔH_{des} , T_{des}) which are related to the hydride stability. Measured weight capacity, ΔH_{des} and T_{des} obtained from DSC experiments are summarized in Table 5.

It was found that T_{des} and ΔH_{des} for the orthorhombic β -TbMgNi_{4-x}Co_xH_y hydrides ($x = 0-3$ and $y = 3.7-4.1$) varies in a narrow T and ΔH_{des} range: 69.5–84.4 °C and 18.3–31.6 kJ/mol H₂, respectively. The hydride of TbMgNi₄ has the lowest stability among studied hydrides. The β -TbMgCo₄H_{3.3} has the highest values of T_{des} (117.1 °C) while the highest ΔH_{des} was found for the β -TbMgNiCo₃H_{3.7} hydride (31.6 kJ/mol H₂). The results of DSC experiments (Table 5) show that β -hydrides more stable than γ -hydrides. These observations agree with the

results of the *PCT* measurements, demonstrating that increasing Co content leads to a significant decrease in the equilibrium plateau pressure and increasing stability of the hydrides (Fig. 2a).

The values of ΔH_{des} are close to that for LaNi₅ hydride, which enthalpy of formation is ranging from about 29 to 32 kJ/mol H₂³⁶. The values of the hydrogen absorption enthalpy determined from the slope of van't Hoff plot for YMgNi_{4-x}Co_x-H₂ systems varies from 27.9 to 33.1 kJmol⁻¹ H₂²⁰.

Table 5. Comparison of desorption temperature and enthalpy of the TbMgNi_{4-x}Co_xH_y hydrides.

Hydride	C _H , wt. %	T _{onset} , °C	Enthalpy, J/g	Enthalpy, kJ/mol H(D) ₂
β -TbMgNi ₄ H _{3.8}	0.91	69.5	82.8	18.3
β -TbMgNi ₃ CoH _{4.1}	0.98	84.4	138.5	28.5
β -TbMgNi ₂ Co ₂ H _{3.7}	0.88	70.7	129.5	29.7
β -TbMgNiCo ₃ H _{3.7}	0.88	76.2	138.1	31.6
γ -TbMgNiCo ₃ D _{5.4}	1.28	93.4	166.0	26.1
β -TbMgCo ₄ H _{3.3}	0.79	117.1	113.5	29.0
γ -TbMgCo ₄ H _{5.3}	1.27	99.6	181.7	28.8

3.5. DFT Calculations of TbMgNi_{4-x}Co_x compounds and TbMgNi_{4-x}Co_xH₆ hydrides

First principles calculations were performed on TbMgNi_{4-x}Co_x compounds and cubic TbMgNi_{4-x}Co_xH₆ hydrides, with a given model for $x = 0, 2$ and 4 . The partial substitution cells ($x = 2$) were obtained by choosing the most randomized distribution of the 16 atoms (8 Co + 8 Ni) in 16e site of *F43m* space group. Similar to the Special quasirandom structure (SQS) approach³⁷, the cell was chosen by comparison of the correlation functions of a set of clusters (5 nearest pairs, 6 nearest triplets and 2 tetrahedra) of all possible atom configurations with the perfect randomized cell. To get a general picture of a relative and simple comparison, the hydride form was considered only in an ideal cubic model (γ -form) with a partial occupancy of H in 24g and 4b sites, representative of the experimental results of TbMgCo₄D₆, *i.e.* 21/24 and 3/4 atoms respectively in the conventional cell (48 atoms in total). The distribution of H was considered with relative positions far of each other with the highest symmetry possible case. As an example, the structural model of TbMgNi₂Co₂H₆ is given in supporting information (Table S2 and Fig S3, with additional VESTA file).

