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SECONDARY-ION MASS SPECTROMETRY STUDY OF LaNi$_5$-HYDROGEN-OXYGEN SYSTEM

The results obtained while studying the surface of the LaNi$_5$ alloy using secondary ion mass spectrometry are reported. It has been shown that the simultaneous action of hydrogen and oxygen on the alloy surface leads to the formation of a complex chemical surface structure consisting of hydrides, hydroxides, and oxides of lanthanum and nickel. The stoichiometric ratios of elements in those compounds depend on the hydrogen and oxygen fractions in the gas mixture. Oxygen interaction with the alloy surface stimulates the surface segregation and grouping of nickel atoms into large clusters. Until there remain sites free from oxides and hydroxides on the surface of such nickel clusters, they serve as catalytically active centers for dissociative chemisorption of hydrogen molecules, thus promoting hydrogenation processes.

Keywords: secondary ion mass spectrometry, surface, hydrogen storage alloys, hydrogen, oxygen, hydrides.

1. Introduction

According to contemporary ideas [1–3], the formation of metal hydrides under the action of hydrogen atmosphere is a multistage process. At the first stage, a hydrogen molecule, when getting to a metal surface, can be physisorbed or dissociatively chemisorbed depending on its kinetic energy and the activation energy barrier height. At the next stage, the chemisorbed hydrogen atoms penetrate through the surface and dissolve in bulk. As a result of the bulk diffusion and the diffusion along the grain boundaries, a solid penetration solution (α-phase) and, then, a metal hydride (β-phase) are formed. The formation of the hydride phase passes through the stages of nucleation, grain growth, and solid-phase transformations. The metal hydride is usually characterized by a substantially higher content of hydrogen atoms and their ordered arrangement in the crystal lattice.

Thus, the dissociative chemisorption of hydrogen is a necessary important step in the formation of metal hydrides. Clean surfaces of a lot of transition metals and alloys can dissociatively chemisorb hydrogen. However, the presence of adsorbates, including oxygen, on them considerably changes their properties. In particular, the coefficient of hydrogen sticking becomes significantly reduced. This occurs owing to the saturation of broken bonds at the surface sections covered with the adsorbate. At those regions, the activation energy of hydrogen chemisorption is higher in comparison with the clean surface. If the whole surface is covered with the adsorbate, it becomes inert, the activation energy of hydrogen chemisorption is high, and the reaction rate is low. The surface can become reactive again only if the adsorbed atoms are removed or the surface and the adsorbed atoms are regrouped so that there arises a specific surface layer not interfering with the dissociative chemisorption of hydrogen [2].

Therefore, it is assumed that impurity gases that are present in hydrogen, being adsorbed on the sur-

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face of a metal or an alloy, form a certain surface structure that reduces the catalytic properties of the material surface. This structure prevents the dissociation of hydrogen molecules in hydrogenation processes and the association of hydrogen atoms into molecules in the dehydrogenation processes [4]. Since the absorption and desorption of hydrogen in the hydrogenation (dehydrogenation) processes strongly depend on the surface structure and state, the chemisorption of impurity gases, by modifying the structure and state of the surface, can affect those processes as well [5].

Despite that the insufficient resistance of intermetallic hydride-forming compounds to poisoning with gaseous impurities – such as O_2, H_2O vapor, CO, CO_2, and others – is the major problem for technological applications, there is little information on the fundamental mechanisms of surface poisoning today [4, 6]. Such a situation forms a basis for continuing the research concerning the influence of the state of the surface modified by adsorbed impurities on the processes of its interaction with hydrogen [7, 8].

The intermetallic alloy $LaNi_5$ is widely used in various technological applications in which metal hydrides are used. Being characterized by a high hydrogen capacity and an excellent sorption-desorption kinetics, it has a relatively low sensitivity to impurities in the gaseous hydrogen. Even if the alloy surface is covered with a thick layer consisting of various oxides and hydroxides of the alloy components, the reactivity of hydrogen with $LaNi_5$ still remains higher than that with oxide-coated transition metals. This circumstance favorably distinguishes $LaNi_5$ from most hydrogen storage alloys.

By analyzing the reasons for this situation, the authors of works [2, 9–13] have proposed a model of the hydrogen interaction with $LaNi_5$, the determining factor of which is the surface segregation, i.e. such a reconstruction of the metal surface of the initial intermetallide that gives rise to the formation of pure metals or their oxides. According to this model, the $LaNi_5$ surface is lanthanum-enriched, as compared with the bulk, in the initial state, because the surface energy of lanthanum is lower than that of nickel [2]. Selective oxidation of lanthanum at the surface additionally reduces its surface energy and promotes the segregation [14]. Lanthanum diffuses to the surface and binds with oxygen. As lanthanum is oxidized, nickel atoms group together to form large clusters, which come out in some cases to the surface [15]. As a result, the surface is a mixture of lanthanum oxide and metallic nickel. When contacting with hydrogen, atomic hydrogen is formed at the uncovered and catalytically active nickel atoms. Then, it migrates into oxide grains and transforms them into hydroxide. In work [15], it was emphasized that since hydrogen is poorly soluble in nickel, it reaches $LaNi_5$, which is located beneath, by migrating along the interface between Ni and La_2O_3 [$La(OH)_3$]. Hence, the chemisorption of reactive impurities – in particular, oxygen – on the surface does not block the process of dissociative chemisorption at hydrogenation.

