

Hydrogen-stabilized $\text{Mg}_2\text{RhH}_{1.1}$ with filled Ti_2Ni -type structure

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Abstract

$\text{Mg}_2\text{RhH}_{1.1}$ is the first example for a hydrogen stabilized binary metal compound with filled Ti_2Ni -type structure. Its composition was refined from X-ray and neutron powder diffraction data on the deuteride and found to be $\text{Mg}_2\text{RhD}_{1.1}$. The deuterium atoms in the structure occupy octahedral holes formed by Mg atoms and tetrahedral holes formed by Mg and/or Rh atoms. Retrieval of hydrogen by desorption destabilizes the structure and leads to a hitherto unknown binary metal compound of composition Mg_2Rh which crystallizes with the Ti_2Pd -type structure, a branch of the MoSi_2 -type structure.

1. Introduction

Intermetallic compounds that crystallize with the Ti_2Ni -type structure (or the closely related η -carbide-type structures) are often stabilized by impurities such as carbon, nitrogen and oxygen (for earlier studies see for example, ref. 1 and references therein). The nonmetal atoms in these structures occupy octahedral holes formed by the transition metal atoms of the majority component. So far, no Ti_2Ni -type compound is known which is stabilized by a nonmetal of small atomic size such as hydrogen. In this paper we report on the synthesis and structural characterization of the first such compound in the Mg–Rh–H system.

2. Experimental details

Samples of nominal composition $\text{Mg}_{2.1}\text{Rh}$ were prepared from powder mixtures of magnesium (CERAC 99.6% purity, –400 mesh) and rhodium (Johnson Matthey 3N). They were compacted under 16 t cm^{-2} to pellets 4 mm in diameter and 6 mm in height, placed in a nickel crucible and treated in a high-pressure autoclave at 450°C and a pressure of 36 bar hydrogen (Air Liquide, 99.9999%) or deuterium (Air Liquide, 99.8%) for 5 days. After

the reaction the pellets had transformed into a fine powder of light-grey colour which was stable in air.

X-ray powder diffraction (Guinier diffractometer, Cu $K\alpha_1$ radiation, internal standard: silicon, $a = 5.430825 \text{ \AA}$) revealed the presence of two phases in the sample. The majority component crystallized with the Ti_2Ni -type structure (Mg_2Rh : cubic, $a = 12.1893(2) \text{ \AA}$ (deuteride), space group $Fd\bar{3}m$ [2], origin at centre, Mg1 on site 16c: 0, 0, 0 etc., Mg2 on 48f: $x, \frac{1}{2}, \frac{1}{2}$ etc. with $x = 0.418$, Rh on 32e: x, x, x etc. with $x = 0.217$) and the minority component with the CsCl-type structure (MgRh : cubic, $a = 3.1812(2) \text{ \AA}$, space group $Pm\bar{3}m$ [2], Rh in 1a: 0, 0, 0; Mg in 1b: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). No other phases were detected, in particular no binary MgH_2 (or MgD_2) and no metal element. A binary Mg_2Rh phase (or an impurity-stabilized ternary phase) with Ti_2Ni -type structure has so far not been reported in the literature, whereas a binary MgRh phase with CsCl-type structure is known to exist [3]. The cell parameter reported for the latter phase ($a = 3.099(2) \text{ \AA}$) is significantly smaller than that observed in our sample, which suggests that our CsCl-type phase contains hydrogen (deuterium).

X-ray Rietveld analysis using the computer program DBW3.2S [4] confirmed the structure (Mg_2RhD_x : $x(\text{Mg}_2) = 0.4183(5)$, $x(\text{Rh}) = 0.2169(1)$, residuals: $R_B = 0.076$; MgRhD_x : $R_B = 0.085$; total profile: $R_p = 0.117$) and allowed us to assign the Mg and Rh atoms to the various metal sites in the structures. These assignments could not be made from the neutron diffraction because of the similar scattering lengths [5] of Mg ($b = 0.5375 \times 10^{-12} \text{ cm}$) and Rh ($b = 0.593 \times 10^{-12} \text{ cm}$).

