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SIMS STUDY OF THE SURFACE OF LANTHANUM-BASED ALLOYS

The results of researches of the surfaces of intermetallic alloys $LaNi_5$*,* $LaNi_{4.75}Al_{0.25}$*, and* $LaNi_{4.5}Al_{0.5}$ *with the use of secondary ion mass spectrometry are presented. It is shown that, at hydrogen partial pressures of* 10^{-7}*–*10^{-2} *Pa and temperatures of 300–900 K, the processes of hydrogen interaction with the examined alloys take place only at the alloy surface and in its near-surface region. In the temperature interval from the room one to 500 K, hydrogen diffuses in appreciable amounts to depths of up to 10 monolayers. As the temperature increases, the amount of hydrogen-containing chemical compounds on the surface and in the near-surface region decreases, whereas the amount of carbides and oxides of the alloy components increases. As hydrogen is accumulated on the surface, a hydrogen-containing structure is formed, in which nickel atoms are chemically bonded with two, and lanthanum atoms with more than two hydrogen atoms.*

Keywords: SIMS, surface, hydrogen, hydrides, hydrogen storage alloys.

1. Introduction

Some transition metals and their alloys reversibly react with gaseous hydrogen to form metal hydrides. Such reversible hydrogenation reactions make those metals and their alloys to be potential materials for the development of metal hydride technologies, e.g., the accumulation of hydrogen, its compact and safe storage, thermosorption compression, hydrogen extraction from gas mixtures, hydrogen purification, isotope separation, *etc.* The hydrogenation/dehydrogenation reaction of those materials can be driven in either direction. Its rate can be controlled by changing the temperature and/or the pressure. An increase in the pressure of gaseous hydrogen and a decrease in its temperature shift the reaction equilibrium point toward the hydride formation, whereas a decrease in the pressure and an increase in the temperature stimulate the hydride decomposition [1].

The intermetallic alloy $LaNi_5$ is a bright example of such materials. Owing to its high hydrogen capacity, high cyclic stability, and activation simplicity, materials fabricated on its basis occupy one of the leading places among those applied in metal hydride power technologies. $LaNi_5$ alloy can absorb and desorb a large amount of hydrogen at temperatures close to room one and at rather low pressures [2–5]. The hydride of the alloy, $LaNi_5H_{6,7}$, contains 1.4 wt% of hydrogen. The enthalpy of hydride formation equals -15.7 kJ/mol H, and the enthalpy of alloy decomposition is -15.1 kJ/mol H [6].

The properties of $LaNi_5$ intermetallic compound can be varied in a wide interval by substituting lanthanum or nickel, completely or partially, by atoms of other metals. Since lanthanum is rather expensive, it is substituted by mischmetal (Mm) containing La, Ce, Pr, Nd, Sm, and Gd in various ratios. This substitution allows the cost of the intermetallic compound to be substantially reduced without a considerable change in its properties. In order to change the hy-

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drogen sorption characteristics of alloys of the $LaNi_5$ type ($MmNi_5$), to reduce the number of their activation cycles, to increase the stability of their exploitation parameters, and to decrease their cost, they are doped by substituting nickel atoms with atoms of various elements (Mg, Al, Ti, Zr, Mn, Mo, Cr, V, Fe, Co, Si, Zn, and Sn) [1, 3, 7]. Various variants of $Mm(Ni, Co, Mn, Al)_5$ alloys form a basis for the majority of modern commercial anodes in nickel-metal hydride batteries.

Various hydrogen sorption characteristics of those doped alloys were rather extensively studied experimentally. However, despite the considerable efforts of experimenters, the mechanisms responsible for the doping effects still remain insufficiently studied. In this work, $LaNi_5$ alloy and alloys on its basis, in which some of nickel atoms were substituted by aluminum or manganese atoms – $LaNi_{4.75}Al_{0.25}$ and $LaNi_{4.5}Mn_{0.5}$ – are studied.

Summarizing the results of a large number of works devoted to the study of the influence of the aluminum- and manganese-doping, the following conclusions can be drawn. The partial substitution of Ni atoms in $LaNi_5$ intermetallic compound by Al or Mn makes it possible to significantly reduce the equilibrium pressure in the plateau interval and to decrease the absorption/desorption pressure hysteresis with an insignificant reduction of the hydrogen capacity. The kinetics of the sorption processes also changes insignificantly, although the relevant data are controversial [1, 8–11].

The alloy with aluminum was found to have a higher cyclic stability than $LaNi_5$. It is also characterized by a higher resistance to the presence of oxygen or water. A partial substitution of nickel atoms by aluminum ones enhances the material resistance with respect to both internal and external degradations [12–15]. A research of the influence of Al on the hydrogen diffusion in the aluminum-doped alloy hydride demonstrated a substantial growth in the hydrogen diffusion activation energy at room temperature and, accordingly, a reduction of the diffusion rate by more than two orders of magnitude in comparison with that in the undoped alloy hydride [16, 17].

When discussing the cause for the pressure drop, which corresponds to the plateau in the sorption/desorption isotherm observed in the case where nickel is substituted by aluminum or manganese, many authors (see, e.g., works [10, 18, 19]) came to a conclusion that its main cause is the growth of the size of a unit crystal cell in the alloy, because the atomic radii of Al and Mn exceed that of Ni. In work [18], it was shown that the pressure corresponding to the plateau in the pressure-composition-temperature diagram is reciprocal to the volume of those interstitial voids in the crystal lattice that contain hydrogen. Owing to the growth of the alloy crystal cell parameters, hydrogen atoms can be more easily built into the crystal lattice to form thermodynamically more stable hydrides. As a result, the hydride decomposition enthalpy increases, and the equilibrium pressure of the hydride formation decreases. Hence, the substitution of nickel atoms in $LaNi_5$ by larger atoms stabilizes the hydride phase of those materials and gives rise to the formation of more stable hydrides. In the technological aspect, this substitution is a convenient method to expand the operational temperature interval of those materials. Unfortunately, the substitution of nickel atoms by larger atoms is accompanied, as a rule, by a reduction, although insignificant, in the hydrogen capacity of the material [20].

The combination of hydrogen sorption properties inherent in the hydride forming intermetallic alloys is a result of several factors. Among them, there are the electron configuration and size of atoms constituting the alloy components, crystal lattice parameters, thermal conductivity, surface reactivity, and others. In most cases, the properties of such materials were optimized by changing their bulk parameters. The optimization by varying surface parameters was restricted to the surface activation with the use of various methods. In particular, this is the cleaning of the surface, to some extent, from chemical compounds, which is performed by heating the surface several times in vacuum or in the H_2 atmosphere in order to bring the surface into a reactive state. The bulk material parameters, which depend on the composition, the crystal lattice parameters, and so on, are responsible for such stages of the hydride formation as the transition of hydrogen atoms from the surface layer into the near-surface one. This is the diffusion of hydrogen atoms in the alloy volume giving rise to the formation of a solid solution of atomic hydrogen (the α-phase) in it, the ordering of a solid solution, and its transformation into hydride (the β-phase). The surface plays a crucial role at the initial stages of hydride formation, at the stage of hydrogen physical adsorption onto active surface centers, at the dissociation of hydrogen molecules into atoms, and their further diffusion from the near-surface region into the bulk [21]. Taking all that into account, the research of the surface properties should make it possible not only to extend general ideas concerning the processes of hydride formation, but also to elaborate recommendations for their optimization.

The aim of this work was to study the chemical composition of the surface of some lanthanum-based hydride forming alloys and the variations of this composition depending on experimental conditions, to study the initial stages of interaction between those alloys and hydrogen, to analyze the role of main alloy components, to determine the role of ligature in the hydride formation, and to study the processes of hydrogen diffusion in the near-surface region of specimens at various temperatures and pressures.

