La-Ni BASED ALLOYS PREPARATION FOR HYDROGEN STORAGE

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Abstract

One of the alternative and topical ways of intermetallic and nonferrous materials application is a metal hydrides formation. Metal hydrides allow storage of hydrogen; carry out gas purification and compression.

Development of powder metallurgy provides new possibility for investigations in the field of alternative way of hydrogen storage. Solid form of hydrogen storage with the possibility of reversible sorption, gives opportunity for creation autonomous energy storage systems and use hydrogen like a modern energy carrier.

Lanthanum-nickel based alloys allow hydrogen storing at ambient temperatures and pressure not higher than 15 bar, which makes the application of these alloys quite practical. The disadvantages of these alloys are the high cost of the initial powdered pure metals and the relatively low mass content of hydrogen in the final alloy. Despite this, La-NI alloys are quite interesting and prospects for further study and modifications.

Keywords: Intermetallic compounds, lanthanum-nickel alloy, metal hydrides, hydrogen storage, XRD analysis

1. METAL HYDRIDES - ALTERNATIVE WAY OF HYDROGEN STORAGE

As it is known, palladium is one of the best metals for hydrogen storage [1], but the price of this material does not allow its use widely [2]. Other materials for hydrogen storage could be complex hydrides since they have a greater storage density in comparison with other types of metal hydrides. **Figure 1** described the different ways of hydrogen storage. However, another important characteristic of hydrogen storage systems based on metal hydrides is the possibility of reversible hydrogen sorption and complex hydrides are not allow to achieve a reversible sorption. The micro porous adsorbents and interstitial hydrides have similar hydrogen densities and volumetric capacity but the second one could work at an ambient temperature which gives a great advantage in practical use. **Table 1** shows main working characteristics of various hydrogen storage ways.

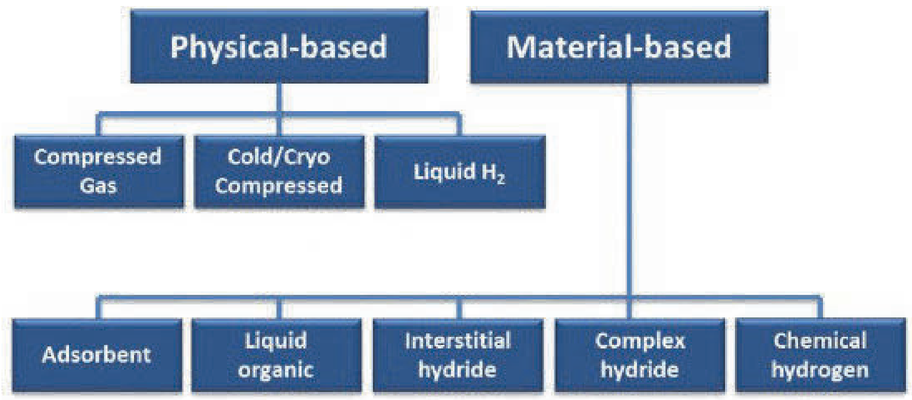

Figure 1 Possible ways of hydrogen storage

Table 1 Comparison of hydrogen storage ways and their main working characteristics [3]

Ways of hydrogen storage	Gravimetric capacity (wt.%)	Volumetric capacity (kg/m^3)	Working temperature (K)
Microporous adsorbents: Zeolites	≤ 7.5	≤ 48	77
Intermetallic hydrides: $LaNi_5$	1.49	87	close to ambient
Complex hydrides: Mg_2NiH_4, $NaAlH_4$, $LiBH_4$	3.6	98.8	373-473

Reaction of metal hydride reversible formation can be described by the following equations:

$$Me + nH_2 \leftrightarrow MeH_n + Q \quad (1)$$

$$Me + nH_2O + e^- \leftrightarrow MeH_n + nOH^- \quad (2)$$

2. PROBLEMATIC OF METAL HYDRIDE PREPARATION AND PRACTICAL USING

Base on personal working experience with $(LaCe)Ni_5$ based alloy and hydrogen storage system HBond-1500, made by LabTech company, few problematic aspects of this alloy practical using were determined.

