THE PHASE TRANSFORMATIONS IN $LaNi_{5-x}Al_x$–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=Cr, Mn, Fe, Co) during HDDR [2].

The aim of the given work is establishing of the conditions and character of phase transformations in $LaNi_{5-x}Al_x$–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 20-920 °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 Cu K_α radiation).

Results and discussion

$LaNi_{5-x}Al_x$-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 $LaNi_{5-x}Al_x$–H_2 (x=0; 0.2; 0.4) system at the indicated above interaction conditions. The thermogram of heating of $LaNi_5$–H_2 system (Fig. 1*a*) also is typical for systems where the aluminium content is 0.2 and 0.4 at./f.un. The phase composition of compounds with 0-0.4 at.Al/f.un. was not changed after heating and cooling in hydrogen.

$LaNi_{4.4}Al_{0.6}$-H_2 system. The character of interaction with hydrogen is changed with the increase of Al amount in $LaNi_{5-x}Al_x$ compound.

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

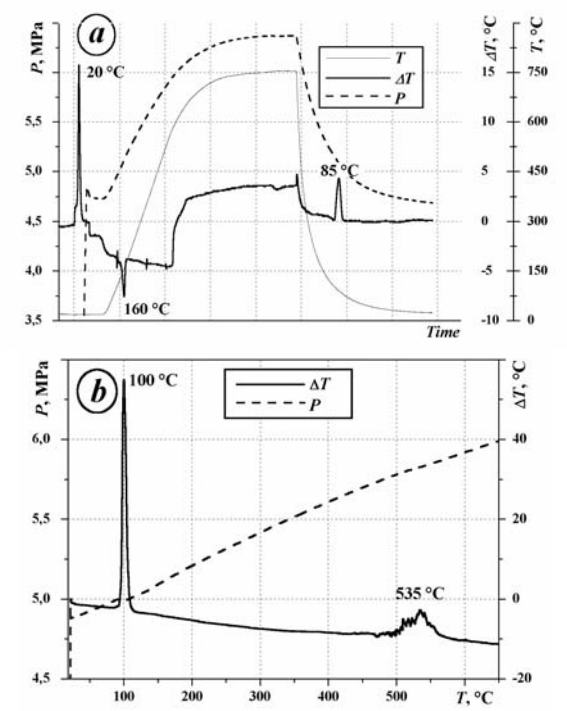

Fig. 1. The thermograms of heating of $LaNi_{5-x}Al_x$-H_2 system: x=0 (*a*)*;* 1.5 (*b*), where *P* is hydrogen pressure; *T* is temperature and ΔT is DTA signal.

$LaNi_{5-x}Al_x$-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 $LaNi_{4.2}Al_{0.8}$-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 650-800 °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.Al/f.un. LaH_x, Ni_3Al and traces of the initial phase were revealed in the case when x=1.0 at.Al/f.un. The initial compound completely decomposes into LaH_x and Ni_3Al at x=1.5 at.Al/f.un. The heating of the investigated compounds to 840 °C with holding for 1.5 h results in formation of products of the same composition when x=0.8 and 1.0 at.Al/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.Al/f.un.

The increase of heating temperature to 910 °C with holding for 2 h leads to formation, in

The conditions and products of interaction in $LaNi_{5-x}Al_x$-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)
		Ni_3Al + ?	0.3582(2)	—
	HD: 840 °C, τ=1.5 h	T.str. $CaCu_5$	0.50315(7)	0.40212(9)
		LaH_x	0.5656(1)	—
		Ni_3Al + ?	0.36071(5)	—
	HD: 910 °C, τ=2 h	LaH_x	0.5647(3)	—
		Ni_3Al	0.3598(5)	—
		$La(Ni,Al)_5H_x$	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, τ=1.5 h	T.str. $CaCu_5$	0.5033(2)	0.4014(3)
		LaH_x	0.5643(2)	—
		Ni_3Al + ?	0.35993(9)	—
	HD: 910 °C, τ=2 h	LaH_x	0.5599(2)	—
		Ni_3Al	0.3596(5)	—
		$La(Ni,Al)_5H_x$	0.5321(1)	0.8396(4)
1.5	HD: 653 °C	LaH_x	0.5640(1)	—
		Ni_3Al + ?	0.3560(1)	—
	HD: 840 °C, τ=1.5 h	LaH_x	0.5647(1)	—
		Ni_3Al	0.3601(1)	—
		?		
	DR 880°C	T.str.$CaCu_5$+?	0.5071(1)	0.4072(2)

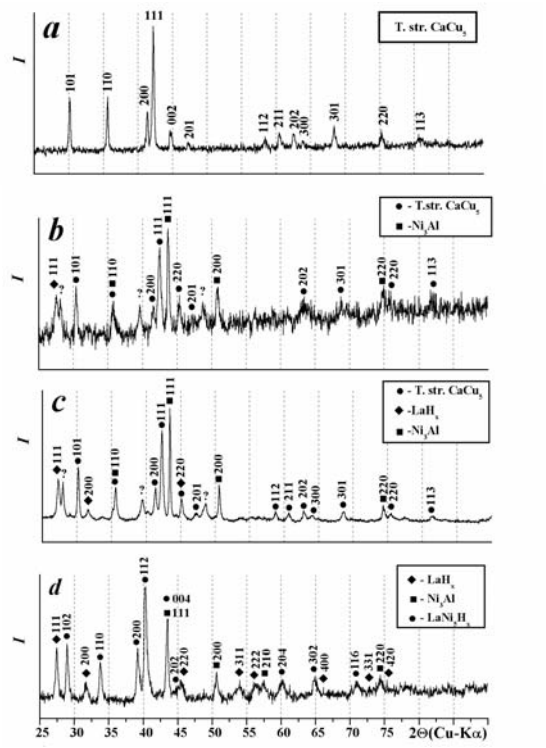

Fig. 2. XRD patterns of the initial $LaNi_{4.2}Al_{0.8}$ alloys (*a*) and products of interaction in $LaNi_{4.2}Al_{0.8}$-H_2 after its heating to temperature ~ 800 °C (*b*), 840 °C and holding for 1.5 h at this temperature (*c*); and to 910 C and holding for 2 h at this temperature (*d*) [4].

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.Al/f.un. According to the data [3], the same lattice parameters are typical for hydrides based on $LaNi_5$ compound with hydrogen content more then 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.Al/f.un.).

Conclusion

It was found that at $P_{H_2} \leq 5{,}7$ MPa, in $LaNi_{5-x}Al_x$-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 $LaNi_{5-x}Al_x$ (x=0; 0.2 and 0.4) compound in hydrogen (P_{H_2} =0.1-5.0 MPa) results in homogenization without a change of symmetry of the initial phase.

In the first time it was found that $LaNi_{5-x}Al_x$ (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 $LaNi_{3.5}Al_{1.5}$ compound fully recombine after heating in vacuum.

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

Fax: 38 (0322) 64 94 27 E-mail: bulyk@ah.ipm.lviv.ua