

THE PHASE TRANSFORMATIONS IN $\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0; 0.2; 0.4; 0.6; 0.8; 1.0$ and 1.5)

Bulyk I.I.^{*}, **Panasuyk V.V.**, **Trostianchyn A.M.**

Karpenko Physico-Mechanical Institute of National Academy of Sciences of Ukraine,
5 Naukova St., 79053 Lviv, Ukraine

Introduction

The authors [1] have made a supposition, that the hydrogenation, disproportionation, desorption, recombination (HDDR) process can be applied not only to the treatment of ferromagnetic alloys, but also to a change of the properties of hydrogen-storing materials. It has been obtained the first data about the particularities of phase transformations in Laves phases ZrT_2 -type ($T=\text{Cr, Mn, Fe, Co}$) during HDDR [2].

The aim of the given work is establishing of the conditions and character of phase transformations in $\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0; 0.2; 0.4; 0.6; 0.8; 1.0$ and 1.5) system depending on temperature.

The HDDR process was studied by means of differential thermal analysis (DTA) with the measurement of pressure change in the temperature range $20\text{-}920\text{ }^\circ\text{C}$ at the initial hydrogen pressure up to 5.7 MPa . A sample was placed into the autoclave, the autoclave was evacuated and filled with hydrogen to given (initial) pressure and heated.

The X-ray phase analysis of materials was carried out by XRD patterns recorded from DRON-4 diffractometer (with $\text{Cu K}\alpha$ radiation).

Results and discussion

$\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0; 0.2; 0.4$) system. According to the data of DTA, the formation of hydride at room temperature, its decomposition during heating and repeated formation during cooling were revealed in $\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0; 0.2; 0.4$) system at the indicated above interaction conditions. The thermogram of heating of $\text{LaNi}_5\text{-H}_2$ system (Fig. 1a) also is typical for systems where the aluminium content is 0.2 and 0.4 at./f.un. The phase composition of compounds with $0\text{-}0.4$ at./f.un. was not changed after heating and cooling in hydrogen.

$\text{LaNi}_{4.4}\text{Al}_{0.6}\text{-H}_2$ system. The character of interaction with hydrogen is changed with the increase of Al amount in $\text{LaNi}_{5-x}\text{Al}_x$ compound.

The initial sample of compound with 0.6 at./f.un is single phase. The disproportionation starts after heating up to $700\text{ }^\circ\text{C}$. In addition to the base phase, lanthanum hydride (LaH_x) and Ni_3Al intermetallic were revealed among disproportionation products (see in table).

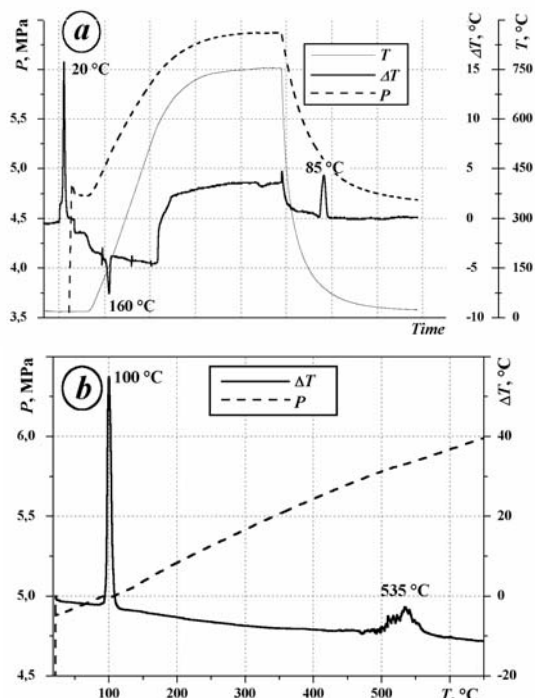


Fig. 1. The thermograms of heating of $\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ system: $x=0$ (a); 1.5 (b), where P is hydrogen pressure; T is temperature and ΔT is DTA signal.

