

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

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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 Mg₂Ni), 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_α radiation). The neutron powder diffraction data were collected at the PSI Villigen, Switzerland (HRPT, $\lambda=1.494$ Å).

Results and discussion

The Mg₃MnNi₂ compound has been synthesized in our previous work [2-3]. Structural analysis showed that this compound crystallize in the Nb₃Ni₂Si type structure, which is an ordered derivative of the Ti₂Ni type of structure [4]. In order to improve absorption characteristics of alloys with higher magnesium contents we synthesized Mg₈₈Mn₄Ni₈ 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 MgH₂ (350 °C for individual hydride) can be attributed to catalytic action of Mg₃MnNi₂ and to synergism of processes in the Mg-Mg₃MnNi₂-H₂ system.

Therefore the hydrogenation of this phase has been studied in details. P-C-T measurements of the Mg₃MnNi₂-H₂ system (Fig.1) demonstrated the formation of three hydride phases: β_1 -Mg₃MnNi₂H₁, β_2 -Mg₃MnNi₂H_{1.5} and γ -Mg₃MnNi₂H₃. ΔH and ΔS 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 Mg₃MnNi₂ hydrides is close to that of MgH₂. Both these hydrides are more stable than Mg₂NiH₄.

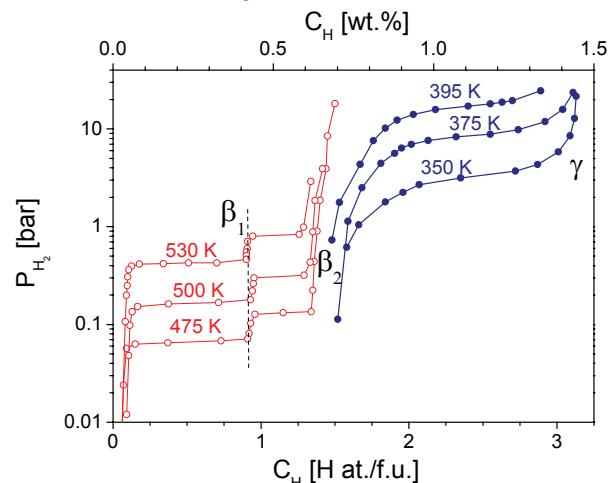


Fig. 1. Desorption isotherms for the Mg₃MnNi₂-H₂ system.

Table 1. Thermodynamic parameters for the Mg₃MnNi₂-H₂ system.

Transformation	ΔH_{des} , kJ·mol ⁻¹ H ₂	ΔS_{des} , J·K ⁻¹ ·mol ⁻¹
Mg ₃ MnNi ₂ \leftrightarrow Mg ₃ MnNi ₂ H ($\alpha \leftrightarrow \beta_1$)	74.2±1.9	133.2±3.9
Mg ₃ MnNi ₂ H \leftrightarrow Mg ₃ MnNi ₂ H _{1.5} ($\beta_1 \leftrightarrow \beta_2$)	72.7±0.6	136±1.2
Mg ₃ MnNi ₂ H _{1.5} \leftrightarrow Mg ₃ MnNi ₂ H ₃ ($\beta_2 \leftrightarrow \gamma$)	41.0±0.2	127.0±0.7

At temperatures above 300°C in hydrogen Mg₃MnNi₂ disproportionates into Mg₂NiH₄

hydride and Mn-Ni phase. Disproportionation reaction occurs at pressures exceeding equilibrium of Mg_2NiH_4 formation (~10 bars at 350°C). Complete hydrogen desorption from Mg_2NiH_4 leads to recombination of Mg_3MnNi_2 .

