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Letter

Hydrogen absorption–desorption and crystallographic characteristics of $RCo_{3-x}Ga_x(R \equiv Y,\ Gd;\ x=0.6–1.2)$ intermetallics

V. A. Yartys' and I. I. Bulyk
Physico-Mechanical Institute, Academy of Sciences of Ukraine, Naukova str. 5, 290601, Lviv (Ukraine)

O. M. Sichevich and N. I. Tomaszczuk
Institute of Inorganic Chemistry, Lviv State University, Lomonosova str. 6, 290005, Lviv (Ukraine)

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Abstract

The replacement of cobalt by gallium in RCo_3 intermetallics ($R \equiv Y$, Gd) leads to a decrease in the hydrogen absorption capacity from $H/RCo_3 = 3.7$ to 2.0–2.5 atoms of H per formula unit (at.H/f.u.) in the case of $RCo_{2.4}Ga_{0.6}$ compounds. The increase of Ga content in the intermetallics $(Y, Gd)Co_{3-x}Ga_x$ from $x=0.6$ to 1.2 is accompanied by a gradual fall in their hydrogen capacity and by a noticeable complication of their activation behaviour, and leads to a decrease in the hydrogen sorption rate. Hydride phases $(Y, Gd)Co_{3-x}Ga_xH_y$ contain 1.5–2.5 at.H/f.u. Their formation proceeds by means of an isotropic expansion of the original lattice of the $CeNi_3$-type structures ($\Delta a/a_0=2.1–3.5\%$, $\Delta c/c_0=2.6–5.1\%$, $\Delta V/V=7.2–12.6\%$). The increase in the gallium content is accompanied by a rise in the thermal stability of the hydride and by a considerable fall in hydrogen capacity during sorption–desorption cycling.

1. Introduction

The binary YCo_3 and $GdCo_3$ intermetallics crystallize in $PuNi_3$-type structure and interact with hydrogen to form $(Y, Gd)Co_3H_{3.7}$ tetrahydride phases [1] stable at ambient temperatures. Hydride formation is accompanied by the expansion of rhombohedral unit cells of the initial structures, both in the basal plane and in the [001] direction, which leads to an increase in their volume of 20–21%. Thermal decomposition of both hydrides has two stages. Firstly, $(Y, Gd)Co_3H_{2.0}$ dihydrides are formed (at 460 and 420 K respectively), for which the intermetallic structure expansion in the [001] direction only is characteristic. The second stage (at 510 and 450 K) is characterized by the removal of all of the hydrogen from the metallic matrix and the formation of initial intermetallics.

In the ternary {Y, Gd}–Co–Ga systems at compositions $(Co+Ga)/(R=3.0)RCo_{3-x}Ga_x$ intermetallics with a wide homogeneity range ($x=0.6–1.2$) and with the structure of the $CeNi_3$ type [2] are formed. As a result of the replacement of cobalt atoms by larger gallium atoms the structures of these ternary gallides are characterized by a noticeable expansion in the basal plane of the hexagonal lattices. The investigation of hydrogen–intermetallic interaction of $RCo_{3-x}Ga_x$ compounds with the smallest initial gallium contents – $RCo_{2.4}Ga_{0.6}$ ($R \equiv$ Gd, Tb, Dy, Ho, Er) – [3] showed that replacement of cobalt by gallium in RCo_3 intermetallics leads to a decrease in the hydrogen absorption capacity from $RCo_3H_{3.7}$ tetrahydrides to the trihydride with $H/RCo_{2.4}Ga_{0.6}=2.5$ in the case of the Gd-containing compound. There is no noticeable change in the thermal stability of the hydride phases. However, in contrast with RCo_3 compounds, there is a fall in hydrogen absorption capacity during the repetition of hydrogenation–dehydrogenation cycles. Hydride formation leads to the isotropic expansion of the initial lattices (by 11.7%). Dehydrogenation is accompanied by the removal of all of the hydrogen from the metallic matrix and the formation of initial intermetallics. The purpose of this work is to investigate the influence of gallium content in $YCo_{3-x}Ga_x$ and $GdCo_{3-x}Ga_x$ intermetallics on their hydrogen absorption–desorption properties.

For the alloys investigated, metals of the following purity (mass parts of the main component) were used: Y and Gd not lower than 0.999; electrolytic cobalt 0.999; gallium 0.9999. The alloys were obtained by arc melting of the components in argon atmosphere. Annealing was carried out in evacuated quartz ampoules at 870 K for 340 h. X-ray investigation was carried out using a DRON-3 diffractometer using Cu Kα radiation. Calculations of X-ray diagrams and unit cell period refinements were carried out on an IBM PC AT using program batch CSD. Hydrogen absorption was measured by a volumetric method and the thermal stability of the hydrides was studied by thermal desorption of hydrogen in a vacuum of 1 Pa by gradual heating of the samples.