The neutron diffraction experiments were performed on a deuterated sample on the DMC powder diffractometer [6] in the high-resolution mode (Ge(511) monochromator, $\lambda = 1.0909 \text{ \AA}$, $\sin(\theta/\lambda)_{\max} = 0.70 \text{ \AA}^{-1}$). The sample consisted of a majority phase with Ti_2Ni -type metal substructure and a minority phase with CsCl-type metal substructure. For both structures the presence of deuterium was checked on all possible interstitial sites. Those found occupied in the Ti_2Ni -type structure were (in order of decreasing occupancy) the tetrahedrally coordinated sites 32e (x, x, x etc., $x = 0.2949(3)$) and 8a ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ etc.), and the octahedrally coordinated site 16d ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ etc.), corresponding to the formula $\text{Mg}_2\text{RhD}_{1.14(6)}$. The octahedrally coordinated sites 8b ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$ etc.) were practically empty. In the CsCl-type structure the octahedrally coordinated site 3d ($\frac{1}{2}, 0, 0$ etc.), *i.e.* that coordinated by four Mg and two Rh atoms, was found to be partially occupied, corresponding to the formula $\text{MgRhD}_{0.8(1)}$. The agreement indices obtained were: $R_B = 0.103$ ($\text{Mg}_2\text{RhD}_{1.1}$) and 0.079 ($\text{MgRhD}_{0.8}$), $R_p = 0.036$ (total profile).

3. Results and conclusions

The positions and environments of the interstitial sites are summarized in Tables 1 and 2 and their occupancies compared with those reported for other hydrogen (deuterium)-containing Ti_2Ni -type compounds such as Ti_2NiH

TABLE 1

Coordinates of metal positions (standardized description [7]) and major interstitial sites (metal environment of occupied sites in brackets) in hydrides (deuterides) with Ti_2Ni -type metal substructure, space group $Fd\bar{3}m$, (inversion centre at the origin)

	$Mg_2RhD_{1.14}$	Ti_2NiH	$Ti_4Fe_2OD_{2.25}$	$Zr_3V_3OD_x$
<i>Metal positions</i>				
48f: $x, \frac{1}{2}, \frac{1}{2}; x \approx 0.41$	Mg	Ti	Ti	Zr
32e: $x, x, x; x \approx 0.22$	Rh	Ni	Fe	V
16c: 0, 0, 0	Mg	Ti	Ti	V
<i>Interstitial sites</i>				
8a: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	[Rh ₄]	[Ni ₄]		
8b: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	[Mg ₆]	[Ti ₆]	[Ti ₆]	
16d: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	[Mg ₆]	[Ti ₆]	[Ti ₆]	[Zr ₆]
32e: $x, x, x; x \approx 0.29$	[Mg ₃ Rh]			[Zr ₃ V]
96g: $x, x, z; x \approx 0.35, z \approx 0.03$			[Ti ₃ Fe]	
192i: $x, y, z; x \approx 0.02, y \approx 0.13, z \approx 0.31$				[Zr ₂ V ₂]

[8] and $Ti_4Fe_2OD_x$ [9] (filled Ti_2Ni -type structure), and the closely related compound $Zr_3V_3OD_x$ [10] (η -carbide W_3Fe_3C -type structure). The occupancies of corresponding interstitial sites in these compounds show striking differences. The tetrahedrally coordinated 8a sites are occupied in $Mg_2RhD_{1.1}$ and Ti_2NiH , but empty in oxygen-stabilized $Ti_4Fe_2OD_x$ and $Zr_3V_3OD_x$. The octahedrally coordinated 16d sites are occupied by deuterium (hydrogen) in $Mg_2RhD_{1.1}$ and Ti_2NiH , and by oxygen in the other compounds. The tetrahedrally coordinated 32e sites are occupied by deuterium (hydrogen) in $Mg_2RhD_{1.1}$ and $Zr_3V_3OD_x$, but empty in $Ti_4Fe_2OD_x$ and Ti_2NiH . Finally, the tetrahedrally coordinated 96g and 192i sites are occupied only in $Ti_4Fe_2OD_x$ and $Zr_3V_3OD_x$ respectively. The reasons for these differences are not yet clear. Repulsive interactions between the nonmetals [11], in particular between hydrogen and oxygen, may play a role, but a study of their exact influence on the site occupancies requires further structural data.

