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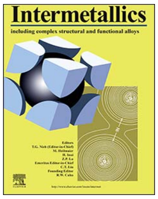

Phase equilibria in the Nd–Mg–Co system at 300 and 500 °C, crystal structure and hydrogenation behavior of selected compounds

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ABSTRACT

The isothermal sections of the Nd–Mg–Co phase diagram at 300 and 500 °C have been constructed on the basis of X-ray diffraction (XRD), Wavelength Dispersive Spectrometry (WDS) and Electron Probe Micro Analyzer (EPMA) analysis. The existence of two ternary compounds $Nd_4Mg_3Co_2$ (own structure type) and Nd_4MgCo (Gd_4RhIn type) was confirmed. The latter has homogeneity range defined as $Nd_{4-x}Mg_{1+x}Co$ with $0 \le x \le 0.2$ at 300 °C and $0 \le x \le 0.3$ at 500 °C. Four new ternary compounds were identified in this work: $Nd_{23-x}Mg_{4+x}Co_7$ ($Pr_{23}Mg_4Ir_7$ type; $-1.5 \le x \le 0.1$ at 300 °C and $-0.6 \le x \le 0.3$ at 500 °C); $NdMg_2Co_9$ (YIn_2Ni_9 type), $\sim Nd_{77}Mg_{14}Co_9$ (cubic) and $\sim Nd_{56}Mg_6Co_{38}$ (unknown crystal structure). Two binary compounds, $NdCo_2$ and $NdCo_3$, were found to dissolve significant amount of Mg with the formation of substitutional solid solutions $Nd_{1-x}Mg_xCo_2$ ($MgCu_2$ type; $x \le 0.1$ at 300 °C and $x \le 0.15$ at 500 °C) and $Nd_{1-x}Mg_xCo_3$ ($PuNi_3$ type; $x \le 0.33$ at 300 °C and $x \le 0.5$ at 500 °C), respectively. The $Nd_4Mg_3Co_2$, $Nd_{4-x}Mg_{1+x}Co$, $Nd_{23-x}Mg_{4+x}Co_7$ and $Nd_{1-x}Mg_xCo_2$ compounds irreversibly absorb hydrogen at room temperature and pressure 1–10 bar to form crystalline or amorphous hydrides with hydrogen content 1.6–2.1 wt. %. Hydrogen thermal desorption from these hydrides in vacuum results in their disproportionation with formation of binary NdH_2 hydride. The $Nd_{1-x}Mg_xCo_3$ ($0 \le x \le 0.5$) alloys reversibly absorb up to 1.3 wt. % of hydrogen. $NdMg_2Co_9$ compound has small hydrogenation capacity, absorbing only 0.5 wt. % at room temperature and hydrogen pressure 185 bar.

1. Introduction

The R–Mg–Ni (R = rare earth) alloys have attracted interest as hydrogen absorbing materials and particularly as effective negative electrodes for Ni–MH batteries [1–4]. Recently, it has been shown that partial replacement of R by Mg in binary intermetallic compounds RNi_2, RNi_3, R_2Ni_7 and R_5Ni_{19} leads to significant changes in characteristics of their hydrides [4]. Compared with binary R_xNi_y phases, Mg-containing alloys ($R_{x-z}Mg_zNi_y$) have higher resistance to hydrogen induced amorphization processes and thus form crystalline hydrides [5]. RNi_3, R_2Ni_7 and R_5Ni_{19} compounds have *hybrid* crystal structure that can be described as a stacking of Laves phase type (RNi_2) and Haucke phase type (RNi_5) layers along [001] direction. Such compounds and their substituted derivatives (R→Mg) are intensively studied as candidate electrode materials for Ni-MH batteries [6,7].

Despite the great interest to R–Mg–Ni alloys, the phase diagrams for most of these systems have not been studied yet. The phase equilibria were investigated and the isothermal sections were established only for four systems so far: Ce–Mg–Ni at 200 °C [8] and at 400 °C [9], La–Mg–Ni at 500 °C [10,11], Tb–Mg–Ni at 400 °C [12] and Y–Mg–Ni at 400 °C [13,14]. Several works are focused on the formation of ternary compounds in the Ni-rich region of R–Mg–Ni (R = Y, Ce, Nd, Pr) systems [15–18].