First of all, it is a problematic of full system charging or complete hydrogen sorption in $(LaCe)Ni_5$ alloy. Completeness of hydrogen sorption depends on the accurate thermoregulation of ongoing hydride formation process. In addition, maximal hydrogen weight capacity of unmodified $LaNi_5$ and $(LaCe)Ni_5$ alloys is not more than 1.6-1.8 wt.%.

The second problematic aspect is a complexity of alloys producing. This issue has become a significant obstacle for the project realization. The classic method of alloy production is a direct fusion from the pure bulk metals in the oven. The same method is used by «LabTech» company. Alloys synthesis, by carrying out joint chemical and heat treatment transformations and using metal oxides or chlorides, instead of bulk metals, is not typical and common method of alloys production. In this regard, lack of equipment for the synthesis of $LaNi_5$ based alloys was appeared. Further analysis of the practical works of other authors shows that the chemical method of $LaNi_5$ alloy production from metal oxides and chlorides is applicable in practice. In the work of G. Giresan, S.R. Sankaranarayanan, L.J. Berchman [4] was described an example of $LaNi_5$ alloy production by thermo-chemical synthesis and using magnesium (Mg) as a reducing agent:

$$La_2O_3 + 10\ Ni + 3\ Mg \rightarrow 2\ LaNi_5 + 3\ MgO \quad (3)$$

Moreover, in the work of S. Kamasaki, Y. Misaki, T.Kanayama, M.Yamada method of alloy modification by additional metal powders of Co and Al for alloy lifetime increasing during operation was described [5].

3. THE MEASUREMENTS AND TEST RESULTS

3.1. LaNi5 alloy preparation at VSB-TUO, Nanotechnology Centre

To perform the alloys synthesis, the new system was assembled. Graphite crucible with reagents, covered by the lid should be placed to the furnace. The crucible lid has two holes for gas pipes connection. One end of the tube is connected to a source of inert gas cylinder with argon. The second tube is used for gas byproducts removing from the reaction zone of the furnace.

Preparation of alloys was carried out in an induction furnace. The lanthanum and nickel chlorides together with lithium hydride were premixed in the required quantitative proportions (**Table 2**).

Table 2 Reactants composition for La-Ni based alloys preparation

Alloys	Reactants weights (g)									
	For 1 kg of alloy					Based on 1.25 g of LiH				
	$LaCl_3$	$CeCl_3$	$NiCl_2$	LiH	Mm	$LaCl_3$	$CeCl_3$	$NiCl_2$	LiH	Mm
$LaNi_5$	566.55	-	1496.42	238.44	-	2.97	-	7.845	1.25	-
$(LaCe)Ni_5$	429.20	431.34	1133.65	222.60	-	2.41	2.42	6.365	1.25	-
$(LaMm)Ni_5$	431.66	-	1140.13	181.90	241.30	2.97	-	7.83	1.25	1.66

Note: MM = Mischmetall

Mixing of the initial components was conducted under an inert atmosphere in glow-box to prevent oxidation and saturation of air moisture. Temperature measurement in the reaction zone of the furnace was carried out by using a thermocouple. **Figure 2** shows basic view of the reactor which was used for the alloys preparation.