In order to investigate the possibility of $Mg_2RhD_{1.1}$ being stabilized by nonmetal impurities such as oxygen, nitrogen or carbon, we performed desorption experiments. After heating the sample to 510 °C and degassing at 0.1 mb for 12 h the Ti_2Ni -type phase had disappeared and a new hitherto unknown phase with tetragonal cell parameters $a = 3.1899(1)$ Å and $c = 10.080(1)$ Å had formed. Its structure was found to belong to the Ti_2Pd structure branch, which is a branch of the $MoSi_2$ -type structure with $c:a > 3$ (see below).

In order to check whether this new phase was metastable, attempts were made to synthesize it directly from the elements using two different methods. One consisted of sintering elemental Mg and Rh metal powders in evacuated and argon-filled quartz tubes at 500 °C for 2 weeks (nominal metal ratio Mg:Rh = 2.3; Mg purity 99.6%), and the other by induction melting of rhodium ingots with high-purity magnesium ingots (nominal metal ratio Mg:Rh = 2.5;

TABLE 2
Hydrogen (deuterium) and oxygen occupancies^a of major interstitial sites in hydrides (deuterides) with Ti₂Ni-type metal substructure

Compound/site ^b	8a	8b	16d	32e	96g	192i	Reference
Mg ₂ RhD _{1.14}	64(4)	9(3)	31(3)	80(2)			— ^c
Ti ₂ NiH	100(-)	100(-)	100(-)				7
Ti ₄ Fe ₂ OD _{2.25}		100(-)	100(-)		28(3)		8
Zr ₃ V ₃ OD _{1.86}			98(1)	90(1)		0.6(2)	9
Zr ₃ V ₃ OD _{2.86}			95(1)	97(1)		8(1)	9
Zr ₃ V ₃ OD _{4.93}			98(1)	100(1)		22(1)	9

^aIn bold type. Estimated standard deviations in parentheses. (-) Value not refined.

^bSpace group *Fd* $\bar{3}m$ (No. 227), inversion centre at origin. For coordinates see Table 1.

^cThis work.

Mg Purity 99.99%), followed by annealing at 500 °C for 10 days. The first method yielded an almost single-phase sample containing the tetragonal phase (Mg_2Rh : space group $I4/mmm$, $a = 3.1880(6)$ Å, $c = 10.0667(3)$ Å, Rh in $2a$ (0, 0, 0 etc.), Mg in $4e$ (0, 0, z) etc. with $z = 0.3564(3)$, $R_p = 0.084$, $R_B = 0.030$), and a small amount of impurity phase with a tetragonally distorted CsCl-type structure (MgRh : $a = 3.1636(1)$ Å, $c = 3.1222(1)$ Å). The second method yielded the tetragonal phase and a higher content of the tetragonally distorted CsCl-type phase. Thus tetragonal Mg_2Rh with Ti_2Pd -type structure is a stable binary compound that also forms in the absence of hydrogen. Finally, an attempt was made to hydrogenate tetragonal Mg_2Rh in order to study its possible transformation to the cubic Mg_2RhH_x phase. After hydrogenation the former had indeed converted into the latter (Mg_2RhH_x : $a = 12.1938(6)$ Å). These experiments confirm that cubic Mg_2RhH_x is stabilized by hydrogen.

Interestingly, a different situation occurs in the palladium-containing hydride system Mg-Pd-H for which a Ti_2Ni -type phase was recently identified from neutron diffraction work [12]. Independent work by Noréus *et al.* [13] showed that such a phase can also be stabilized by carbon (Mg_2PdC_x : $a = 12.0480(4)$ Å, $x = 0.1$). Our latest experiments on nonmetal-free samples, however, suggest that this phase already forms in the binary Mg-Pd system (Mg_2Pd : $a = 12.0458(8)$ Å; synthesized by induction melting from Mg ingots with a purity of 99.99%, and subsequent annealing at 350 °C for 16 days), and need not be stabilized by significant amounts of nonmetal impurities. In contrast to Mg_2Rh , this phase does not absorb significant amounts of hydrogen.

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