Recently, we have observed significant improvement of hydrogenation properties of $RMgNi_4$ alloys ($MgCu_4Sn$-type) by substitution of Ni with Co [19–21]. This raised interest in the studies of R–Mg–Co alloys. Up to now, phase equilibria were established for two such systems: La–Mg–Co [22] and Tb–Mg–Co [23]. This paper is a continuation of the systematic study of R–Mg–Co ternary alloys. We report the phase equilibria in the Nd–Mg–Co system at 300 and 500 °C, crystal structure of new ternary compounds and their hydrogenation properties.

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Table 1
Literature data for binary phases of the Nd–Mg–Co system.

Phase	Stability range (°C)	Prototype	Space group	Lattice parameters (Å)			Reference	Presence in this work
				a	*b*	*c*		
Nd–Mg system								
NdMg	< 800	CsCl	$Pm\bar{3}m$	3.869	–	–	[29]	+
$NdMg_2$	750–660	$MgCu_2$	$Fd\bar{3}m$	8.671	–	–	[29]	–
$NdMg_3$	< 780	BiF_3	$Fm\bar{3}m$	7.399	–	–	[29]	+
Nd_5Mg_{41}	< 560	Ce_5Mg_{41}	$I4/m$	14.741	–	10.396	[29]	+
$NdMg_{12}$	*metastable*	$ThMn_{12}$	$I4/mmm$	10.307	–	5.947	[29]	–
Nd–Co system								
Nd_3Co	< 646	Fe_3C	*Pnma*	7.125	9.764	6.408	[30]	+
Nd_5Co_2	–	Mn_5C_2	$C2/c$	16.370	6.430 $\beta = 96.7°$	7.080	[34]	+
Nd_7Co_3	< 596	Th_7Fe_3	$P6_3mc$	9.888	–	5.937	[35]	–
$Nd_{24}Co_{11}$	–	$Ce_{24}Co_{11}$	$P6_3mc$	9.796	–	21.7	[35]	–
Nd_4Co_3	–	–	*hexagonal*	5.853	–	9.580	[35]	–
$Nd_2Co_{1.7}$	< 599	–	*hexagonal*	4.795	–	4.08	[30]	–
	–	$La_2Co_{1.7}$	$C2/m$	8.300(7)	4.799(3) $\beta = 89.47(3)°$	4.138(1)	This work	+
α-Nd_2Co_3	< 583	La_2Ni_3	*Cmca*	4.963	10.006	7.569	[30]	+
β-Nd_2Co_3	650–583	–	–	–	–	–	[30]	–
$NdCo_2$	< 1050	$MgCu_2$	$Fd\bar{3}m$	7.297	–	–	[30]	+
$NdCo_3$	< 1100	$PuNi_3$	$R\bar{3}m$	5.070	–	24.750	[30]	+
Nd_2Co_7	< 1143	Gd_2Co_7	$R\bar{3}m$	5.038	–	36.600	[35]	+
		Ce_2Ni_7	$P6_3/mmc$	5.063	–	24.45	[30]	+
Nd_5Co_{19}	< 1152	Ce_5Co_{19}	$R\bar{3}m$	5.052	–	48.666	[36]	+
$NdCo_5$	< 1266	$CaCu_5$	$P6/mmm$	5.028	–	3.977	[30]	+
Nd_2Co_{17}	< 1370	Th_2Zn_{17}	$R\bar{3}m$	8.426	–	12.245	[30]	+
Mg–Co system								
$MgCo_2$	< 970	$MgZn_2$	$P6_3/mmc$	4.859	–	7.954	[32]	+
δ-MgCo	~350–480	CdNi	$Fd\bar{3}m$	11.434	–	–	[33]	–