2. Research Methods

The chemical composition of the surface of researched alloys and a modification of this composition by varying experimental conditions were studied, by using the secondary ion mass-spectrometry (SIMS) method. Unlike the vast majority of experimental techniques applied to study the surface, this method allows hydrogen and its compounds to be detected directly, and the changes in the composition of those compounds to be studied depending on experimental conditions.

Polycrystalline specimens of $LaNi_5$, $LaNi_{4.75}Al_{0.25}$, and $LaNi_{4.5}Mn_{0.5}$ alloys were analyzed. As primary ions, Ar^+ ions with the energy of 8 keV were used to examine positive secondary ions, and 16 keV to examine negative ones. The current density in the primary beam amounted to 0.9–4.5 $\mu A/cm^2$, which corresponded to the dynamic SIMS mode. The residual vacuum in the target chamber was about 4×10^{-6} Pa.

The experimental installation had an energy filter with a transmission window width not exceeding 10 eV, which allowed the emission intensities of only low-energy secondary ions to be measured in a narrow energy interval. Just those ions mostly characterize the presence of chemical compounds on the examined surface, as well as their composition [22]. The resolution exceeded 1000 at the half-height of a peak. The intensities of secondary ion emissions were measured in a dynamic range not narrower than six orders of magnitude. If the secondary ion emissions were overlapped by mass, their partial contributions were calculated, by following the standard procedure using the natural isotopic abundances.

Before the measurements, the specimens were annealed in a residual vacuum at the temperature of 750–1000 K in order to partially clean the surface from chemical compounds. During the annealing, those compounds were either desorbed from the surface or dissolved in the material bulk. After the annealing the surface was cleaned by using the primary ion beam until the mass-spectra composition and the intensities of secondary ion emissions were completely stabilized. The gas phase composition and low partial pressures of gases in a vacuum chamber were monitored and measured, by using a gas mass spectrometer.

3. Experimental Results and Their Discussion

Our measurements showed that the mass spectra of positive and negative secondary ions sputtered from the surface of researched specimens contained a large number of various emissions. The latter were associated with both the alloy components – atomic and clustered ions of lanthanum, nickel, aluminum, and manganese, as well as ions that are combinations of those elements – and the alloy impurities. The mass spectra also included emissions associated with the interaction with the gas phase, i.e. emissions corresponding to hydrogen- and oxygen-containing compounds. The emissions associated with lanthanum prevailed in the spectra of positive secondary ions. The emission of LaO^+ ions turned out the most intense one in the spectra of positive ions for all three specimens. The spectra of negative secondary ions contained intense emissions associated with nickel including its compounds with oxygen.

When the specimens were annealed in the absence of a primary beam, the emission of positive thermal ions was observed. In particular, the emission of positive thermal ions of alkaline metals Na^+, K^+, Rb^+, and Cs^+ took place for all three specimens. Furthermore, at temperatures higher than 700 K, the emission of La^+ and LaO^+ thermal ions was registered for all three specimens and, besides that, the emission of Al^+ thermal ions for the $LaNi_{4.75}Al_{0.25}$ specimen, and Mn^+ for the $LaNi_{4.5}Mn_{0.5}$ was observed.

The emission of those thermal ions can be a result of the decomposition and desorption of oxides that were presented on the surface from the very beginning. It is their removal, complete or partial, from the surface in order to achieve its high reactivity, i.e. a high absorption rate and a maximum hydrogen capacity, that is aimed at the activation of specimens in technologies connected with hydrogen storage alloys. The annealing and the following irradiation of the surface with a primary beam resulted in a substantial cleaning of the specimen surface. Some emissions, which are mainly associated with compounds, disappear from the mass spectra, whereas the intensities of some emissions decrease. However, even after the annealing and the beam-assisted cleaning of the surface, the mass spectra contained the emissions of ions of oxygen-, hydrogen-, and carbon-containing compounds with the components of the alloys. Since the sputtered secondary ions were fragments of surface monolayers of the solid, they undoubtedly characterized the composition and the amount of chemical compounds on the surface and in the near-surface layer. Thus, the analysis of the measured mass spectra testified that the surface of studied specimens was covered, to some extent, with chemical compounds, which included oxides, hydrides, hydroxides, and carbides of alloy components. Similar results concerning the presence of chemical compounds on the surface, which included the both alloy components, were obtained in work [23] for the zirconium-vanadium alloy.

The main interest in the examined alloys concerned their interaction with hydrogen. Therefore, the dependences of the emission intensity of various hydrogen-containing secondary ions sputtered from the specimen surface on the partial hydrogen pressure were measured in the target chamber, first of all. These are those emissions that allow one to draw a conclusion about the presence and composition of hydrogen-containing chemical compounds on the surface. The mass spectra obtained at higher partial hydrogen pressures contained a large set of hydrogen-containing emissions of both positive and negative secondary ions. In the spectra of positive ions, the most intense were the emissions of hydrogen-containing ions that included lanthanum atoms. The spectra of negative ions contained ions that included nickel atoms. The electron affinity energy equals 0.5 eV for lanthanum and 1.15 eV for nickel atoms [24].

The analysis of the results obtained showed that the compositions of mass spectra and the dependences of the emission intensity on the partial hydrogen pressure for the secondary ions containing the main alloy components (lanthanum and nickel) were similar for all studied specimens. The mass spectra contained the emissions of positive hydrogen-containing ions LaH_n^+, $\mathrm{La_2H}_n^+$ $(n = 1,2)$, $\mathrm{Ni}_m\mathrm{H}^+$ $(m = 1,2,3)$, negative hydrogen-containing ions LaH_n^- $(n = 1,2,3,4)$, NiH_m^- $(m = 1,2)$, $\mathrm{Ni}_n\mathrm{H}^-$ $(n = 2,3,4)$, and some others with low intensities. Furthermore, there were the emissions of complex hydrogen-containing lanthanum-nickel $\mathrm{LaNiH}^\pm$ and $\mathrm{LaNi_2H}^\pm$ ions, as well as LaOH^+, LaCH^+, NiOH^-, and NiCH^- ones. The presence of the emissions of hydrogen-containing ions with both lanthanum and nickel, as well as complex lanthanum-nickel ions, is a direct confirmation that hydrogen, when being absorbed on the surface, forms chemical bonds with the both main alloy components. This situation is somewhat different from the existing viewpoint that nickel atoms in such alloys serve only for the dissociation of hydrogen molecules, whereas lanthanum is a hydride-forming component.

Since the dependences of the emission intensity for positive and negative hydrogen-containing secondary ions with lanthanum and nickel on the partial hydrogen pressure are similar for all studied specimens, only the results of a series of measurements obtained for the $\mathrm{LaNi_5}$ specimen are depicted in Fig. 1 as an example.

