

# STRUCTURE AND HYDROGENATION PROPERTIES OF NOVEL Mg-BASED INTERMETALLIC COMPOUNDS AND ALLOYS

Denys R.V., Berezovets V.V., Koval'chuk I.V., Paul-Boncour V.<sup>(1)</sup>, Cerny R.<sup>(2)</sup>, Zavaliy I.Yu.\*

Physico-Mechanical Institute, NAS Ukraine, 5, Naukova St., Lviv, 79601

<sup>(1)</sup> ICMPE, CNRS, 2-8 rue Henri Dunant, 94320 Thiais Cedex, France

<sup>(2)</sup> University of Geneva, Laboratory of Crystallography, 24 quai E.-Ansermet, Geneva, Switzerland

\*E-mail: zavaliy@ipm.lviv.ua

## Introduction

Magnesium and its alloys are very attractive materials for hydrogen storage and negative electrodes of Ni-MH batteries due to high hydrogenation capacity (7.6 wt.% for pure Mg, 3.6 wt.% for Mg<sub>2</sub>Ni), low cost, abundance and non-toxicity [1]. However, their application is still hindered by such obstacles as high temperatures (250-300°C), slow kinetics of the hydrogen absorption-desorption processes and low corrosion stability. One of the most promising methods for improvement of hydrogenation properties of magnesium alloys is high-energy ball milling (HEBM), which allows not only to obtain material in the amorphous/nanocrystalline state, but also to synthesise new compounds. The present work is focused on the synthesis, hydrogenation properties and crystal structure of new intermetallic compounds in the Mg-Mn-Ni and RE-Co-Mg systems (RE=Y,Ce).

## Experimental details

The alloys were prepared from the powders of Mg, Ni, Co, Mn and RE-metals (with purity  $\geq 99.9\%$ ). The powder mixtures were mechanically alloyed in Fritsch "Pulverisette-6" mill. After milling the powders were annealed at temperatures 400-800°C in argon atmosphere. Phase-structural analysis of the samples has been performed by powder X-ray diffraction (DRON-3.0 diffractometer, Cu-K $\alpha$  radiation). The neutron powder diffraction data were collected at the PSI Villigen, Switzerland (HRPT,  $\lambda=1.494$  Å).

## Results and discussion

The Mg<sub>3</sub>MnNi<sub>2</sub> compound has been synthesized in our previous work [2-3]. Structural analysis showed that this compound crystallize in the Nb<sub>3</sub>Ni<sub>2</sub>Si type structure, which is an ordered derivative of the Ti<sub>2</sub>Ni type of structure [4]. In order to improve absorption characteristics of alloys with higher magnesium contents we synthesized Mg<sub>88</sub>Mn<sub>4</sub>Ni<sub>8</sub> alloy from powders of original components (Mg, Mn, Ni) by 12-hour HEBM in argon. Hydrogenation capacity of the saturated alloy was 5.4 wt. % H. The thermal desorption of hydrogen from the obtained material

into vacuum occurred between 150 and 250 °C (a low-temperature shoulder at 180 °C and a main peak at 230 °C). Such a substantial decrease in the temperature of decomposition of MgH<sub>2</sub> (350 °C for individual hydride) can be attributed to catalytic action of Mg<sub>3</sub>MnNi<sub>2</sub> and to synergism of processes in the Mg-Mg<sub>3</sub>MnNi<sub>2</sub>-H<sub>2</sub> system.

Therefore the hydrogenation of this phase has been studied in details. P-C-T measurements of the Mg<sub>3</sub>MnNi<sub>2</sub>-H<sub>2</sub> system (Fig.1) demonstrated the formation of three hydride phases:  $\beta_1$ -Mg<sub>3</sub>MnNi<sub>2</sub>H<sub>-1</sub>,  $\beta_2$ -Mg<sub>3</sub>MnNi<sub>2</sub>H<sub>-1.5</sub> and  $\gamma$ -Mg<sub>3</sub>MnNi<sub>2</sub>H<sub>-3</sub>.  $\Delta H$  and  $\Delta S$  were determined from Vant Hoff relation for the  $\alpha \leftrightarrow \beta_1 \leftrightarrow \beta_2 \leftrightarrow \gamma$  transformations (Table 1). Thermodynamic stability of the lower Mg<sub>3</sub>MnNi<sub>2</sub> hydrides is close to that of MgH<sub>2</sub>. Both these hydrides are more stable than Mg<sub>2</sub>NiH<sub>4</sub>.

