Journal of Alloys and Compounds, 190 (1993) L45–L46
JALCOM 528

Letter

On the composition and structure of the cubic δ-phase in the Mg–Co–H system

M. Yoshida*, F. Bonhomme and K. Yvon
Laboratoire de Cristallographie, Université de Genève, 24 Quai E. Ansermet, CH-1211 Genève (Switzerland)

P. Fischer
Labor für Neutronenstreuung, ETH-Zürich, CH-5232 Villigen PSI (Switzerland)

(Received September 23, 1992)

Three phases are known to exist in the Mg–Co–H system: tetragonal β-Mg_2CoH_5 [1, 2], orthorhombic γ-$Mg_6Co_2H_{11}$ [1, 3] and cubic δ-$Mg_{2-x}CoH_\epsilon$ ($\epsilon \approx 0$, $a = 11.426(8)$ Å [1], 11.43 Å [4]). The latter phase forms by decomposition of the β-phase but its exact composition and structure are unknown. Here we show that the δ-phase derives from a binary compound of composition MgCo which can be obtained by direct synthesis and crystallizes with the CdNi structure type.

Samples of β-Mg_2CoH_5 and its deuteride (for synthesis see ref. 2) were dehydrogenated (dedeuterated) on a thermobalance (type M25-D-P, Sartorius GmbH, Goettingen, Germany) at various temperatures (378–459 °C) and pressures (19–1 bar). Reactions at 398 °C and above showed two plateaux in the pressure region 5–15 bar, whereas reactions at 398 °C and 378 °C showed one plateau at about 3 and 1 bar pressure respectively (Fig. 1). X-ray powder diffraction analysis (Guinier camera and Philips diffractometer, Co Kα radiation, internal standard: silicon, $a = 5.4308$ Å, room temperature) after desorption at 378 °C and 438 °C showed the presence of the δ-phase, Mg and Co phase, and after desorption at 459 °C the presence of the δ-phase, Mg, Co and hexagonal $MgCo_2$ ($MgZn_2$-type structure).

X-ray Rietveld analysis (program DBWS-9006 [5]) on a sample dedeuterated at 1 bar and $T = 398$ °C revealed that the metal atom substructure of the δ-phase was that of the CdNi type (a substitution variant of the Ti_2Ni type), corresponding to the formula MgCo (space group $Fd3m$, $a = 11.434(2)$ Å; dedeuter sample: $a = 11.4356(6)$ Å; dehydrided sample). Refinement results are summarized in Table 1. Dehydrogenation at higher pressures yielded slightly larger cell parameters for the δ-phase, thus confirming the ability of this phase to absorb small quantities of hydrogen (deuterium).

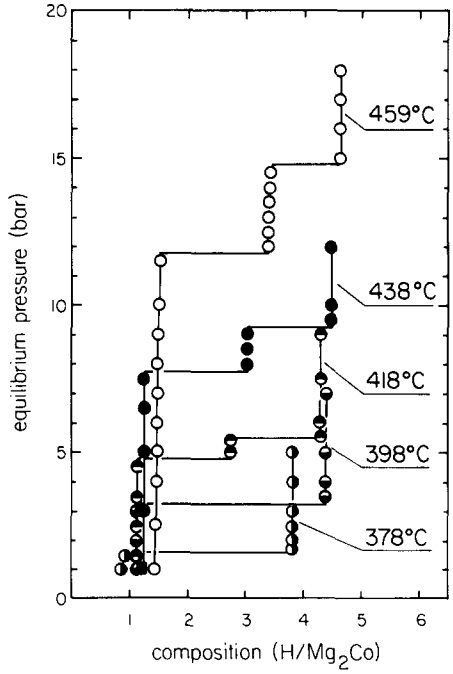

Fig. 1. Pressure–composition isotherms for a β-Mg_2CoH_5 sample. Estimated ΔH values for desorption: upper plateau −108(3) kJ mol^{-1} H_2; lower plateau −95(5) kJ mol^{-1} H_2.

