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The Influence of Mechanical Activation on Hydrogen Absorption by Intermetallic Compound $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$

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Abstract—The influence of mechanical activation in a high energy planetary ball mill on hydrogen sorption and structural properties of intermetallic compound $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$ in relation to its application as a filler in composite metal-polymer membranes for hydrogen separation from gas mixtures was studied. It has been determined that the basic results of performed processing are the decrease of the coherently diffracting domain size and the increase of lattice microstrain while the unit cell parameters remain unchanged. In the temperature range of 298–333 K, the hydrogen absorption and desorption isotherms were measured, and the values of the related enthalpy and entropy, which do not depend on mechanical activation time, were determined. The results of this work allow us to consider the obtained data as reference values to describe the hydrogen sorption behavior of a metal-hydride component in composite membranes with satisfactory accuracy.

Keywords: hydrides, hydrogen, mechanical activation

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INTRODUCTION

The unique ability of some intermetallic compounds (IMCs) to interact reversibly with hydrogen in relatively mild conditions opens wide opportunities of their application in hydrogen energy. This means not only hydrogen storage, but also thermosorption compression, hydrogen sensors and getters, Ni-MH batteries, hydrogen extraction from gas mixtures and its purification [1]. The last direction is of particular importance due to the increasing demand of high-purity hydrogen to power fuel cells. However, the direct application of metal hydride materials in the most promising (membrane) systems for hydrogen separation is hindered by their known ability to pulverize during the interaction with hydrogen. The exception is a small group of palladium-based alloys, but their implementation is severely limited by high cost and short service life [2]. The adaptation of a wide range of metal hydride materials to membrane technology for hydrogen-containing gas mixture separation is a technical and scientific objective. As recently shown, a possible solution of this problem is the production of metal-polymer composite membranes, where a hydride forming component (e.g. AB_5 -type IMCs) performs the function of active disperse filler in a polymer matrix [3]. To achieve the optimal adhesion between membrane components and, as a consequence, the efficiency of the gas separation process, the crucial factor is their preliminary mechanical acti-

vation in a ball mill. The detailed research showed that the energy transfer to the material during the high-energy mechanical treatment leads to the accumulation of structural defects in the bulk and at the surface of metal particles [5]. As a result, the adhesive ability of the material increases, and this promotes good interfacing in metal-polymer composites [6, 7] and even low-temperature intermetallic powder compaction without a binder [8].

The high-energy mechanical activation affects significantly not only physical properties, but also hydrogen sorption ability of metal-hydride materials. While the kinetics of hydrogen absorption and desorption is obviously related to the particle size reduction and additional reaction surface formation, the change of hydrogenation thermodynamic parameters has a more complicated nature. The different aspects of this influence were analyzed, for example, in works [9–11], and summarized in [12]. Most authors note the decrease of absorption capacity, the expansion of hydrogen solid solution area and the reduction of plateau region at higher doses of deformation impact. The increased concentration of crystal structure defects and the appearance of amorphous regions particularly at the grain boundaries are considered as possible reasons for the observed phenomena. The preparation of metal-polymer membrane materials involves the short mechanical treatment (for several minutes [4]), and the extent of influence of aforementioned factors at

Table 1. The influence of mechanical activation time on crystal lattice parameters of $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$ samples and their β -hydride phases

	Milling time, min	a , nm	c , nm	V , nm ³	$\Delta V/V_0$, %	D , nm	ϵ , %
Pristine alloy	—	0.513	0.395	0.0899	—	41	0.3
	1	0.507	0.400	0.0889	—	25	0.5
	3	0.505	0.400	0.0882	—	7	2.5
β -hydride	—	0.531	0.416	0.1014	12.8	32	0.3
	1	0.533	0.404	0.0992	11.4	12	0.4
	3	0.531	0.407	0.0992	12.5	10	1.2

such small doses of impact has not been investigated in details to date.

The choice of the work object was determined by a set of parameters that are most critical for adaptation of metal hydride materials to membrane gas separation. First, this is the value of hydride formation equilibrium pressure, which should not exceed 1 atm within the working temperature range (up to 60°C). Second, the minimal specific volume increase during hydrogen absorption is required for preserving the adhesion at the metal/polymer interface. Third, a specific form of metal hydride system phase diagram is beneficial for high stability after multiple hydrogenation-dehydrogenation cycles – namely, the increased solid solution area and the short plateau [13]. The multicomponent alloy $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$ described earlier in [14] meets all these requirements, but there is no information about the effect of ball milling on its structure and properties. Hence, the aim of our work is to obtain new experimental data on the influence of high energy mechanical treatment on microstructure and hydrogen sorption features of $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$.