The spin polarized band structure calculations were carried out by using the DFT scheme implemented in the projector-augmented wave (PAW) method, performed with the VASP package^{38,39}, using the Generalized Gradient Approximation (GGA) for the exchange and correlation energy of Perdew-Burke-Ernzerhof (PBE) functional⁴⁰. Terbium was considered with "ghost-state" approach using a special pseudopotential in which the *f* electrons are kept frozen in the core (only 9 valence electrons). A plane wave basis set with a cutoff energy of 600 eV was used in all calculations converging within 0.1 meV in the total energy.

From the energies difference related to pure elements in their reference state, the heats of formation of intermetallics and hydrides are given in Table 6. In agreement with the conventional Miedema rules for hydride, the less stable compound (richer in Co) forms the most stable hydride. The opposite applies to the Ni-based

compound to be very stable (about -40 kJ/mol) whereas the TbMgNi₄H₆ hydride is not stable in ambient conditions ($P_{eq} > 400$ bar).

Table 6. Heat of formation of TbMgNi_{4-x}Co_x compounds and TbMgNi_{4-x}Co_xH₆ hydrides calculated by DFT.

x	Compound	Enthalpy, kJ/mol	Hydride	Enthalpy, kJ/mol H ₂
0	TbMgNi ₄	-38.8	TbMgNi ₄ H ₆	-10.9
2	TbMgNi ₂ Co ₂	-24.4	TbMgNi ₂ Co ₂ H ₆	-18.4
4	TbMgCo ₄	-13.1	TbMgCo ₄ H ₆	-18.8