It is worth to note that the mass spectra of negative secondary ions for all three studied alloys contain rather an intense emission of LaH_4^- ions. A similar emission was also observed in works [25, 26], in which various variants of SIMS were applied to study the hydrogen-saturated $\mathrm{LaNi_5}$ alloy. Considering the issue about the origin of such ions, one may suppose that, according to work [27], LaH_4^- ions are formed as a result of the combination of LaH_2^- ions with hydrogen molecules in the gas phase. In this case, however, the intensity dependences of those ions on the partial hydrogen pressure would have been substantially different. In an interval of rather high pressures, where this recombination is most probable, a considerable growth of the LaH_4^- emission intensity relative to the LaH_2^- one would have been observed. However, the experimental pressure dependences obtained for those ions (Fig. 1) are very similar, especially in the

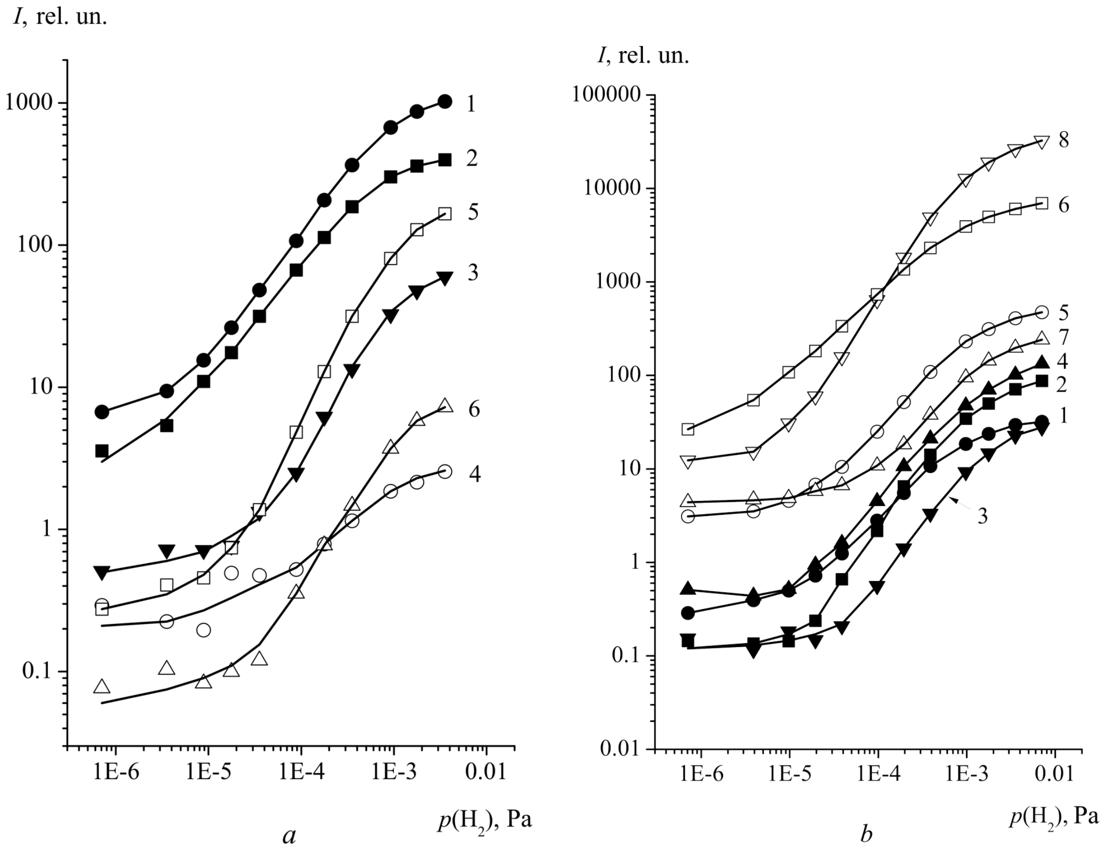

Fig. 1. Dependences of the emission intensity on the partial hydrogen pressure for positive and negative hydrogen-containing secondary ions sputtered from the $LaNi_5$ surface. Measurements were carried out at room temperature and the current density of primary ions $j = 4.5\ \mu A/cm^2$. Panel *a*: (*1*) LaH^+, (*2*) La_2H^+, (*3*) LaH_2^+, (*4*) $^{58}NiH^+$, (*5*) $^{58}Ni_2H^+$, and (*6*) Ni_3H^+ ($m = 175$ amu); panel *b*: (1) LaH^-, (2) LaH_2^-, (3) LaH_3^-, (4) LaH_4^-, (5) $^{58}NiH^-$, (6) $^{58}Ni_2H^-$, (7) Ni_3H^- ($m = 177$ amu), and (8) $^{58}NiH_2^-$

interval of high partial pressures, where the recombination should be the most expectable. This similarity means that, under our experimental conditions, the interaction between secondary ions and hydrogen molecules in the gas phase does not affect significantly the composition of hydrogen-containing secondary ions, and their qualitative and quantitative compositions are governed by the processes of sputtering from the surface and the surface composition.

However, the appearance of LaH_4^- ions in the mass spectra should not be interpreted as the presence of a chemical compound on a surface, in which a trivalent lanthanum is chemically bonded with four hydrogen atoms. Most likely, this emission reflects the fact that this secondary ion is a fragment of a hydrogen-containing surface structure, in which the lanthanum atom has no less than four hydrogen atoms in its nearest vicinity.

A specific feature of specimens with a ligature is the presence of some additional emissions associated with manganese or aluminum. The mass spectra of secondary ions sputtered from the surface of $LaNi_{4.5}Mn_{0.5}$ alloy, besides ions that included the main alloy components, contained the emissions of secondary ions with Mn. These were positive ions Mn_n^+, Mn_nH^+ ($n = 1, 2$), $NiMn^+$, $NiMnH^+$, $LaMn^+$, and $LaMnH^+$, as well as negative ions MnH^-, MnH_2^-, $MnNiH^-$, and $MnNiH_2^-$. Furthermore, the emission of ions including manganese and oxygen (MnO^- and $MnOH^-$) was also observed. This fact testifies that, provided the indicated experimental conditions, the composition of the chemical compounds, including oxygen-containing ones, that were present on the sur-