TABLE 1. X-ray refinement results on δ-MgCo

Atom	x	y	z	$U_{iso}(10^{-2}$ Å$^2)$
Co1 (16c)	0.0	0.0	0.0	3.00(4)
Co2 (32e)	0.2020(1)	x	x	U_{iso}(Co1)
Mg (48f)	0.4209(2)	1/8	1/8	2.36(8)

Space group $Fd\bar{3}m$ (No. 227)
Cell parameter $a = 11.434(2)$ Å
$R_B = 7.4\%$, $R_p = 3.2\%$, $R_{WP} = 4.5\%$
Form of temperature factor: $T = \exp[-8\pi^2 U_{iso}(\sin^2\theta/\lambda^2)$

Neutron diffraction experiments on the dedeuterated sample (1 bar, $T = 398$ °C) were performed on the DMC powder diffractometer [6] in the high-intensity mode at the reactor SAPHIR at PSI, Villigen, $\lambda = 1.7001$ Å. The purpose was to check the presence of deuterium (or oxygen) on one of the possible interstitial sites of δ-MgCo as analysed for the structurally related compound $Zr_3V_3OD_x$ (filled W_3Fe_3C-type structure [7]). The sample contained δ-MgCo and the impurity phases Mg, Co and MgO. Rietveld analysis (program DBWS-

*Permanent address: Hitachi Chemical Co. Ltd., Tsukuba Research Lab., 48 Wadai, Tsukuba-city Ibaraki, 300-42, Japan.

0925-8388/93/$6.00

9006 [5]) showed no evidence for the presence of deuterium or oxygen on any of the possible interstitial sites of δ-MgCo. The estimated upper limits for the deuterium and oxygen contents correspond to the formula $MgCoD_{0.01(1)}O_{0.01(1)}$.

In order to check whether δ-MgCo is a stable binary compound (no intermetallic phase of composition close to MgCo has so far been reported in the Mg–Co binary phase diagram [8]), attempts were made to synthesize it directly from the elements. A mixture of Mg powder (Cerac, 99.6%) and Co(Merck, 99.998%), of nominal composition $Mg_{1.05}Co$, was compacted under 16 ton cm^{-2} to form pellets, sealed into a quartz tube and heated to 350 °C (13 weeks), 400 °C (4 weeks) and 500 °C (2 weeks). X-ray analysis of the 350 °C and 400 °C samples revealed the presence of the δ-phase with a cell parameter ($a = 11.426(1)$ Å) slightly smaller than that of the dehydrided sample, elemental Mg and Co, and binary $MgCo_2$. The 500 °C sample consisted of a mixture of $MgCo_2$ and Mg but did not contain significant amounts of δ-phase. Thus cubic δ-MgCo can be considered as a stable binary compound that forms at relatively low temperature and does not require the presence of significant amounts of hydrogen and oxygen.

As to the decomposition of tetragonal β-Mg_2CoH_5, the pressure composition isotherms shown in Fig. 1 clearly confirm a two-step reaction, as suggested previously [4]. However, the data do not allow us to specify reaction mechanisms.

Acknowledgment

We thank Dr. R. E. Gladyshevskii for the translation of the Russian literature, and Mrs. B. Künzler for help with the drawing.

References

1 P. Zolliker, Synthèse, structure et propriétés des hydrures métalliques ternaires Mg_2FeH_6, Mg_2CoH_5 et Mg_2NiH_4, *Thèse No. 2246, Genève, 1987.*
2 P. Zolliker, K. Yvon, P. Fischer and J. Schefer, *Inorg. Chem., 24* (1985) 4177.
3 R. Cerny, F. Bonhomme, K. Yvon, P. Fischer, P. Zolliker, D. E. Cox and A. Hewat, *J. Alloys Comp., 187* (1992) 233.
4 I. G. Konstanchuk, E. Yu. Ivanov, A. A. Stepanov and T. I. Samsonova, *Izv. Nauk SSSR, Ser. Khim. Nauk, 3* (1989) 93 (in Russian).
5 D. B. Wiles and R. A .Young, *J. Appl. Cryst., 14* (1981) 149. A. Sakthivel and R. A. Young, *Program* DBWS-9006, 1990, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, USA.
6 J. Schefer, P. Fischer, H. Heer, A. Isacson, M. Koch and R. Thut, *Nucl. Instrum. Methods Phys. Res. A, 288* (1990) 477.
7 F. J. Rotella, H. E. Flotow and J. D. Jorgensen, *J. Chem. Phys., 79* (1983) 4522.
8 W. G. Moffatt, *The Handbook of Binary Phase Diagrams,* Genium, New York, 1984.