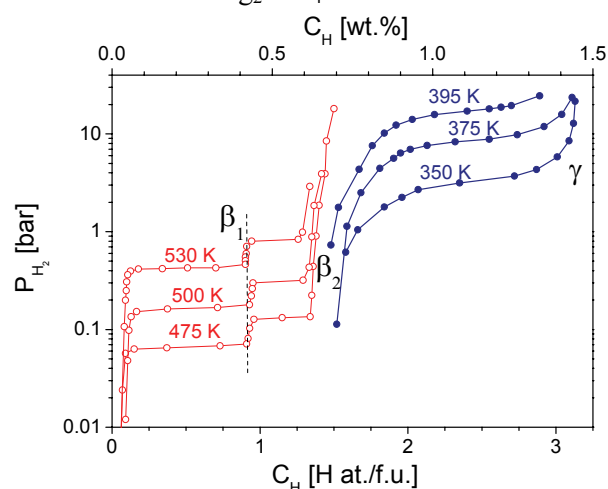


Fig. 1. Desorption isotherms for the Mg<sub>3</sub>MnNi<sub>2</sub>-H<sub>2</sub> system.

Table 1. Thermodynamic parameters for the Mg<sub>3</sub>MnNi<sub>2</sub>-H<sub>2</sub> system.

Transformation	$\Delta H_{des}$ , kJ·mol <sup>-1</sup> H <sub>2</sub>	$\Delta S_{des}$ , J·K <sup>-1</sup> ·mol <sup>-1</sup>
Mg <sub>3</sub> MnNi <sub>2</sub> $\leftrightarrow$ Mg <sub>3</sub> MnNi <sub>2</sub> H ( $\alpha \leftrightarrow \beta_1$ )	74.2±1.9	133.2±3.9
Mg <sub>3</sub> MnNi <sub>2</sub> H $\leftrightarrow$ Mg <sub>3</sub> MnNi <sub>2</sub> H <sub>1.5</sub> ( $\beta_1 \leftrightarrow \beta_2$ )	72.7±0.6	136±1.2
Mg <sub>3</sub> MnNi <sub>2</sub> H <sub>1.5</sub> $\leftrightarrow$ Mg <sub>3</sub> MnNi <sub>2</sub> H <sub>3</sub> ( $\beta_2 \leftrightarrow \gamma$ )	41.0±0.2	127.0±0.7

At temperatures above 300°C in hydrogen Mg<sub>3</sub>MnNi<sub>2</sub> disproportionates into Mg<sub>2</sub>NiH<sub>4</sub>

hydride and Mn-Ni phase. Disproportionation reaction occurs at pressures exceeding equilibrium of  $\text{Mg}_2\text{NiH}_4$  formation ( $\sim 10$  bars at  $350^\circ\text{C}$ ). Complete hydrogen desorption from  $\text{Mg}_2\text{NiH}_4$  leads to recombination of  $\text{Mg}_3\text{MnNi}_2$ .

In other system studied in this work, RE-Co-Mg, we have synthesized new intermetallic compounds  $\text{REMgCo}_4$  and  $\text{RE}_2\text{MgCo}_9$  (RE=Y, Ce). The hydrogenation properties have been studied for  $\text{REMgCo}_4$ . Formation of two phases  $\beta$ - $\text{CeMgCo}_4\text{H}_{\sim 4}$  and  $\gamma$ - $\text{CeMgCo}_4\text{H}_{\sim 6}$  has been observed in  $\text{CeMgCo}_4\text{-H}_2$  system (Fig.2). The structure of more stable  $\beta$ - $\text{CeMgCo}_4\text{D}_4$  deuteride has been studied by powder neutron diffraction (Fig.3). It retains initial cubic symmetry of  $\text{CeMgCo}_4$  compound with unit cell expansion  $\Delta V/V=20\%$ . The crystallographic parameters and fragment of crystal structure of this deuteride are presented in Table 2 and Fig.4 respectively.

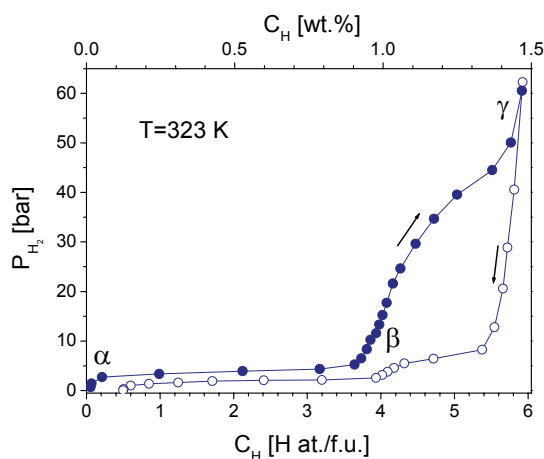


Fig. 2. Absorption-desorption isotherm for the  $\text{CeMgCo}_4\text{-H}_2$  system at  $50^\circ\text{C}$ .