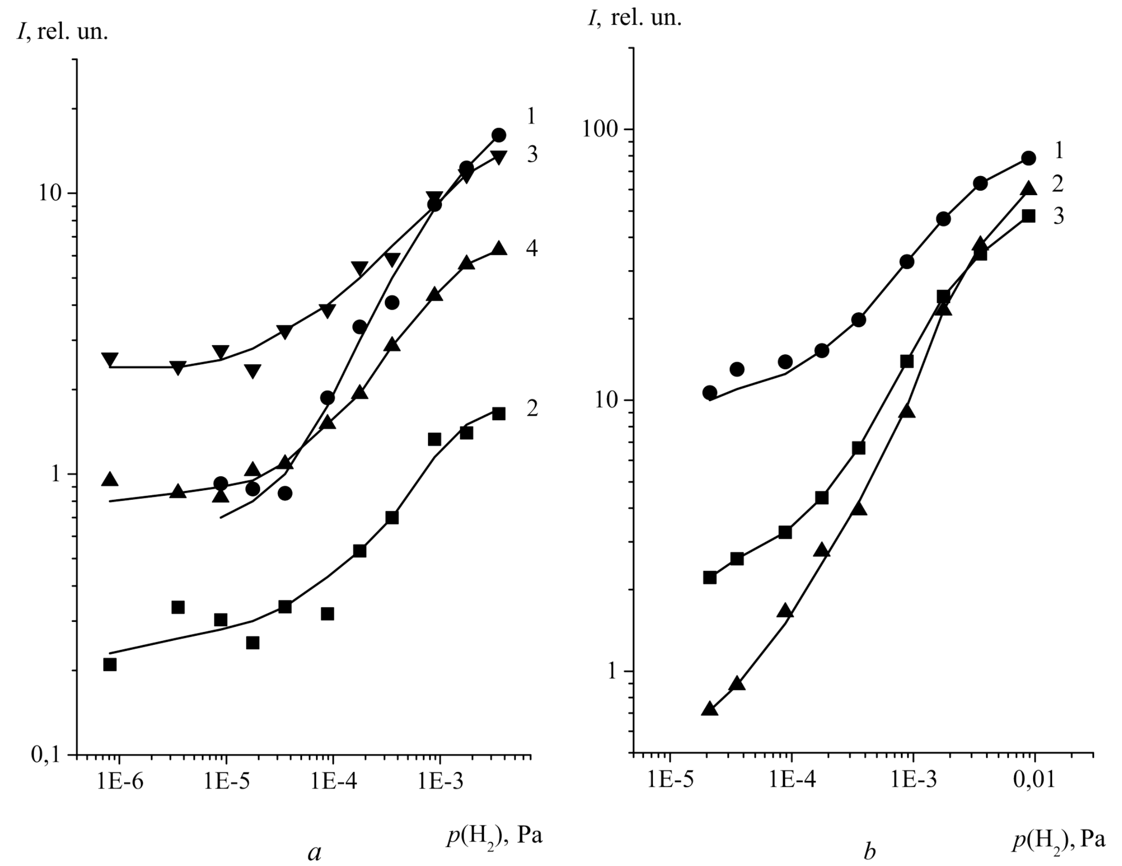

Fig. 2. Dependences of the emission intensity on the partial hydrogen pressure for positive manganese-containing secondary ions sputtered from the $LaNi_{4.5}Mn_{0.5}$ surface and negative hydrogen-containing secondary ions with aluminum sputtered from the $LaNi_{4.75}Al_{0.25}$ surface. Measurements were carried out at room temperature and the current density of primary ions $j = 4.5\ \mu A/cm^2$. Panel *a*: (*1*) MnH^+, (*2*) Mn_2H^+, (*3*) $LaMnH^+$, and (*4*) $^{58}NiMnH^+$; panel *b*: (*1*) $^{58}NiAlH^-$, (*2*) $^{58}NiAlH_2^-$, and (*3*) $^{58}Ni_2AlH^-$

face of the specimen included all alloy components, including manganese.

In the mass spectra of the secondary ions sputtered from the surface of the aluminum-doped alloy $LaNi_{4.75}Al_{0.25}$, the additional emissions of Al^+, $NiAl^+$, $LaAl^+$, $LaAlO^+$, and Ni_2Al^- are observed, as well as the hydrogen-containing emissions of complex nickel-aluminum and lanthanum-aluminum ions $NiAlH^+$, $LaAlH^+$, $LaAlOH^+$, $NiAlH^-$, $NiAlH_2^-$, and Ni_2AlH^-. At the same time, there are no emissions corresponding to the compounds of aluminum, as a ligature, and hydrogen ($Al_nH_m^\pm$), at least their number is not sufficient to make an unequivocal interpretation. Since complex hydrogen-containing aluminum ions with nickel or lanthanum are fragments of surface chemical compounds, the absence of $Al_nH_m^\pm$ ions allows a conclusion to be made that, at high pressures, hydrogen on the surface is bonded with nickel or lanthanum atoms rather than with aluminum ones. This is the essential difference from the alloy with manganese, for which the presence of the emissions of secondary ions of manganese, as a ligature, and hydrogen ($Mn_nH_m^\pm$) gives ground to assume that manganese, together with nickel and lanthanum, directly participates in the hydride formation. Figure 2 exhibits some examples of the emission intensity dependences on the partial hydrogen pressure for hydrogen-containing ions with either manganese or aluminum.

The dependences of the emission intensities on the partial hydrogen pressure measured for all studied alloys testify to the following. As the partial hydrogen pressure grows, the intensities of the majority of observed positive and negative hydrogen-containing secondary ions significantly increase. The growing character of those dependences points to a larger amount of hydrogen-containing compounds containing all alloy components on the surface and in the near-surface region. As was marked above, the specific feature of the aluminum-doped alloy consists in that, under the given experimental conditions, hydrogen does not form chemical bonds directly with aluminum, unlike nickel, lanthanum, and manganese.

The analysis of our results shows that, among a large number of sputtered hydrogen-containing secondary ions, a group of ions containing more than one hydrogen atom stands out. For the NiH_2^-, $La_2H_2^+$, LaH_2^+, LaH_2^-, LaH_3^-, LaH_4^-, $LaNiH_2^-$, and $LaNiH_3^-$ ions, the dependence of the emission intensity on the partial hydrogen pressure can be approximated by a power function with a power exponent larger than 1 in a pressure interval from about 10^{-5} to about 10^{-3} Pa. For another numerous group of hydrogen-containing ions, such as La_2H^+, $LaH^\pm$, Ni_nH^- ($n = 1, 2, 3, 4$), $MnH^\pm$, as well as complex ions $LaNiH^\pm$, $LaNi_2H^\pm$, and $NiMnH^\pm$, this approximation is also possible; however, the corresponding power exponents are different and less than 1 for all those ions.

The existence of the group of secondary ions containing more than one hydrogen atom and different from other ions by the value of the power exponent in the power function approximating the dependence of the emission intensity on the partial hydrogen pressure gives us grounds to assume the following scenario. As hydrogen is accumulated on the surface and in the near-surface region of the specimen, a hydrogen-containing parent structure is formed, the characteristic fragments of which are secondary ions containing more than one hydrogen atom. A characteristic feature of this compound consists in that nickel, which is bivalent in the majority of chemical compounds, has strong bonds with two hydrogen atoms, whereas trivalent lanthanum with more than two hydrogen atoms. The fact that the ions typical of this compound include the complex ion $LaNiH_2^-$ testifies that the formed hydrogen-containing structure includes the both main components of the alloy.

Therefore, we may assume that, under the indicated experimental conditions, a hydrogen-containing intermetallic compound is formed on the surface and in the near-surface region of the specimen. This compound is a result of the chemisorption interaction between hydrogen and alloy atoms at the specimen surface. It is characterized by a definite stoichiometric ratio. This compound should not be identified with the bulk hydride phase of the alloy (β-phase), which is formed in the specimen bulk under significantly higher pressures and is characterized by a number of thermodynamic and crystallographic parameters.

The emissions of the secondary ions containing less than two hydrogen atoms are a result of the fragmentation of hydrogen-containing structures located on the surface, in which the alloy components do not manifest their maximum valence. The growth in the intensity of those emissions reflects only the larger number of relevant structures or, actually, the growth in the number of hydrogen atoms that created bonds with alloy components in various combinations.

At room temperature and partial hydrogen pressures higher than about 7×10^{-3} Pa, a hydrogen-containing structure is formed on the surface and in the near-surface region. Since the curves in Figs. 1 and 2 have a tendency to the saturation, the composition of this structure does not undergo qualitative or quantitative changes, as the partial hydrogen pressure grows further.

The temperature is not a less important parameter than the hydrogen pressure for the processes of intermetallic alloy hydrogenation. Therefore, the dependences of the emission intensities of hydrogen-containing secondary ions on the specimen temperature were measured. The measurements were performed at a residual hydrogen pressure and, for illustrative purposes, at the elevated partial hydrogen pressure $P_{H_2} = 3.54 \times 10^{-4}$ Pa. As was in the case of the dependences on the partial hydrogen pressure, the temperature dependences for secondary ions including the main alloy components, i.e. lanthanum and nickel, are similar for all three studied specimens. As an example, some of those dependences obtained for secondary ions sputtered from the surface of $LaNi_5$ specimen are depicted in Fig. 3.