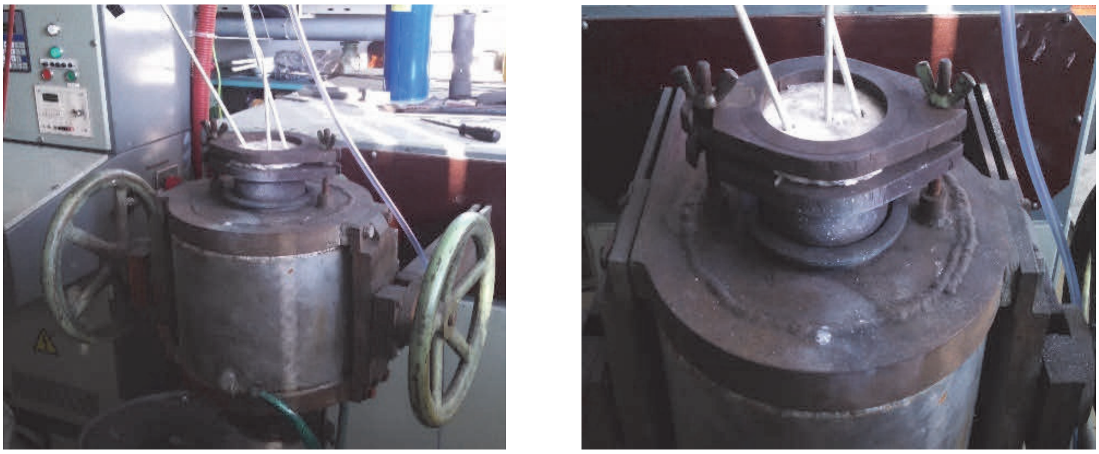

Figure 2 Basic view of the reactor for alloys preparation

La-Ni based alloys syntheses were carried out at following working parameters:

A - sample (1)
Reagents heating up to 750 °C during 80 minutes; sample holding during 80 minutes at 750 °C.

B - sample (2)
Increasing of working temperature up to 900°C and duration of heating process
Reagents heating up to 900 °C during 100 minutes; sample holding during 80 minutes at 900 °C.

C - sample (3A and 3B)
Increasing of sample holding time up to 90 minutes; sample (3A) - with LiH, sample (3B) - without LiH.
Reagents heating up to 900 °C during 80 minutes; sample holding during 90 minutes at 900 °C.

Figure 3 shows the time-temperature curves of alloys preparation. After temperature holding all alloy samples were cooling down close to the ambient temperature and placed in a desiccator before subsequent qualitative analysis.

Three $LaNi_5$ samples in crucibles: $LaNi_5$ sample (2), LaNi5 alloy sample (3A) made with LiH and $LaNi_5$ alloy sample (3B) made without LiH were putted in the oven for heating during night. Samples in the oven placed under vacuum and heated up till 110 °C for complete drying. Two samples, which were made with LiH show the grey colour of alloy and monolithic structure, $LaNi_5$ sample (2) - with visible oxidation white points on the surface of alloy. $LaNi_5$ sample (3A) - without visible oxidation. $LaNi_5$ sample (3B) which was made without LiH looks amorphous with visible phase separation and brown-orange/dirty-yellow colour of sample. **Figure 4** shows photos of the three samples described above.