$\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0.8; 1.0; 1.5$) system. The interaction in the mentioned systems was studied at different conditions (see in table). The XRD patterns shown in Fig.2 were obtained for $\text{LaNi}_{4.2}\text{Al}_{0.8}\text{-H}_2$ and are typical for systems where the aluminium content is 1.0 and 1.5 at./f.un. The heating of the initial single phase compounds to $650\text{-}800\text{ }^\circ\text{C}$ leads to different degree of their disproportionation. The beginning of disproportionation of the initial phase and extraction of Ni_3Al compound were found when $x=0.8$ at./f.un. LaH_x , Ni_3Al and traces of the initial phase were revealed in the case when $x=1.0$ at./f.un. The initial compound completely decomposes into LaH_x and Ni_3Al at $x=1.5$ at./f.un. The heating of the investigated compounds to $840\text{ }^\circ\text{C}$ with holding for 1.5 h results in formation of products of the same composition when $x=0.8$ and 1.0 at./f.un. (LaH_x and Ni_3Al with remainder of initial phase) and complete decomposition of the initial compound into LaH_x and Ni_3Al when $x=1.5$ at./f.un.

The increase of heating temperature to $910\text{ }^\circ\text{C}$ with holding for 2 h leads to formation, in

The conditions and products of interaction in $\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0.6; 0.8; 1.0$ and 1.5) system

x	Interaction conditions	Phase	Lattice parameters, nm	
			a	c
0.6	HD: 700 °C	T.str. CaCu_5	0.5026(3)	0.3982(3)
		LaH_x	0.5706(3)	—
		Ni_3Al	0.3558(2)	—
0.8	HD: 800 °C	T.str. CaCu_5	0.5019(2)	0.3998(2)
		$\text{Ni}_3\text{Al} + ?$	0.3582(2)	—
	HD: 840 °C, $\tau=1.5$ h	T.str. CaCu_5	0.50315(7)	0.40212(9)
		LaH_x	0.5656(1)	—
		$\text{Ni}_3\text{Al} + ?$	0.36071(5)	—
HD: 910 °C, $\tau=2$ h	LaH_x	0.5647(3)	—	
	$\text{La}(\text{Ni},\text{Al})_5\text{H}_x$	0.5295(3)	0.8316(4)	
1.0	HD: 720 °C	T.str. CaCu_5	Traces	—
		LaH_x	0.5627(1)	—
		Ni_3Al	0.3571(1)	—
	HD: 840 °C, $\tau=1.5$ h	T.str. CaCu_5	0.5033(2)	0.4014(3)
		LaH_x	0.5643(2)	—
		$\text{Ni}_3\text{Al} + ?$	0.35993(9)	—
HD: 910 °C, $\tau=2$ h	LaH_x	0.5599(2)	—	
	$\text{La}(\text{Ni},\text{Al})_5\text{H}_x$	0.5321(1)	0.8396(4)	
1.5	HD: 653 °C	LaH_x	0.5640(1)	—
		$\text{Ni}_3\text{Al} + ?$	0.3560(1)	—
	HD: 840 °C, $\tau=1.5$ h	LaH_x	0.5647(1)	—
		Ni_3Al	0.3601(1)	—
DR 880°C	T.str. $\text{CaCu}_5 + ?$	0.5071(1)	0.4072(2)	