MATERIALS AND METHODS

The intermetallic compound $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$ was synthesized from high-purity metals (La – 99.8%, Ni – 99.96%, Co – 99.9%; Mn was employed in the form of NiMn ligature) in an electric arc furnace with a non-consumable W electrode in pure argon. To achieve homogeneity, the ingot was remelted 3 times.

The mechanical activation of the samples was performed in a water-cooled high-energy planetary ball mill AGO-2U for 1 and 3 min. The obtained alloy (8 g) was put into metal cylindrical drums with internal ceramic coating and ceramic (ZrO_2) milling balls with a diameter of 6 mm and total mass of 66 g. The handling of raw and mechanically activated powders was carried out in an argon glove box MBraun.

X-ray diffraction (XRD) study was done on a Thermo ARLX'TRA diffractometer using CuK_α radi-

ation ($\lambda = 0.15405$ nm, reflection geometry, semiconducting detector with Peltier cooling, angle range of $2\theta = 20^\circ\text{--}50^\circ$, scan rate $0.5^\circ/\text{min}$). The accuracy of crystal lattice parameter determination was 0.003 nm. The size of coherently diffracting domains (D) and the value of root-mean-square lattice strain (ϵ) were estimated by the approximation method from the XRD peak broadening [15]. To determine the structure parameters of the hydride phases, the hydrogen-saturated samples were cooled in liquid nitrogen under pressure and then exposed to air at the same temperature. This treatment leads to the passivation of the sample surface and prevents the hydride decomposition during several hours, which is enough to conduct *ex situ* XRD.

Hydrogen used in this work was obtained by desorption from hydride phase of a LaNi_5 -type alloy, the amount of impurities did not exceed 10^{-5} vol %.

Before sorption experiments, the samples (non-milled, milled for 1 min and milled for 3 min, respectively) were subjected to two cycles of hydrogenation-dehydrogenation to achieve reproducible values of studied parameters. The hydrogen sorption/desorption isotherms were measured at 298, 313 and 333 K. The reaction temperature was maintained accurate to 1 K.

The investigation of absorption and desorption processes was carried out in an experimental Sieverts-type setup [16]. The samples were put to a steel autoclave and attached to a gas measuring system. The amount of absorbed and released hydrogen was determined using van-der-Waals equation from the pressure changes in the system.

RESULTS AND DISCUSSION

X-ray diffraction data for the raw cast alloy $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$, the samples, which were mechanically activated for 1 and 3 min, and related hydride phases are presented in Table 1. In all cases, including hydrogen-saturated hydrides, the hexagonal CaCu_5 -

Table 2. The influence of mechanical activation time on p – C – T parameters of $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}\text{--H}_2$ system

T , K	Milling time, min	p , atm		$p_{\text{abs}}/p_{\text{des}}$	H/M		
		p_{abs}^*	p_{des}^*		$p = 0.5$ atm	$p = 1$ atm	$p = 10$ atm
298	—	0.24	0.23	1.04	3.6	4.3	5.4
	1	0.25	0.22	1.14	3.2	3.7	4.8
	3	0.25	0.21	1.19	2.2	2.4	3.5
313	—	0.40	0.37	1.08	3.6	4.0	5.3
	1	0.42	0.34	1.24	3.2	3.7	5.2
	3	0.43	0.35	1.23	1.8	2.3	3.2
333	—	0.91	0.70	1.30	2.4	3.4	4.8
	1	0.94	0.70	1.34	1.2	2.1	3.2
	3	0.95	0.72	1.27	0.8	1.4	2.6

* — the pressure corresponds to the middle of the isotherm plateau.