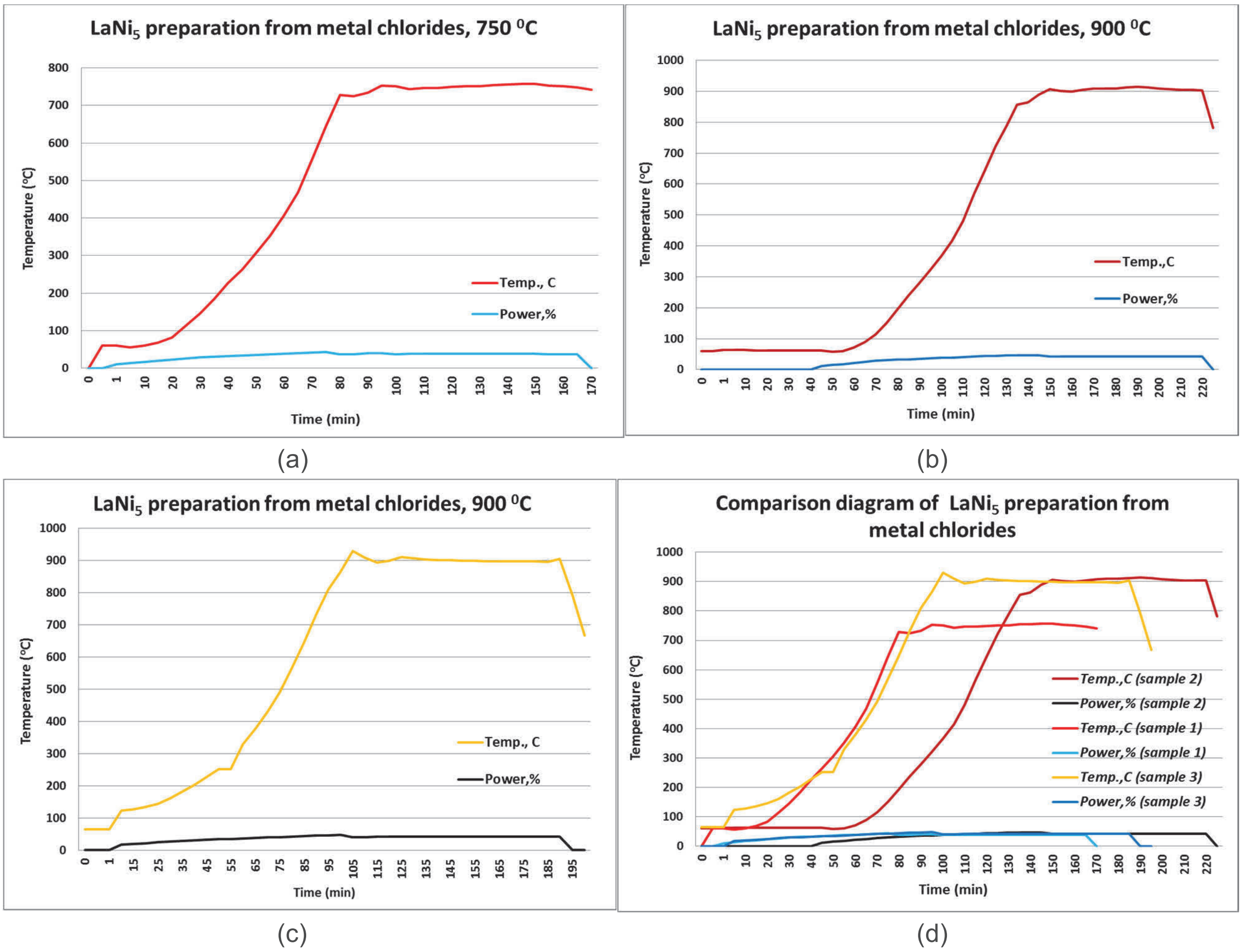

Figure 3 The time-temperature curves of alloys preparation

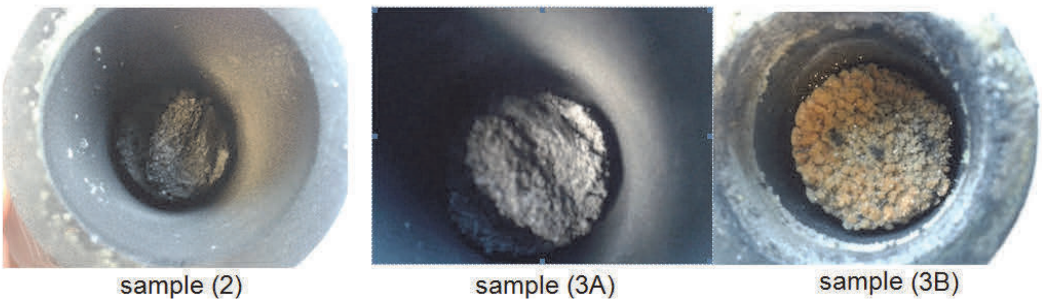

Figure 4 General wiev of three La-Ni samples: sample (2) and sample sample (3A) made with LiH; sample (3B) without LiH

3.2. Sample analysis

Information about chemical composition and structure of prepared alloys were obtained from XRD analysis of relevant samples. Measured samples were evaluated using appropriate software and compared with ICCD database. Measured sample was not stable under the ambient conditions. From this reason sample was gently grinded under flow of nitrogen and covered with 6 μm thick Mylar foil to eliminate exhibition of air humidity. The

XRD diagram of LaNi5 phase is shown in **Figure 5**. Broad diffraction at positions 16.0, 19.3 and 30.0° 2theta corresponds to the Mylar foil.