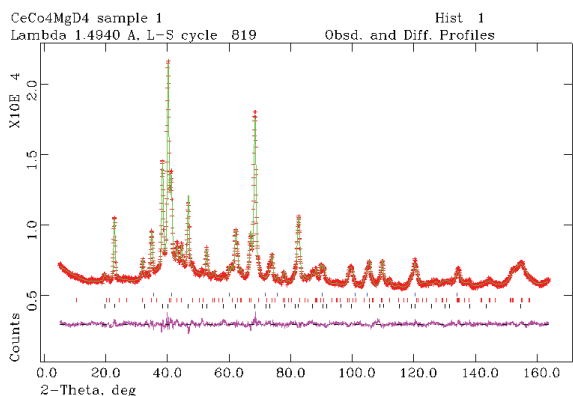


Fig. 3. Powder neutron diffraction pattern of the  $\text{CeMgCo}_4\text{D}_4$  deuteride ( $\lambda=1.494$  Å). Impurity phases:  $\text{Ce}_2\text{MgNi}_9$  and  $\text{MgO}$ .

It is shown that the D atoms are located in the 24g site only. D atoms occupy triangular  $\text{MgCo}_2$  face between tetragonal  $\text{CeMgCo}_2$  interstices forming the  $\text{D}_6$  octahedra around Mg atoms. We should note the rather short Mg-D distances,

1.87 Å, which can be attributed to strong Mg-H bonding in this type of hydrides.

Hydrogenation and structural studies of related compound,  $\text{LaMgNi}_4$ , demonstrated the formation of 3 hydrides ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) [5]. The structure of the studied  $\beta$ - $\text{CeMgCo}_4\text{D}_4$  deuteride is similar to that of  $\gamma$ - $\text{LaMgNi}_4\text{D}_{4.85}$ , but the 4b sites are empty. The further studies should clarify the crystal structure of the saturated hydrides  $\text{REMgCo}(\text{Ni})_4$ .

Table 2. Crystallographic data for  $\text{CeMgCo}_4\text{D}_{4.18(1)}$   
Sp.gr.  $F-43m$ ,  $a=7.5010(2)$  Å.

Atom	Site	Coordinates (x,y,z)	$U_{\text{iso}}$ , Å <sup>2</sup>	Occupancy
Ce	4a	0, 0, 0	0.049(1)	1.0
Mg	4c	1/4, 1/4, 1/4	0.062(1)	1.0
Co	16e	0.6265(3), x, x	0.0172(4)	1.0
D	24g	0.0014(4), 1/4, 1/4	0.0398(6)	0.70(1)

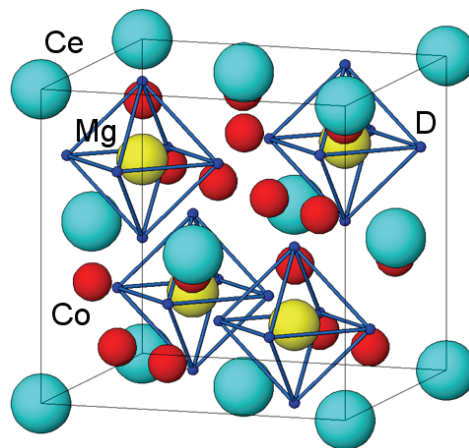


Fig.4. Crystal structure of  $\text{CeMgCo}_4\text{D}_4$ .

The researches were supported in part by INTAS (YSF grant 06-100019-6490). The skilful assistance of Denys Sheptyakov (PSI, Switzerland) with the neutron powder diffraction experiment is highly appreciated.

## References

- Advanced Materials for Energy Storage. MRS Bulletin. November 1999, Vol.24, № 11.
- Denys R.V., Zavalii I.Yu., Paul-Boncour V. *et. al.* New Mg-Mn-Ni alloys as efficient hydrogen storage materials. *Intermetallics*, submitted.
- Denys R.V., Zavalii I.Yu., Paul-Boncour V., *et. al.* New Mg-M-Ni (M=Mn, Ti, Al) alloys as efficient hydrogen storage materials. Astr. of X Int. Conf. ICHMS'2007, Ukraine-Crimea-Sudak, Sept. 22-28, 2007, P. 332-335.
- Gladyshevskiy E.I. *et. al.* Crystal structures of the compounds  $\text{Mn}_3\text{Ni}_2\text{Si}$ ,  $\text{V}_3\text{Ni}_2\text{Si}$ ,  $\text{Nb}_3\text{Ni}_2\text{Si}$  and related chromium and tantalum compounds. *Zh. Strukturnoyi Khimii*. 1963; 4(3): 372-379.
- Chotard J.N., Sheptyakov D., Yvon K. Hydrogen induced site depopulation in the  $\text{LaMgNi}_4$ -hydrogen system. *Z. Kristallogr.* 2008; 223: 690-696.