2. Results and discussion

The velocity of the first absorption of hydrogen by $RCo_{3-x}Ga_x$ intermetallics depends substantially on gal-

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lium content in the metallic matrix. The most active hydride formation occurs in the case of $YCo_{2.4}Ga_{0.6}$ and $GdCo_{2.4}Ga_{0.6}$ intermetallics with minimum gallium content. After activation *in vacuo* at 570 K, these compounds absorbed hydrogen under a pressure of 0.1 MPa, reaching saturation in 1–1.5 h. As is shown in Fig. 1, the increase in Ga content up to concentrations of $0.6 < x < 1.2$ is accompanied by a substantial decrease in the hydrogenation velocity and the appearance of a long induction period of hydrogenation. Moreover, saturated hydrides are formed only after storage of the alloys in hydrogen for several hours. The (Y, Gd)$Co_{1.8}Ga_{1.2}$ alloys with maximum Ga contents do not interact with hydrogen at a pressure of 0.1 MPa. Their hydrogenation takes place only when the pressure is higher than 1 MPa.

After the first absorption–desorption cycle all activated samples interact with hydrogen at a pressure of 0.1 MPa irrespective of their Ga content. In this case an induction period of hydride formation is not required and the time needed for the metallic matrix to reach saturation by hydrogen does not depend substantially on Ga concentration in these intermetallics. At the same time absorption–desorption cycling leads to a gradual fall in the hydrogen absorption capacity, which is displayed most clearly at high Ga contents in the intermetallics. The increase in the Ga content itself is also accompanied by a fall in capacity from $H/RCo_3 = 3.7$ to $H/RCo_{1.8}Ga_{1.2} = 1.5$.

The investigation of the thermal stability of the hydride phases obtained showed that their decomposition takes place in a wide temperature range and usually in two stages.

$$YCo_{2.4}Ga_{0.6}H_{2.0} \xrightarrow{300\ K} YCo_{2.4}Ga_{0.6}H_{1.1} \xrightarrow{425\ K} YCo_{2.4}Ga_{0.6}$$

$$YCo_{2.1}Ga_{0.9}H_{2.0} \xrightarrow{300\ K} YCo_{2.1}Ga_{0.9}H_{1.2} \xrightarrow{450\ K} YCo_{2.1}Ga_{0.9}$$

$$YCo_{1.8}Ga_{1.2}H_{1.6} \xrightarrow{300\ K} YCo_{1.8}Ga_{1.2}H_{1.0} \xrightarrow{400\text{–}850\ K} YCo_{1.8}Ga_{1.2}$$

$$GdCo_{2.4}Ga_{0.6}H_{2.5} \xrightarrow{300\ K} GdCo_{2.4}Ga_{0.6}H_{1.9} \xrightarrow{425\ K} GdCo_{2.4}Ga_{0.6}$$

$$GdCo_{2.2}Ga_{0.8}H_{2.3} \xrightarrow{300\ K} GdCo_{2.2}Ga_{0.8}H_{1.4} \xrightarrow{425\ K} GdCo_{2.2}Ga_{0.8}$$

$$GdCo_{2.0}Ga_{1.0}H_{1.6} \xrightarrow{300\ K} GdCo_{2.0}Ga_{1.0}H_{1.2} \xrightarrow{375\text{–}850\ K} GdCo_{2.0}Ga_{1.0}$$

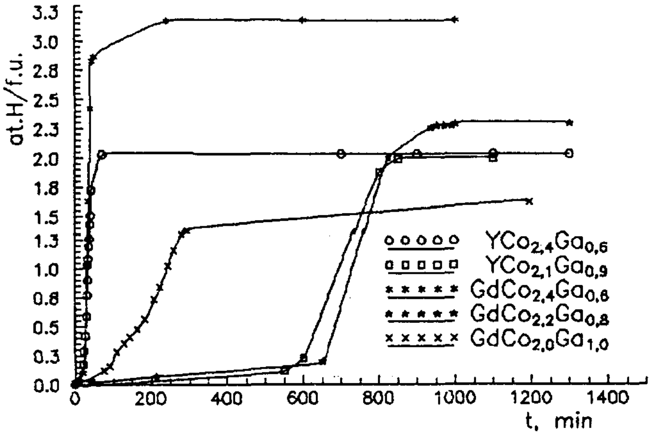

Fig. 1. Time dependence of the first hydrogen absorption ($p_{H_2} = 0.1$ MPa, room temperature) by the intermetallic compounds $YCo_{2.4}Ga_{0.6}$, $YCo_{2.1}Ga_{0.9}$, $GdCo_{2.4}Ga_{0.6}$, $GdCo_{2.2}Ga_{0.8}$ and $GdCo_{2.0}Ga_{1.0}$.