The temperature dependences for hydrogen-containing secondary ions including ligature atoms and sputtered from the $LaNi_{4.5}Mn_{0.5}$ alloys, and negative hydrogen-containing secondary ions with aluminum sputtered from the $LaNi_{4.75}Al_{0.25}$ surface have, in general, the same descending character. For all researched specimens, the main characteristic feature of the temperature dependences measured at the elevated partial hydrogen pressure is a substantial re-

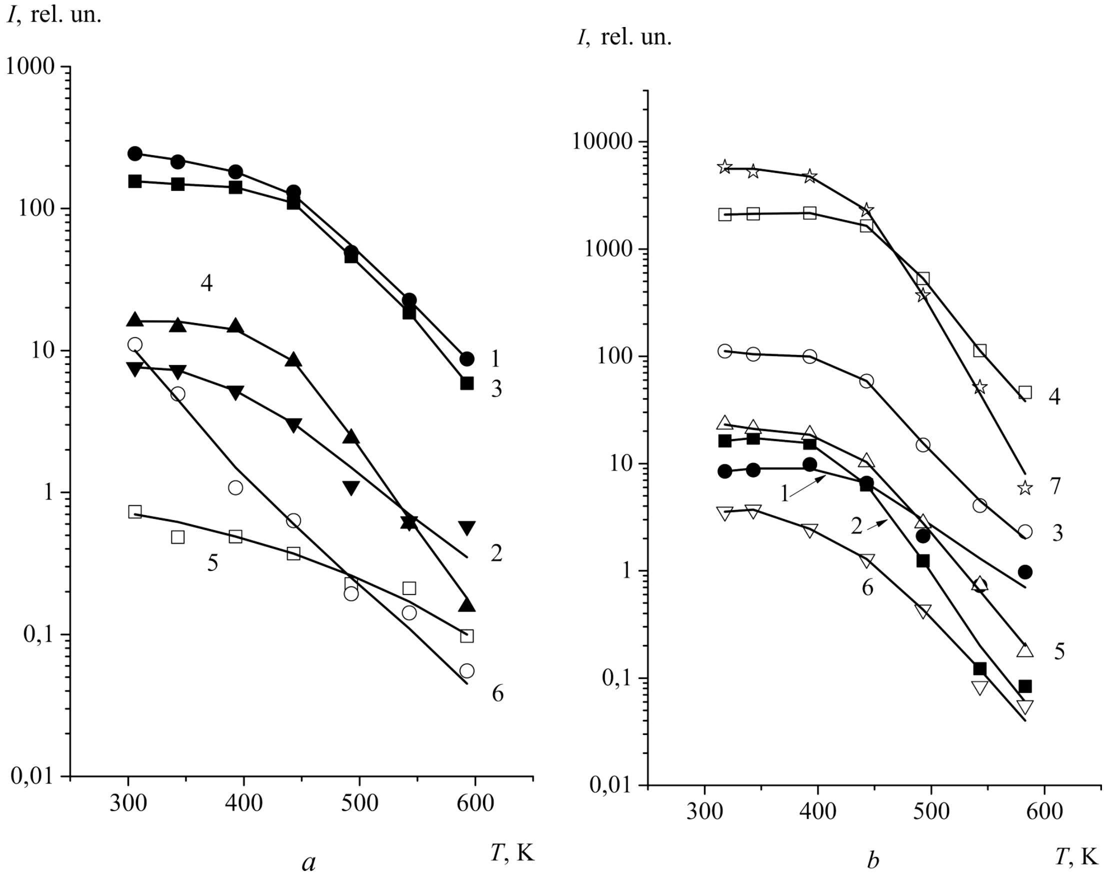

Fig. 3. Temperature dependences of the emission intensity for positive and negative hydrogen-containing secondary ions sputtered from the $LaNi_5$ surface. Measurements were carried out at the elevated hydrogen pressure $p(H_2) = 3.54 \times 10^{-4}$ Pa and the current density of primary ions $j = 4.5$ $\mu A/cm^2$. Panel *a*: (*1*) LaH^+, (*2*) LaH_2^+, (*3*) La_2H^+, (*4*) $La_2H_2^+$, (*5*) $^{58}NiH^+$, and (*6*) $^{58}Ni_2H^+$; panel *b*: (*1*) LaH^-, (*2*) LaH_2^-, (*3*) $^{58}NiH^-$, (*4*) $^{58}Ni_2H^-$, (*5*) Ni_3H^- ($m = 175$ amu), (*6*) Ni_4H^- ($m = 233$ amu), and (*7*) $^{58}NiH_2^-$

duction of the emission intensity with the temperature growth for practically all positive and negative hydrogen-containing ions. The emission intensities of those ions correlate with the amount of hydrogen-containing compounds on the surface. Therefore, the reduction of the intensity of those emissions testifies to the reduction of the amount of hydrogen-containing chemical compounds.

The equilibrium coverage of the surface with adsorbed particles, as well as the products of chemical reactions between those particles and the atoms at the solid surface, is a result of a dynamic equilibrium between several processes. These are the adsorption-desorption processes (because the equilibrium coverage is implemented provided the adsorption-desorption equilibrium between the gas phase and the surface), processes of sputtering by the primary beam, and diffusion of adsorbed particles into bulk. In the first approximation, the parameters of sputtering processes do not change with the temperature in the researched temperature interval. Therefore, the sputtering affects the equilibrium coverage identically at various temperatures. As a rule, the parameters of diffusion processes strongly depend on the temperature, especially in the case of hydride-forming alloys. To elucidate the role of diffusion processes under our experimental conditions, the following experiment was carried out.

The surface of the specimen ($LaNi_5$) was cleaned, by using a high-density primary beam. Then, hydrogen was inlet into a chamber up to a pressure of 1.8×10^{-4} Pa with a settling time about 2 s. Afterward, the time dependence of the emission intensity of the Ni_2H^- ion, which is typical of hydrogen-containing compounds, was measured. The primary current density amounted to $j = 1.13$ μA/cm^2 in this case. A current density lower than that used at the measurement of the temperature dependences was used to diminish the sputtering action of a primary beam. The exposure time amounted to 150 s. The measured time dependences of the emission intensity of the characteristic ion are shown in Fig. 4. After an exposure interval of 150 s, hydrogen was evacuated for about 1 s. The primary beam density was raised to $j = 4.5$ μA/cm^2, and the evolution of the emission intensity in time, i.e. in the course of the sputtering of a layer of formed hydrogen-containing compounds, was measured. This procedure was repeated for various specimen temperatures. The results obtained are depicted in Fig. 5.

The data presented in Fig. 4 testify to the following. First, the emission intensity of secondary ions characteristic of the hydrogen-containing compounds increases in time, that is quite natural. All the curves have a tendency to the saturation. Since the registered ions were sputtered from the upper monolayers, the growth of their number testifies to the increase in the amount of hydrogen-containing compounds, a fragment of which is the Ni_2H^- ion, on the surface. Second, the emission intensity of characteristic ions decreases as the exposure temperature grows. Following the same reasons, this reduction can be explained by the fact that, at a fixed partial hydrogen pressure, the growth of the specimen temperature gives rise to the formation of a smaller amount of hydrogen-containing compounds on the surface. The dynamic equilibrium between the adsorption, desorption, diffusion, and sputtering processes is reached more quickly in this case, and the curves reach a plateau more rapidly.

We roughly estimated the time dependence of the number of sputtered monolayers for a sputtering coefficient value of 4. The analysis of the data obtained (Fig. 5) allows us to draw a conclusion that, during the exposure under the indicated partial pressure and in the examined temperature interval, hydrogen diffuses and forms an appreciable amount of chemical bonds only to the depth of about 10 monolayers.

Besides the aforesaid, the following factors should be emphasized. At various sputtering stages, the amount of hydrogen-containing compounds changes in a complicated manner. If the sputtering is considered to be a process that is responsible for the composition of surface compounds, i.e. if the diffusion of hydrogen at measurements is not taken into consideration, the data obtained in the course of the sputtering may actually be regarded as results of the layer-by-layer analysis. This circumstance makes it possible to trace the dependence of the amount of hydrogen-containing compounds on the exposure temperature at various sputtering stages.