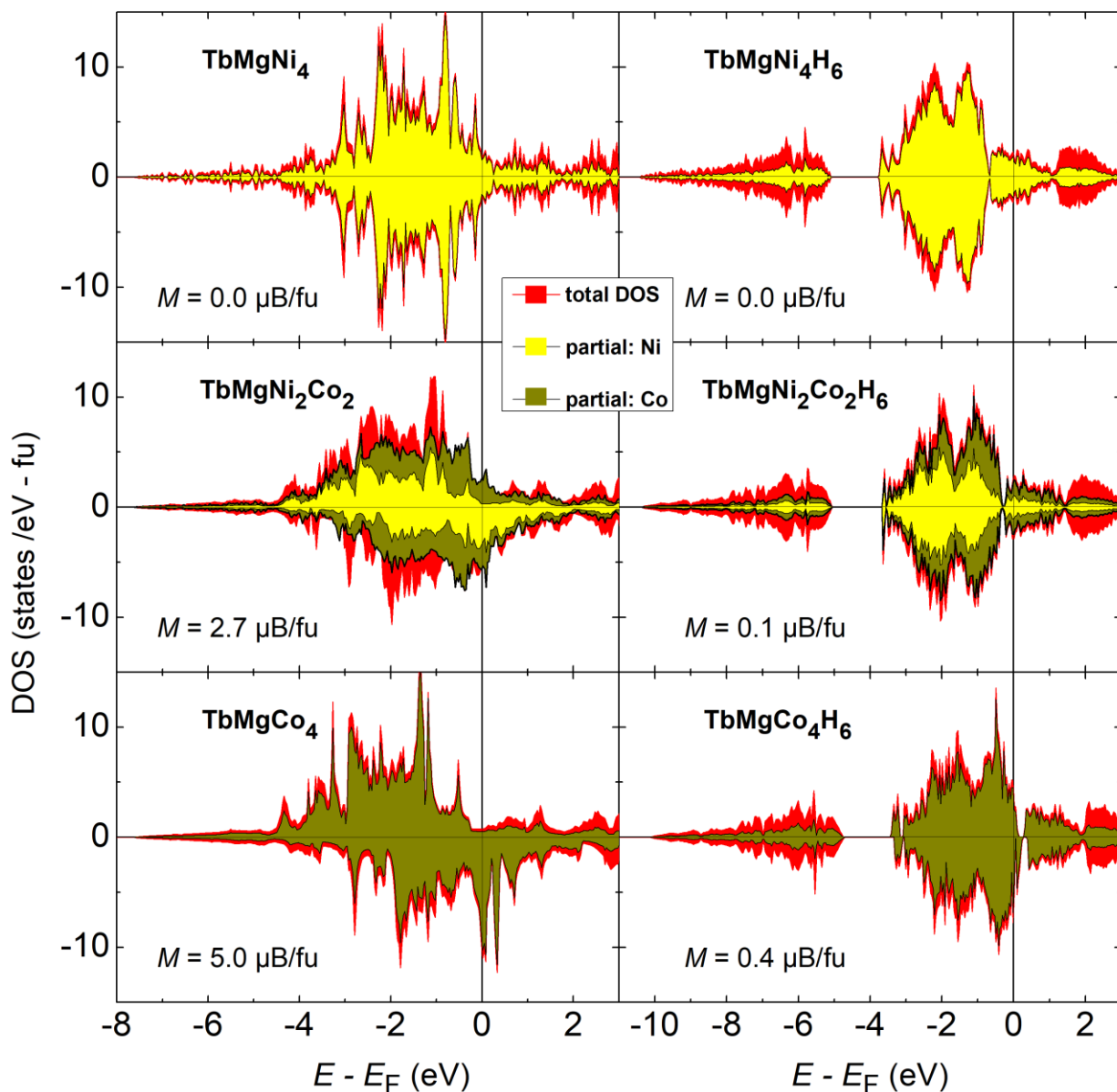


Fig. 5. Density of states of TbMgNi_{4-x}Co_x compounds and TbMgNi_{4-x}Co_xH₆ hydrides for $x = 0, 2, 4$. Red area corresponds to the total contribution whereas yellow and green areas correspond to the Ni and Co parts respectively. The Fermi level has been chosen as the origin of energy.

The electronic structure could be analyzed from the density of states (DOS) representation given in Fig. 5. About the intermetallics, an electron depopulation of the main band is observed with the increase of x (increase

of Co-rate), naturally explained by the number of electrons of Ni and Co. The DOS of hydrides is typical of this kind of phase, characterized by a new broad electronic structure at low energy (around -10 to -5 eV below the Fermi level, E_F). It corresponds mostly to the 6 bands associated with metal-hydrogen bonding dominating by H-(Co,Ni) interactions. Due to the lattice expansion of the hydride (about +18 %), the Tb+Mg and transition metal interaction is weakened, the bands of the main structure are narrower and the valley separating the bonding and anti-bonding states is smeared out. Thanks to the additional electrons from H atoms, the Fermi level is shifted at higher energy for the hydrides and leads to the almost filling of the main structure in $x = 4$ whereas E_F falls in anti-bonding states for $x = 0$.

Whatever the x value, the Bader charge analysis indicated a charge transfer from Mg and Tb to H with a total charge of about $0.45 e^-$ for each H atom, as shown in high density region around H of the electron localization function (ELF) plotted in Fig S4 of Supporting Information. The transition metal charges are most unchanged from their elemental state.

A substantial increase of the calculated enthalpies of formation has been also observed when Ni is replaced by Co in $YMgT_4$ IMC ($T = Ni, Co$)⁴¹ and Y by Nd in $RMgNi_4$ IMC ($R = Y, Nd$)⁴². Previously we assumed that the enthalpy of formation of $NdMgCo_4$ is possibly positive and that $NdMgCo_4$ compound and others with $R = La, Pr, Nd$ are thermodynamically unstable. Moreover, latest publication⁴³ revealed good structural stability with the order: $NdMgCo_4 > NdMgNi_4 > NdMgCu_4$. Calculated cell parameter for $NdMgCo_4$ compound was 7.1078 Å. Besides, it was experimentally found that cell parameters of $NdMgNi_{4-x}Co_x$ compounds increase linearly from 7.0947(5) Å for $x = 0$ to 7.1286(6) Å for $x = 3$. By extrapolation, the cell parameter of $NdMgCo_4$ compound should be 7.1404 Å, but this compound can not be obtained. Meanwhile, calculated enthalpies of formation for $NdMgCo_4$ is -0.08 eV/atom which is close to a positive value and explaining that it is thermodynamically unstable. Finally, formation of the $RMgCo_4$ compounds depends on the nature of rare earth and Mg solubility in the binary RCO_2 compounds.