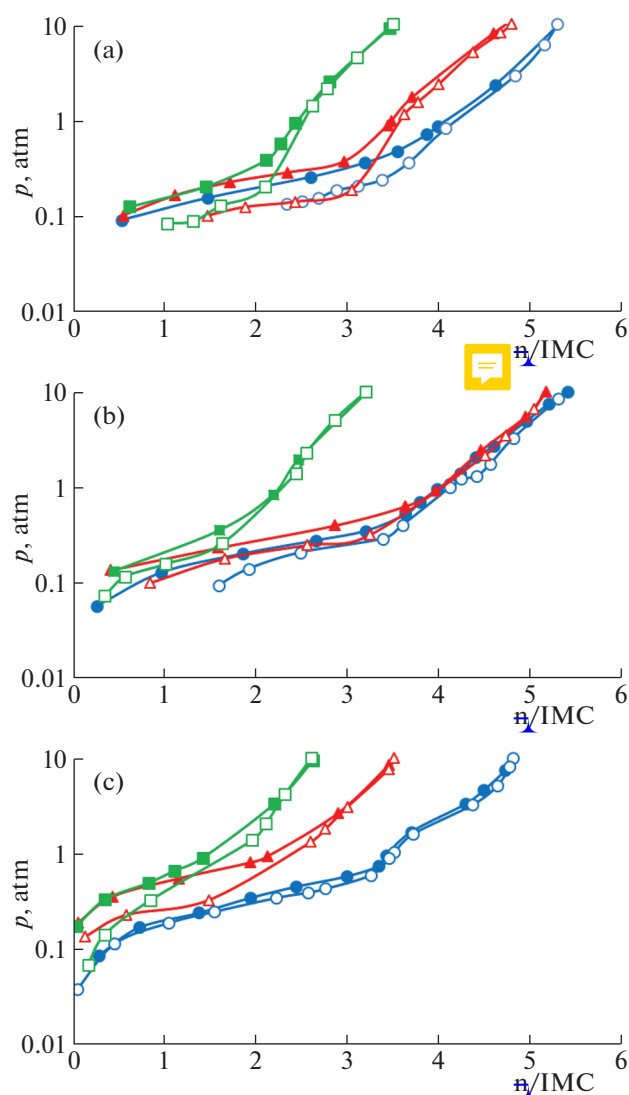


Fig. 1. (Color online) Isotherms of hydrogen absorption/desorption in intermetallic compound $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$. Circles — the non-milled sample, triangles — the sample milled for 1 min, squares — the sample milled for 3 min. Absorption — filled markers, desorption — hollow markers.

type ($P6/mmm$ space group) was recorded. The a parameter and the unit cell volume of the IMC reduce insignificantly after the mechanical activation. As expected, the lattice microstrain increases, and the coherently diffracting domain size decreases, especially at the milling time of 3 min. Herewith, the relative expansion of the crystal lattice during hydride phase formation remains the same within the measurement error.

The isotherms of hydrogen absorption and desorption in $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$ samples treated in the planetary ball mill for 1 and 3 min in comparison with the raw as-cast IMC are presented in Fig. 1. The obtained thermodynamic parameters, dissociation pressures and hydrogen absorption capacity are given in Table 2. The decrease of the total absorption capacity and the reduction of plateau area with the milling time increase can be observed. However, the equilibrium pressure value remains practically unchanged. This trend can be traced at each temperature. It should also be noted that the equilibrium plateau pressure does not exceed 1 atm even at 333 K, which is important for the efficient implementation of the IMC as a filler in gas separation membranes.

The hydrogenation/dehydrogenation enthalpy and entropy values were estimated from the p – C – T measurements data in the temperature range of 298–333 K using the van't Hoff equation. In these calculations, the pressures corresponding to the middle of the two-phase $\alpha \leftrightarrow \beta$ area at the isotherms were chosen as the experimental parameter characterizing the phase equilibrium. The values given in Table 3 indicate that the duration of mechanical activation practically does not affect the thermodynamic parameters.

CONCLUSIONS

The performed study showed that the significant change of the microstructure parameters with minor variations of unit cell size is the main result of short mechanical activation of intermetallic compounds.

Table 3. The influence of milling time on thermodynamic parameters of $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Mn}_{0.1}$ hydration and dehydration

	Milling time	ΔH , kJ/mol	ΔS , J/mol K
Hydrogenation	—	-35 ± 3	-100 ± 5
	1	-33 ± 3	-97 ± 5
	3	-33 ± 3	-95 ± 5
Dehydrogenation	—	26 ± 5	75 ± 8
	1	27 ± 5	79 ± 8
	3	31 ± 5	81 ± 8

The increase of defect concentration (ε value) can be considered as a beneficial factor for making metal–polymer composites with optimal adhesion at the interface. The observed decrease of absorption capacity is critical for hydrogen storage systems, but is not determinative in membrane gas separation processes. Meanwhile, the main thermodynamic parameters of interaction with hydrogen practically do not depend on mechanical activation time. The results of the research allow us to consider the data obtained for initial alloys as reference values with respect to the hydrogen sorption behavior of the metal hydride component in composite membranes.

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