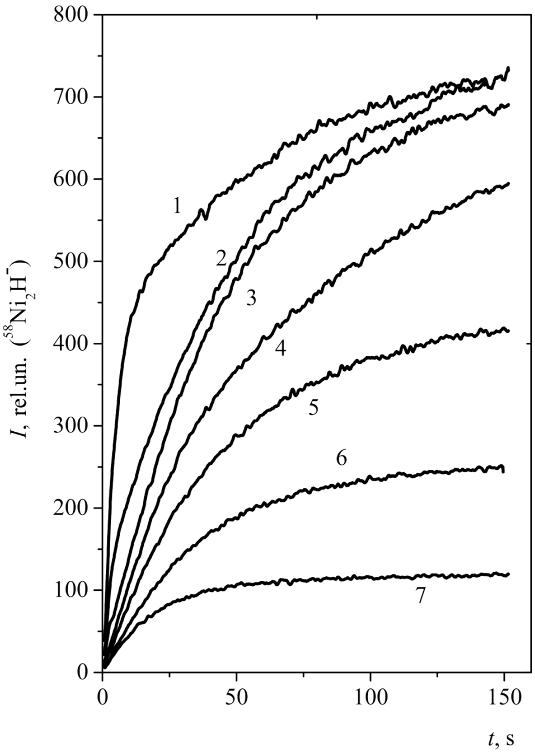

Fig. 4. Time dependences of the emission intensity of Ni_2H^- secondary ions sputtered from the $LaNi_5$ surface. Measurements were carried out at the current density of primary ions $j = 1.13$ μA/cm^2, the partial hydrogen pressure $p(H_2) = 1.8 \times 10^{-4}$ Pa, and various specimen temperatures: (*1*) 313, (*2*) 348, (*3*) 373, (*4*) 423, (*5*) 448, (*6*) 473, and (*7*) 498 K

In Fig. 6, the relevant data are exhibited. The analysis of the depicted dependences testifies that, as the sputtering begins (about 0.2 s), the amount of hydrogen-containing compounds in the first monolayer decreases monotonically (i.e. the curve decreases monotonically) with the temperature growth. The next monolayers demonstrate a tendency to have a maximum of the emission intensity at temperatures above the initial one. In particular, the amount of hydro-

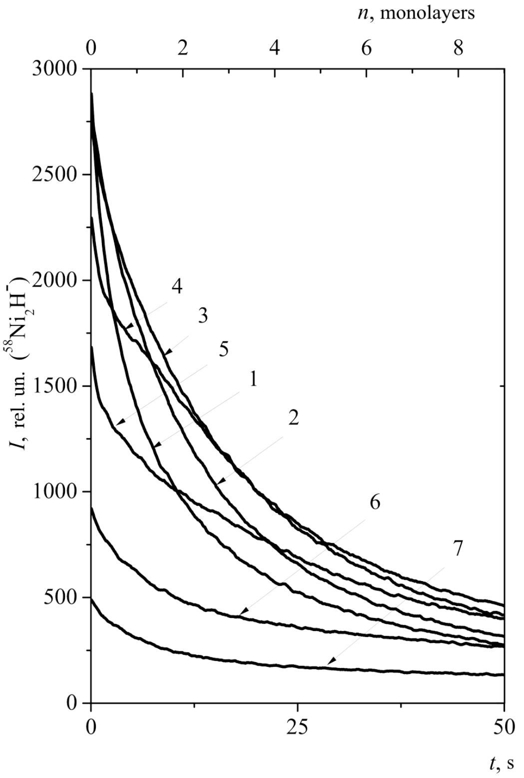

Fig. 5. Dependences of the emission intensity of Ni_2H^- secondary ions on the sputtering time after the exposure under the partial hydrogen pressure $p(H_2) = 1.8\times10^{-4}$ Pa. Measurements were carried out at the current density of primary ions $j = 4.5$ μA/cm^2, and various temperatures: (*1*) 313, (*2*) 348, (*3*) 373, (*4*) 423, (*5*) 448, (*6*) 473, and (*7*) 498 K

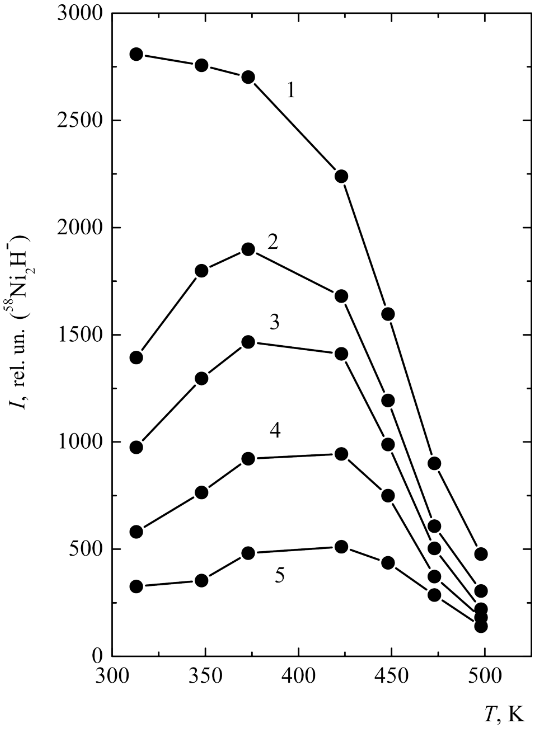

Fig. 6. Dependences of the emission intensity for Ni_2H^- secondary ions sputtered from the $LaNi_5$ surface on the exposure temperature at various sputtering stages: (*1*) 0.2, (*2*) 5.6, (*3*) 11, (*4*) 22, and (*5*) 44 s

gen-containing compounds in the second (after the 5.6-s sputtering), third (after the 11-s sputtering) and fourth (after the 17-s sputtering) monolayers increases with the exposure temperature growing from 313 to 373 K. In the fifth and deeper monolayers, the amount of hydrogen-containing compounds increases with the growth of the exposure temperature up to 423 K. At higher exposure temperatures, the amount of hydrogen-containing compounds decreases for all monolayers. Therefore, in the region from the fifth monolayer and deeper, the maximum of the emission intensity, and, hence, the maximum of the amount of hydrogen-containing compounds fall in a temperature interval of 373–423 K, with each next monolayer demonstrating a general decrease of the emission intensity.

The results presented above allow us to draw the following conclusions. After the 150-s exposure under a partial hydrogen pressure of about 10^{-4} Pa, the amount of chemical compounds on the surface monotonically decreases by several times, if the exposure temperature grows to about 500 K. In deeper monolayers, with the growth of exposure temperature, the amount of hydrogen–containing compounds firstly increases and begins to decrease only above about 423 K. The maximum amount of compounds at a depth of more than five monolayers is formed in a temperature interval of 373–423 K.