Measurement conditions: Diffractometer Rigaku SmartLab; goniometer geometry - Bragg-Brentano theta-2theta; lamp - CoKα (λ_1 = 0.178892 nm, λ_2 = 0.179278 nm); detector - D/teX Ultra 250; range of the measurement - 5 - 90° 2theta; sample holder - glass holder with cavity depth 0.5 mm.

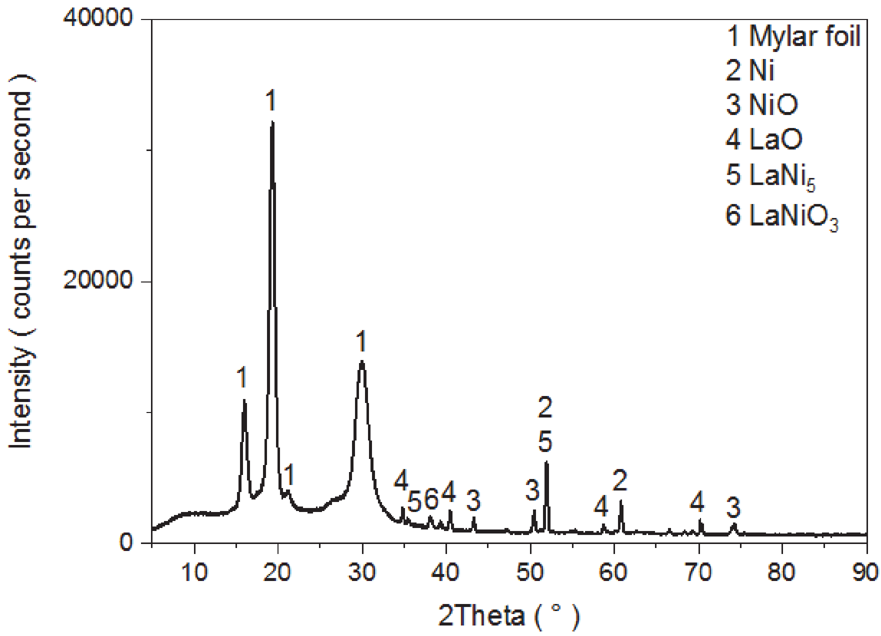

Figure 5 XRD diagram of alloy copmosition (phase $LaNi_5$)

As can be seen from the **Table 3** only one of the alloy samples (sample 3A) represents the $LaNi_5$ phase. The results of the XRD analysis showed that most of the samples were exposed to strong oxidation during sample synthesis or sample preparation for next analysis. Based on the operating parameters of the synthesis of each sample and subsequent analysis, it can be seen that increasing of sample holding time (sample 3) led to the formation of the desired $LaNi_5$ phase. In accordance with this, further synthesis of the samples will be carried out with a longer temperature holding in the furnace. At the same time, the problem of oxidation of samples remains open.

Table 3 Phase compositions of alloys samples getting from XRD analysis

Sample	**Chemical composition**				
$LaNi_5$ (1)	Li_2O	LaOCl	NiO	La_2NiO_4	
$LaNi_5$ (2)	Li_2O	LaOCl	NiO	$La_2(NiO_{4.144})$	
$LaNi_5$ (3)					
$LaNi_5$ (3A)	Ni	LaO	NiO	$LaNiO_3$	$LaNi_5$
$LaNi_5$ (3B) without LiH		LaOCl	$NiCl_2$		

4. CONCLUSION

Results of chemical composition analysis of La-Ni based alloy samples gave useful information about exist problem with alloys synthesis from metal chlorides such as a choosing of optimal time- temperature working parameters of synthesis, which from one side should be enough for creation desired $LaNi_5$ phase during synthesis, and from other side should be as shorter as possible for energy and time consumption reducing of the synthesis process. Cost of the reagents that should be used for alloy preparation and respectively cost of the final alloy is the second important issue and the reason why the La-Ni alloys in this job were synthesized from metal chlorides. Next synthesis should be carried out at increased temperature sample holding stage for fully $LaNi_5$ phase creation.

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