In other system studied in this work, RE-Co-Mg, we have synthesized new intermetallic compounds $REMgCo_4$ and RE_2MgCo_9 ($RE=Y, Ce$). The hydrogenation properties have been studied for $REMgCo_4$. Formation of two phases β - $CeMgCo_4H_{-4}$ and γ - $CeMgCo_4H_{-6}$ has been observed in $CeMgCo_4-H_2$ system (Fig.2). The structure of more stable β - $CeMgCo_4D_4$ deuteride has been studied by powder neutron diffraction (Fig.3). It retains initial cubic symmetry of $CeMgCo_4$ 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.

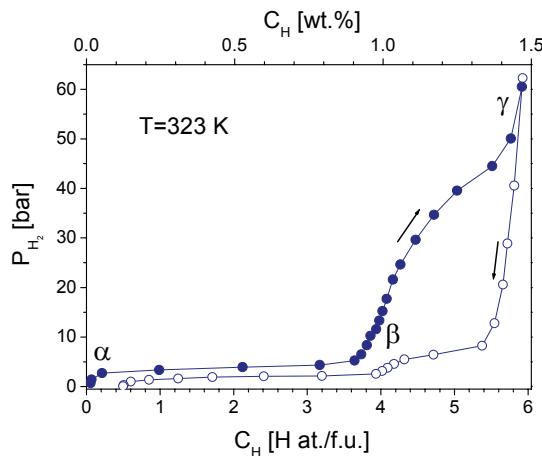


Fig. 2. Absorption-desorption isotherm for the $CeMgCo_4-H_2$ system at 50°C.

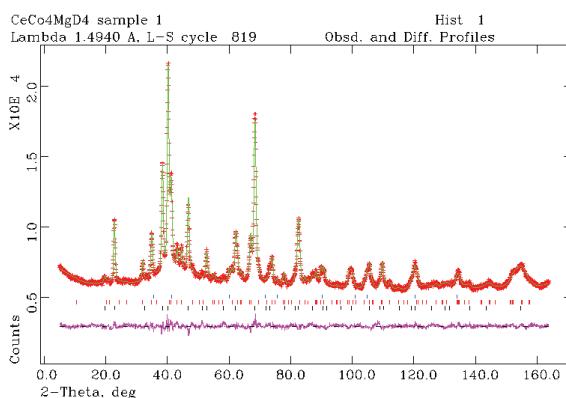


Fig. 3. Powder neutron diffraction pattern of the $CeMgCo_4D_4$ deuteride ($\lambda=1.494 \text{ \AA}$). Impurity phases: Ce_2MgNi_9 and MgO .

It is shown that the D atoms are located in the 24g site only. D atoms occupy triangular $MgCo_2$ face between tetragonal $CeMgCo_2$ interstices forming the D_6 octahedra around Mg atoms. We should note the rather short Mg-D distances,

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

Hydrogenation and structural studies of related compound, $LaMgNi_4$, demonstrated the formation of 3 hydrides (α, β, γ) [5]. The structure of the studied β - $CeMgCo_4D_4$ deuteride is similar to that of γ - $LaMgNi_4D_{4.85}$, but the 4b sites are empty. The further studies should clarify the crystal structure of the saturated hydrides $REMgCo(Ni)_4$.

Table 2. Crystallographic data for $CeMgCo_4D_{4.18(1)}$
Sp.gr. $F-43m$, $a=7.5010(2) \text{ \AA}$.

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

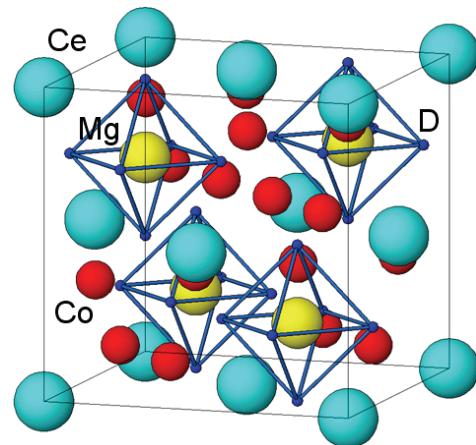


Fig.4. Crystal structure of $CeMgCo_4D_4$.

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