Therefore, we have grounds to assume that, under the experimental conditions of this work, the processes of hydrogen interaction with the researched alloys take place only on the surface and in the closest near-surface region. In turn, this model makes it possible to interpret the obtained results as those describing the initial stages of hydrogen accumulation (hydrogenation) processes, namely, as the interaction of hydrogen with the surface of indicated alloys, neglecting its considerable diffusion into bulk as one of the channels giving rise to the modification of surface

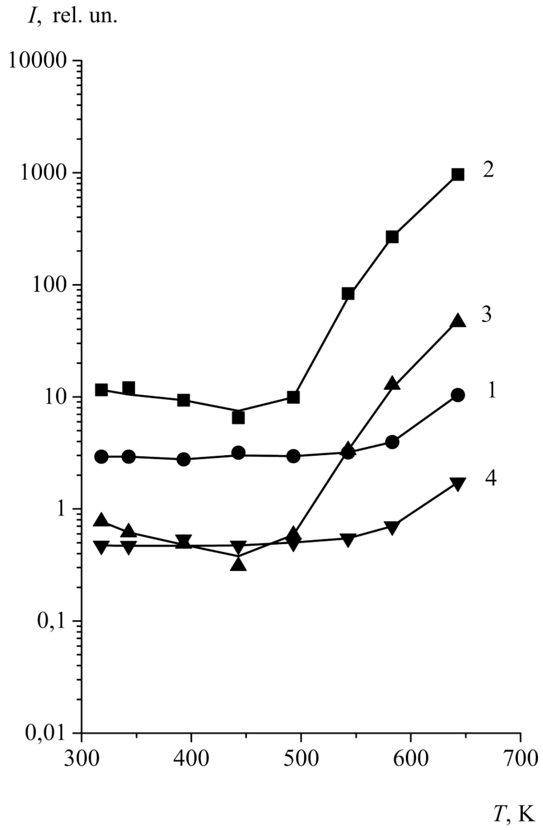

Fig. 7. Temperature dependences of the emission intensity of negative carbon-containing secondary ions sputtered from the $LaNi_5$ surface. Measurements were carried out under the residual partial hydrogen pressure and at the current density of primary ions $j = 4.5\ \mu A/cm^2$: (*1*) $^{58}NiC^-$, (*2*) $^{58}NiC_2^-$, (*3*) LaC_2^-, and (*4*) LaC_4^-

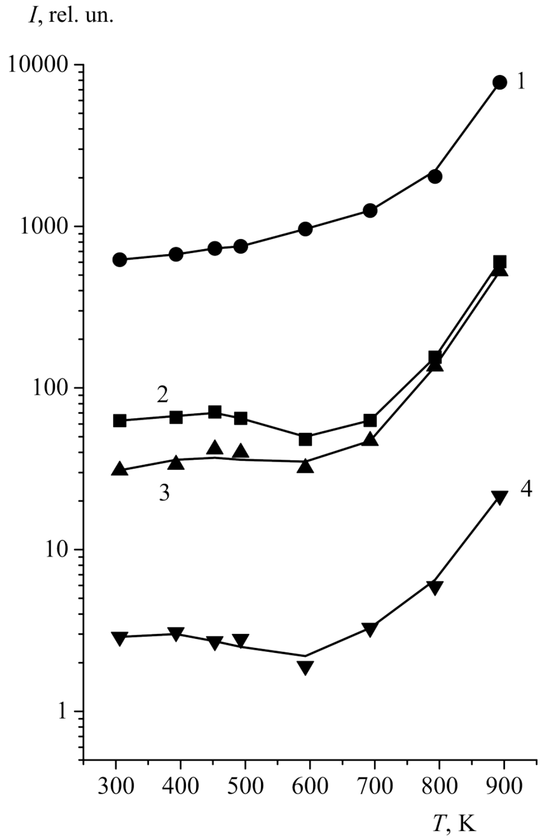

Fig. 8. Temperature dependences of the emission intensity of positive oxygen-containing secondary ions sputtered from the $LaNi_5$ surface. Measurements were carried out under the residual partial hydrogen pressure and at the current density of primary ions $j = 4.5\ \mu A/cm^2$: (*1*) LaO^+, (*2*) La_2O^+, (*3*) $La_2O_2^+$, and (*4*) $La^{58}NiO^+$

composition. Of course, in so doing, one should not forget about the effects caused by a primary beam, namely, the implantation of hydrogen recoil atoms located on the surfaces and the ion beam mixing.

Besides the temperature dependences of the emission intensity for hydrogen-containing secondary ions, we also measured the temperature dependences for oxygen-containing ions of the main components of examined alloys and carbon-containing ions. As an example, Figs. 7 and 8 exhibit the temperature dependences for those secondary ions sputtered from the $LaNi_5$ surface, which were measured under a residual partial hydrogen pressure.

The presence of the emissions of carbon-containing ions is explained by the fact that carbon is present in the bulk of polycrystalline specimens as an impurity. A common feature of all temperature dependences of the emissions for carbon-containing ions is a more or less strong growth of the emission intensities with the temperature (see Fig. 7). This growth is especially intensive at temperatures above about 450 K ($^{58}NiC_2^-$, LaC_2^-), which is most likely explained by the fact that, at those temperatures, carbon starts to diffuse from the bulk to the surface, where it forms chemical bonds with alloy components.

The presence of oxygen-containing ion emissions in the mass spectra of secondary ions is a result of the presence of oxides as impurities in the specimen bulk and, to a less extent, a result of the oxygen sorption from the gas phase. As follows from Fig. 8, the emission intensities of oxide ions at temperatures higher than about 600 K have a general tendency to grow with the temperature. It is reasonable to associate the observed growth of the emission intensities of oxygen-containing ions with the intensification of oxide formation processes at those temperatures.

4. Conclusions

Our researches show that, under ordinary conditions, the surface of the specimens of $\mathrm{LaNi_5}$, $\mathrm{LaNi_{4.75}Al_{0.25}}$, and $\mathrm{LaNi_{4.5}Mn_{0.5}}$ alloys, which are mainly used as hydrogen storage materials, is covered with a layer of chemical compounds including oxides, hydrides, hydroxides, and carbides of alloy components. The research of the initial stages of interaction processes between those alloys and hydrogen indicates that, in the course of hydrogen accumulation, a hydrogen-containing structure is formed on the surface and in the closest near-surface region. The characteristic fragments of this structure are secondary ions that contain more than one hydrogen atom. As follows from the composition of secondary ions and the dependences of the intensities of their emission on the partial hydrogen pressure, a characteristic feature of this surface structure consists in that nickel atoms are bound with two neighbor hydrogen atoms, whereas lanthanum atoms with more than two neighbor hydrogen atoms.

The formed hydrogen-containing structure includes the both main alloy components (La and Ni) for all studied alloys, although only lanthanum is conventionally considered to be a hydride-forming element in such alloys. In the case of $\mathrm{LaNi_{4.5}Mn_{0.5}}$ alloy, manganese, being an additional alloy component, also enters the composition of this hydrogen-containing structure and directly participates in the hydride formation processes. In the case of $\mathrm{LaNi_{4.75}Al_{0.25}}$ specimen, aluminum, unlike manganese, forms no direct chemical bonds with hydrogen in appreciable amounts. In other words, the aluminum atoms in this alloy do not directly participate in the hydride formation processes, in a sense that they do not form chemical bonds. Their main role consists in a reconstruction of the crystal lattice.

The research of the temperature dependences of the emission intensity for hydrogen-containing secondary ions showed that the amount of hydrogen-containing compounds on the surface and in the near-surface region decreases, as the temperature grows. This reduction is associated, first of all, with a reduction of the sticking coefficient for hydrogen molecules.

The research of the time dependences of the emission intensity for secondary ions that characterize the presence of hydrogen-containing compounds on the surface, which were measured at various specimen temperatures during the hydrogen adsorption stage, and when the formed surface compounds were sputtered, showed the following. In the course of the hydrogen adsorption, the amount of hydrogen-containing compounds formed on the surface and in the near-surface region monotonically decreases, as the temperature increases, and the equilibrium coating by those compounds is attained more rapidly. In the examined temperature interval, hydrogen diffuses in appreciable amounts to the depth of about 10 monolayers. Therefore, under the experimental conditions realized in this work, the processes of hydrogen interaction with the studied alloys take place only at the surface and in the closest near-surface region. In turn, this conclusion makes it possible to interpret the obtained results as the initial stages of hydrogenation processes, neglecting the substantial hydrogen diffusion into bulk as one of the channels to change the surface composition.