In these cases the desorption of hydrogen from the metal hydrides begins at ambient temperatures and the first stage of the desorption is completed at 370 K. In most cases the second stage of thermal desorption takes place at 425–450 K. However, in the case of the $YCo_{1.8}Ga_{1.2}H_{1.6}$ and $GdCo_{1.8\text{–}2.0}Ga_{1.2\text{–}1.0}H_x$ hydride phases the second peak of hydrogen release is not a very distinct one – hydrogen desorption takes place gradually in a wide temperature range and reaches completion only at 870 K. The thermal stability of the hydride phases is enhanced by higher Ga content as well as by switching from Y- to Gd-containing compounds.

According to the X-ray investigation data, hydride formation is accompanied by an almost isotropic expansion of the initial hexagonal lattices of the $CeNi_3$ type with a volume increase of 7–11%. The volume increase per hydrogen atom absorbed is 2.8–4.6 Å^3 (see Table 1).

During partial hydrogen desorption from (Y, Gd)$Co_{3-x}Ga_xH_y$ saturated hydride phases $YCo_{2.4}Ga_{0.6}H_{1.1}$, $YCo_{2.1}Ga_{0.9}H_{1.2}$, $GdCo_{2.2}Ga_{0.8}H_{1.4}$ and $GdCo_{2.0}Ga_{1.0}H_{1.2}$ hydrides are formed. Their lattice volumes are between those of the initial and the fully hydrogenated compounds.

The comparison of the crystallographic characteristics of Ga-containing hydride structures with the related characteristics of $RNi_{2.67}Al_{0.33}H_x$ hydrides [4] (formed on the basis of the Ce_3Co_8Si-type intermetallics, that is superstructure for $CeNi_3$ type) shows that in both cases formation of saturated hydride phases is accompanied by an isotropic expansion of the intermetallic matrix. However, Al-containing hydrides with intermediate hydrogen contents are characterized by an anisotropic expansion of the hexagonal structures in the [001] direction. Substantial changes in *c*/*a* ratios are not characteristic for Ga-containing hydride phases in the whole hydrogen concentration range.

TABLE 1. Crystallographic data for $RCo_{3-x}Ga_x$ intermetallics and their hydrides

Compound	Lattice parameters (nm)		$\frac{\Delta a}{a_o}$ (%)	$\frac{\Delta c}{c_o}$ (%)	$\frac{\Delta V}{V_o}$ (%)	$\frac{\Delta V}{\text{at.H}}$ $\times 10^3$ (nm^3)	Hydrogen content (mass.%)
	a	*c*					
$YCo_{2.4}Ga_{0.6}$	0.5052	1.613	–	–	–	–	–
$YCo_{2.4}Ga_{0.6}H_{1.1}$	0.5180	1.674	2.53	3.78	9.11	4.92	0.5
$YCo_{2.4}Ga_{0.6}H_2$	0.5235	1.691	3.62	4.84	12.57	3.73	0.9
$YCo_{2.1}Ga_{0.9}$	0.5132	1.626	–	–	–	–	–
$YCo_{2.1}Ga_{0.9}H_{1.2}$	0.5251	1.669	2.32	2.62	7.44	4.6	0.4
$YCo_{2.1}Ga_{0.9}H_2$	0.5297	1.682	3.22	3.42	10.18	3.15	1.1
$YCo_{1.8}Ga_{1.2}$	0.5134	1.606	–	–	–	–	–
$YCo_{1.8}Ga_{1.2}H_{1.6}$	0.5242	1.652	2.1	2.86	7.24	2.76	0.9
$GdCo_{2.4}Ga_{0.6}$	0.5127	1.644	–	–	–	–	–
$GdCo_{2.4}Ga_{0.6}H_{3.2}$	0.5292	1.724	3.22	4.87	11.7	2.28	0.8
$GdCo_{2.2}Ga_{0.8}$	0.5145	1.639	–	–	–	–	–
$GdCo_{2.2}Ga_{0.8}H_{1.4}$	0.5261	1.681	2.25	2.56	7.24	3.2	0.4
$GdCo_{2.2}Ga_{0.8}H_{2.3}$	0.5309	1.700	3.19	3.72	10.4	2.84	0.7
$GdCo_{2.0}Ga_{1.0}$	0.5146	1.609	–	–	–	–	–
$GdCo_{2.0}Ga_{1.0}H_{1.2}$	0.5259	1.671	2.20	3.85	8.46	4.34	0.3
$GdCo_{2.0}Ga_{1.0}H_{1.6}$	0.5272	1.660	2.44	3.17	8.31	3.18	0.7

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