2. Experimental part

The Nd–Mg–Co alloys were prepared by two methods. In the first method, the alloys were synthesized from arc melted Nd–Co pre-alloys and fine Mg powder (325 mesh, 99.8 %). Nd–Co pre-alloys were prepared by arc melting of individual metals (purity > 99.9 %) in purified argon atmosphere. Then they were ground and mixed with Mg powder in certain proportions. Mg was added with 3 wt. % excess in order to compensate its evaporation loss at high temperatures. The obtained powder mixtures were pressed into pellets (8 mm in diameter). The pellets were wrapped in tantalum foil and then placed into stainless steel containers, which were filled with argon and sealed by welding. The samples were heat treated by gradual heating from 500 to 800 °C for 25 h, followed by annealing at 500 °C for 250 h and quenching in cold water. In the second method, the individual metals were mixed and loaded into a small tantalum crucible sealed by arc welding in argon atmosphere. The tantalum crucible was then enclosed in evacuated quartz ampoule. The samples were heated in argon atmosphere from room temperature to 400 °C at 5 °C/min rate, kept at 400 °C for 48 h and then heated to 900 °C. Then, they were cooled to 300 °C, annealed at this temperature for 300 h and rapidly cooled down to room temperature. The weight loss in the samples after heat treatment was less than 2 %. Some Nd-rich and Co-rich (> 50 at. %) alloys were re-melted in arc-furnace with non-consumable tungsten electrode under protective argon atmosphere.

Phase analysis of the samples was carried out with the use of powder X-ray diffraction (XRD) (DRON-3.0M and HZG-4, Bruker D8 diffractometers with Fe- and Cu-$K\alpha$ radiation, respectively) and PowderCell software [24]. Lattice parameters were obtained by a least-squares routine [25]. Indexation and crystal structure solution from X-ray powder diffraction data were performed using TREOR program implemented into Fullprof [26]. The obtained powder diffraction data were analyzed by Rietveld method using Fullprof software [26]. Single crystal diffraction data were collected at 20 °C on an Xcalibur™3 CCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation. The chemical composition of the constituent phases was analyzed by Wavelength Dispersive Spectrometry (WDS) and CAMECA SX-100 Electron Probe Micro Analyzer (EPMA).

Hydrogen absorption-desorption properties of the alloys were studied using a Sieverts type apparatus. Prior to hydrogenation the alloys were heat treated in dynamic vacuum (10^{-5} mbar) at 200 °C. Then they were cooled to room temperature and hydrogenated using high purity H_2 gas (99.999 %). Hydrogen was added with 1 bar step up to full saturation at 10 bar. Some alloys were also hydrogenated at higher temperature and lower hydrogen pressure, 120 °C and 0.5–1 bar H_2.

Hydrogen desorption from the hydrides was studied by means of thermal desorption spectroscopy (TDS) with linear heating of specimens (2 °C/min) in dynamic vacuum from room temperature to 500 °C. A coupled TGA/DSC experiment (up to 1000 °C) was performed using the SETSYS Evolution apparatus from SETARAM instrument.

3. Results and discussion

3.1. Phase equilibria in the Nd–Mg–Co system at 500 °C

Literature data for the binary systems Nd–Mg, Nd–Co and Mg–Co [27,28] were used for the study of phase equilibria in the Nd–Mg–Co system (Table 1). Most of the previously reported binary compounds were detected during study of the Nd–Mg–Co system at 500 °C (Tables 1 and 2, Figs. 1 and 2). We have not observed formation of $NdMg_2$ and $NdMg_{12}$. $NdMg_2$ is stable at higher temperatures (between 660 and 770 °C) [27,28], while $NdMg_{12}$ is a metastable phase [29]. Therefore, these two compounds are not shown in the phase diagram at 500 °C (Fig. 1). Also, the existence of Nd_4Co_3, Nd_7Co_3 and $Nd_{24}Co_{11}$ compounds has not been confirmed. Ray *et al.* reported that $Nd_2Co_{1.7}$ has hexagonal structure [30], however, in this study we used the structure model suggested for isostructural $La_2Co_{1.7}$ by Dusek *et al.* [31], who found that