1. B.A. Kolachev, R.E. Shalin, A.A. Ilyin. *Hydrogen Storage Alloys* (Metallurgiya, 1995) (in Russian).
2. J.H.N. van Vucht, F.A. Kuijpers, H.C.A.M. Bruning. Reversible room-temperature absorption of large quantities of hydrogen by intermetallic compounds. *Philips Res. Repts.* **25**, 133 (1970).
3. V.M. Azhazha, M.A. Tikhonovskii, A.G. Shepelev, Yu.P. Kurilo, T.A. Ponomarenko, D.V. Vinogradov. Materials for hydrogen storage: Analysis of development trends based on information flow data. *Vopr. At. Nauki Tekhn.* No. 1, 145 (2006) (in Russian).
4. P. Dantzer. Properties of intermetallic compounds suitable for hydrogen storage applications. *Mater. Sci. Eng.* **329-331**, 313 (2000).
5. B.P. Tarasov, M.V. Lototskii, V.A. Yartys. The problem of hydrogen storage and the prospects for using hydrides for hydrogen accumulation. *Ross. Khim. Zh.* **50**, No. 6, 34 (2006) (in Russian).
6. S. Luo, J.D. Clewley, T.B. Flanagan, R.C. Bowman, L.A. Wade. Further studies of the isotherms of $\mathrm{LaNi}_{5-x}\mathrm{Sn}_x$–H for $x = 0 - 0.5$. *J. Alloys Compd.* **267**, 171 (1998).
7. A.N. Perevezentsev, B.M. Andreev, V.K. Kapyshev, L.A. Rivkis, M.P. Malek, V.M. Bystritskii, V.A. Stolupin. Hydrides of intermetallic compounds and alloys, their properties and applications in nuclear engineering. *Fiz. Elem. Chast. At. Yadra* **19**, 1386 (1988) (in Russian).

8. T. Takeshita, S.K. Malik, W.E. Wallace. Hydrogen absorption in RNi_4Al (R = rare earth) ternary compounds. *J. Solid State Chem.* **23**, 271 (1978).
9. M.H. Mendelsohn, D.M. Gruen, A.E. Dwight. The effect of aluminum additions on the structural and hydrogen absorption properties of AB_5 alloys with particular reference to the $LaNi_{5-x}Al_x$ ternary alloy system. *J. Less Common Metals* **63**, 193 (1979).
10. L.G. Shcherbakova, Yu.M. Solonin, Ye.N. Severyanina. Influence of metal substitute on electrochemical and sorption characteristics of $LaNi_5$ based alloys. In *Carbon Nanomaterials in Clean Energy Hydrogen Systems,* edited by B. Baranowski, S.Yu. Zaginaichenko, D.V. Schur, V.V. Skorokhod, A.Veziroglu (Springer, 2008), p. 645.
11. H. Diaz, A. Percheron-Guegan, J.C. Achard, C. Chatillon, J.C. Mathieu. Thermodynamic and structural properties of $LaNi_{5-y}Al_y$ compounds and their related hydrides. *Int. J. Hydrogen Energy* **4**, 445 (1979).
12. P.D. Goodell. Cycling hydriding response of $LaNi_5$ in hydrogen containing oxygen as a minor impurity. *J. Less Common Metals* **89**, 45 (1983).
13. K. Suzuki, K. Ishikawa, K. Aoki. Degradation of $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ Hydrogen-absorbing alloys by cycling. *Mater. Trans. JIM* **41**, 581 (2000).
14. J.I. Han, J.Y. Lee. Influence of oxygen impurity on the hydrogenation properties of $LaNi_5$, $LaNi_{4.7}Al_{0.3}$ and $MmNi_{4.5}Al_{0.5}$ during long-term pressure-induced hydriding-dehydriding cycling. *J. Less Common Metals* **152**, 329 (1989).
15. P. Dantzer. Static, dynamic and cycling studies on hydrogen in the intermetallics $LaNi_5$ and $LaNi_{4.77}Al_{0.22}$. *J. Less Common Metals* **131**, 349 (1987).
16. R.C. Bowman, D.M. Gruen, M.H. Mendelsohn. NMR studies of hydrogen diffusion in β-$LaNi_{5-y}Al_y$ hydrides. *Solid State Commun.* **32**, 501 (1979).
17. R.C. Bowman, B.D. Craft, A. Attalla, M.H. Mendelsohn, D.M. Gruen. Role of aluminum substitution on hydrogen diffusion in β-$LaNi_{5-y}Al_yH_x$. *J. Less Common Metals* **73**, 221 (1980).
18. C.E. Lundin, F.E. Lynch, C.B. Magee. A correlation between the interstitial hole sizes in intermetallic compounds and the thermodynamic properties of the hydrides formed from those compounds. *J. Less Common Metals* **56**, 19 (1977).
19. W.E. Wallace, E.B. Boltich. Reduction of hydrogen solubility by alloying RNi_5 systems with Al. *J. Solid State Chem.* **33**, 435 (1980).
20. C. Lartigue, A. Percheron-Guegan, J.C. Achard. Thermodynamic and structural properties of $LaNi_{5-x}Mn_x$ compounds and their related hydrides. *J. Less Common Metals* **75**, 23 (1980).
21. L. Schlapbach, A. Seiler, F. Stucki, H.C. Siegmann. Surface effects and the formation of metal hydrides. *J. Less Common Metals* **73**, 145 (1980).
22. V.A. Litvinov, A.G. Koval, B.M. Fizgeer. On the energy spectra of secondary ions sputtered from the surface of certain metals and their oxides. *Izv. Akad Nauk SSSR Ser. Fiz.* **55**, 2423 (1991) (in Russian).
23. V.A. Litvinov, V.T. Koppe, V.V. Bobkov. SIMS investigations of hydrogen interaction with a zirconium getter alloy surface. *Bull. Russ. Acad. Sci. Phys.* **76**, 553 (2012).
24. A.A. Radtsig and B.M. Smirnov, *Handbook on Atomic and Molecular Physics* (Atomizdat, 1980) (in Russian).
25. R. Dobrileit, H. Zuchner. SIMS investigations on the $SmCo_5D_n$ and $LaNi_5H_n$ systems. *Z. Naturforsch. A* **50**, 533 (1995).
26. H. Zuchner, J. Kintrup, R. Dobrileit, I. Untiedt. Chemical structure and bonding characteristics of metal hydrogen systems studied by the surface analytical techniques SIMS and XPS. *J. Alloys Compd.* **293–295**, 202 (1999).
27. P. Joyes. Sur la formation d'ions polyatomiques secondaires. *J. Phys. (Paris)* **44**, 221 (1983).

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ВІМС ДОСЛІДЖЕННЯ ПОВЕРХНІ СПЛАВІВ НА ОСНОВІ ЛАНТАНУ

Резюме

У роботі представлені результати дослідження поверхні інтерметалевих сплавів $LaNi_5$, $LaNi_{4,75}Al_{0,25}$ та $LaNi_{4,5}Mn_{0,5}$ методом вторинної іонної мас-спектрометрії. Показано, що при парціальних тисках водню 10^{-7}–10^{-2} Па і температурах 300–900 K процеси взаємодії водню з досліджуваними сплавами мають місце тільки на поверхні та у найближчій приповерхневій області. У температурному інтервалі від кімнатної до 500 K водень дифундує в помітних кількостях на глибину до 10 моношарів. При збільшенні температури кількість воденьвмісних сполук на поверхні та в приповерхневій області зменшується, а кількість карбідів і оксидів компонентів сплавів збільшується. З накопиченням водню на поверхні утворюється воденьвмісна структура, у якій атоми нікелю хімічно пов'язані із двома атомами водню, а атоми лантану – більш ніж з двома.