4. Conclusions

$TbMgNi_{4-x}Co_x$ ($x = 0-4$) intermetallics with $SnMgCu_4$ type cubic structure have been synthesized. Their hydrogenation properties have been studied in detail. The structural study of the alloys and their hydrides or deuterides has been performed.

$TbMgNi_{4-x}Co_x$ ($x = 0-4$) compounds reversibly absorb hydrogen. *PCT* curves of $TbMgNi_{4-x}Co_x$ display only one plateau ($x = 0-1$) whereas *PCT* curves of $TbMgNi_{4-x}Co_x$ ($x = 2-4$) compounds are characterized by two absorption/desorption plateaus. Thermodynamic properties of the $TbMgNi_{4-x}Co_xH_y$ ($x = 0-4$) hydrides were studied by *PCT* and DSC measurements. The experimental enthalpies of formation are in good agreement with the DFT calculated ones. It shows a decreasing stability of the alloys upon Co for Ni substitution and the reverse effect on the hydride as expected from the reverse stability rule. Increasing Co content in the $TbMgNi_{4-x}Co_x$ alloys leads to the lowering of desorption plateau pressure and improvement of the kinetics of hydrogen absorption.

The existence of α -, β -, γ -hydrides has been observed in the *PCT* curves. Formation of the β -hydrides is going through the orthorhombic distortion of the cubic $\text{TbMgNi}_{4-x}\text{Co}_x$ ($x = 0-3$) intermetallics. Moreover, β - $\text{TbMgCo}_4\text{H}_{3.3}$ has a monoclinic structure observed for the first time among $\text{RMgNi}_{4-x}\text{Co}_x\text{H}_y$ hydrides. This monoclinic structure corresponds to a distortion of the orthorhombic structure and can be obtained by a lowering of the crystal symmetry. Deuterium has been found to prevent from fast desorption compared to hydrogen. The neutron diffraction study of the $\text{TbMgCo}_4\text{D}_6$ deuteride has revealed significant structural similarity with $\text{LaMgNi}_4\text{D}_{4.85}$ ³¹ with deuterium atoms located inside Tb_2MgCo_2 octahedra and Co_4 tetrahedra.

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Fig. 1. Change of the unit cell volume with Co content for TbMgNi_{4-x}Co_x ($x = 0-4$) compounds.

Fig. 2. Hydrogenation properties of the TbMgNi_{4-x}Co_x alloys: hydrogen absorption isotherms at 25 °C (*a*); evolution of the equilibrium pressure with $x(\text{Co})$ (*b*), comparison of *PCT* curves for the TbMgCo₄-H₂ system at 25 and 50°C (*c*), and first hydrogenation curves for the TbMgNi_{4-x}Co_x (*d*).

Fig. 3. XRD patterns of the selected TbMgNi_{4-x}Co_x hydrides (*a,b*) and evolution of the cell parameters versus Co content (*c,d*).

Fig. 4. Refined NPD pattern (1 – 97 wt.% TbMgCo₄D₆, 2 – 3 wt.% MgO) and unit cell projection of the TbMgCo₄D₆ deuteride with an environment of D atoms around Co and Mg.

Fig. 5. Density of states of TbMgNi_{4-x}Co_x compounds and TbMgNi_{4-x}Co_xH₆ hydrides for $x = 0, 2, 4$. Red area corresponds to the total contribution whereas yellow and green areas correspond to the Ni and Co parts respectively. The Fermi level has been chosen as the origin of energy.