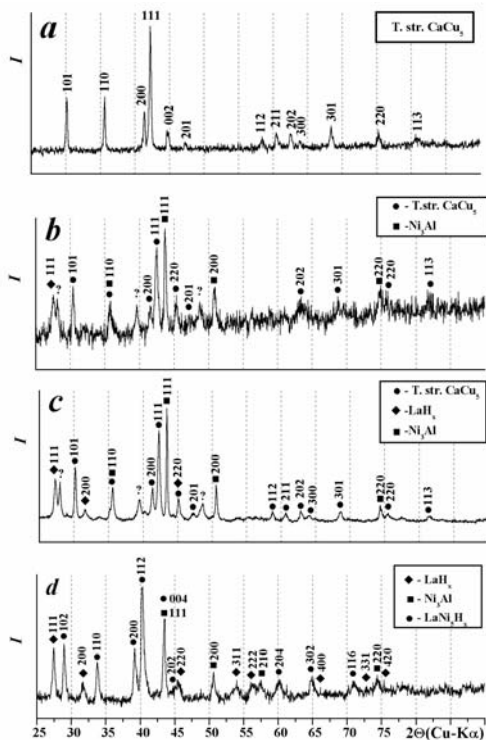


Fig. 2. XRD patterns of the initial $\text{LaNi}_{4.2}\text{Al}_{0.8}$ alloys (a) and products of interaction in $\text{LaNi}_{4.2}\text{Al}_{0.8}\text{-H}_2$ after its heating to temperature ~ 800 °C (b), 840 °C and holding for 1.5 h at this temperature (c); and to 910 C and holding for 2 h at this temperature (d) [4].

Fax: 38 (0322) 64 94 27

addition to LaH_x and Ni_3Al , of phase with structure similar to CaCu_5 but with doubled c spacing in the compounds where $x=0.8$ and 1.0 at./f.un. According to the data [3], the same lattice parameters are typical for hydrides based on LaNi_5 compound with hydrogen content more than 5 at./f.un.

The full recombination with a renewal of the initial structure was achieved in the case of compound with the highest content of aluminium (1.5 at./f.un.).

Conclusion

It was found that at $P_{\text{H}_2} \leq 5,7$ MPa, in $\text{LaNi}_{5-x}\text{Al}_x\text{-H}_2$ ($x=0; 0.2; 0.4; 0.6; 0.8; 1.0$ and 1.5) system, the disproportionation occurs for compounds with the contents of aluminium more than 0.6 at./f.un. (with decomposition of the initial phase into LaH_x and Ni_3Al).

The heating of $\text{LaNi}_{5-x}\text{Al}_x$ ($x=0; 0.2$ and 0.4) compound in hydrogen ($P_{\text{H}_2} = 0.1\text{-}5.0$ MPa) results in homogenization without a change of symmetry of the initial phase.

In the first time it was found that $\text{LaNi}_{5-x}\text{Al}_x$ ($x=0.8; 1.0$ and 1.5) intermetallic compound recombines with the formation of hydride with CaCu_5 -type structure with doubled c spacing during heating in hydrogen to 900 °C and above with holding for 1.5 h at this temperature.

The disproportionation products of $\text{LaNi}_{3.5}\text{Al}_{1.5}$ compound fully recombine after heating in vacuum.

References

- Fruchart D, Liesert S, Perrier de la Bâthie R et al. Hydrogenation-Disproportionation-Dehydrogenation-Recrystallisation: a typical HTM process for anisotropic and coercive Nd-Fe-B magnets. Hydrogen treatment of materials, Book of Abstracts of the Second Int. Conf. "HTM-98", Donetsk, Ukraine, 1998; p.35.
- Bulyk II, Basaraba YuB and Trostianchyn AM. Features of HDDR process in ZrT_2 ($T=\text{Cr, Mn, Fe, Co}$) compounds. Collected Abstracts 7th Int. Conf. on Crystal Chemistry of Intermetallic Compounds. Lviv, Ukraine, 2002; p.20.
- Thompson P, Reilly JJ, Corliss LM et al. The crystal structure of LaNi_5D_7 . J. Physics F. 1986(16): p.675–685.
- Bulyk II, Trostianchyn AM. The peculiarities of structural changes in lanthanum nickel aluminum alloys during heating in hydrogen. Phys.-chem. mechanical of materials. 2003. №1; p.29-34. (In Ukrainian).

Note: in the table x – at./f.un.; T. str. – type of structure; ? – unknown phase; HD – hydrogenation-disproportionation; DR – desorption-recombination.