In works [6, 16], when considering the mechanisms of initial $LaNi_5$ activation, a model was proposed that does not require the presence of an alloy of catalytically active nickel clusters at the surface and in the near-surface region. It was assumed that the catalytic activity for initiating the dissociation of hydrogen on the $LaNi_5$ surface is demonstrated by lanthanum oxides and suboxides, such as LaO_x, La_3O_{3-x}, and $LaNiO_x$. Probably, lanthanum hydroxides or nickel oxides and hydroxides manifest no catalytic activity at the dissociation of hydrogen molecules. Dissociated hydrogen atoms penetrate through the oxide layer and reach $LaNi_5$ located beneath [17].

Thus, there is no common view on the processes of hydride formation in the presence of reactive impurities – in particular, oxygen – in hydrogen. In order to better understand the scope of problems associated with the hydrogen absorption kinetics and the activation problems, additional studies of the influence of surface effects are required. They would stimulate a further progress in the application of alloys that are particularly suitable for the technological usage.

The literature contains plenty of studies dealing with the absorption of hydrogen by metals. However, the influence of the material surface on the characteristics of the hydrogen sorption-desorption processes was considered in very few publications. One of the reasons for this is the fact that the detection of hydrogen making use of the most widespread analytical methods of surface research is very problematic. Electron spectrometry methods (e.g., AES and XPS) cannot always detect hydrogen and its compounds. One of the unique features of mass spectrometric methods is just their ability to detect hydrogen and its compounds [18].

The aim of this work was to analyze the composition of chemical compounds on the surface of the hydrogen storage alloy LaNi$_5$ at the initial stages of its interaction with hydrogen and oxygen, as well as the modification of this composition depending on the partial pressures of hydrogen and oxygen in the gas mixture.

2. Research Methods

In this work, the study was performed making use of the secondary ion mass spectrometry (SIMS) method [19]. Unlike the vast majority of analytical methods to study the surface, this method permits the direct detection of hydrogen and its compounds, as well as studying of the composition variation in such compounds depending on experimental conditions.

The alloy specimens were irradiated with primary Ar$^+$ ions with an energy of 10 keV, when analyzing positive secondary ions, and 18 keV, when analyzing negative ones. The current density of the primary beam was 9 μA cm, when measuring positive secondary ions, and 17 μA cm, when measuring negative ones, which corresponded to the dynamic SIMS mode. Low-energy secondary ions (10 ± 3 eV) sputtered in a narrow energy interval were analyzed. The emission intensities of secondary ions were measured in a dynamic range of more than six orders of magnitude. In the cases where the emissions of polyatomic secondary ions, which characterize the composition of chemical compounds on the surface, overlap by the masses in a complicated way, the resolution of their specific contributions was carried out according to the standard procedure utilizes the natural occurrence of isotopes.

Before the measurements, the specimens were annealed in the residual vacuum in order to partially clean their surface from chemical compounds. After the annealing, the surface was additionally cleaned by the primary ion beam until the complete stabilization of the composition in the mass spectra and the intensity of secondary ion emissions was reached. The gas phase composition and low partial pressures of the gases in the vacuum chamber were controlled and measured making use of a gas mass spectrometer.

In the dynamic SIMS mode, which was used to carry out measurements, the primary beam can affect the composition and the amount of chemical compounds on the specimen surface. Therefore, when analyzing the results obtained, main attention was paid not to the absolute intensity values of the secondary ion emissions, but to the intensity changes depending on the experimental parameters.

3. Experimental Results and Their Discussion

When discussing the influence of oxygen on the hydrogen interaction with the alloy surface, as well as when carrying out the relevant experiments, information concerning how hydrogen and oxygen interact separately with a relatively clean surface and how the chemical composition of the near-surface monolayers in the alloy changes under such interaction would be very useful. In this connection, at the first stage of our research, we studied the composition of chemical compounds on the LaNi$_5$ surface at its interaction separately with hydrogen and oxygen.

The results of measurements showed that the mass spectra of positive and negative secondary ions sputtered from a relatively clean LaNi$_5$ surface under residual partial oxygen and hydrogen pressures contain a large set of emissions of atomic and cluster ions of both alloy components, as well as emissions corresponding to the compounds of the alloy components with hydrogen, oxygen, and carbon. Note that the most intense emission in the spectrum of positive ions was the emission of lanthanum oxide ions. This result may probably be associated with the presence of oxygen as an impurity in the specimen bulk. The experimental composition of the mass spectra indicates that there were some chemical compounds on the surface of the examined specimens from the very beginning, namely, the oxides, hydrides, hydroxides, and carbides of the alloy components.

The research of the LaNi$_5$ interaction with hydrogen at residual partial oxygen pressures showed the following. As the partial pressure of hydrogen was increased from about 7×10^{-7} to $(3{\div}7) \times 10^{-3}$ Pa, the emission intensity substantially increased for the majority of the observed positive and negative hydrogen-containing secondary ions [19], whereas the emission intensities of oxygen-containing ions remained almost unchanged. The presence of rather intense emissions of hydrogen-containing ions with lanthanum and nickel, as well as complex lanthanum-nickel ions, at high partial hydrogen pressures means that hydrogen, being chemisorbed on a clean surface, forms strong chemical bonds with both alloy components. The growth of the intensity of such emissions with the

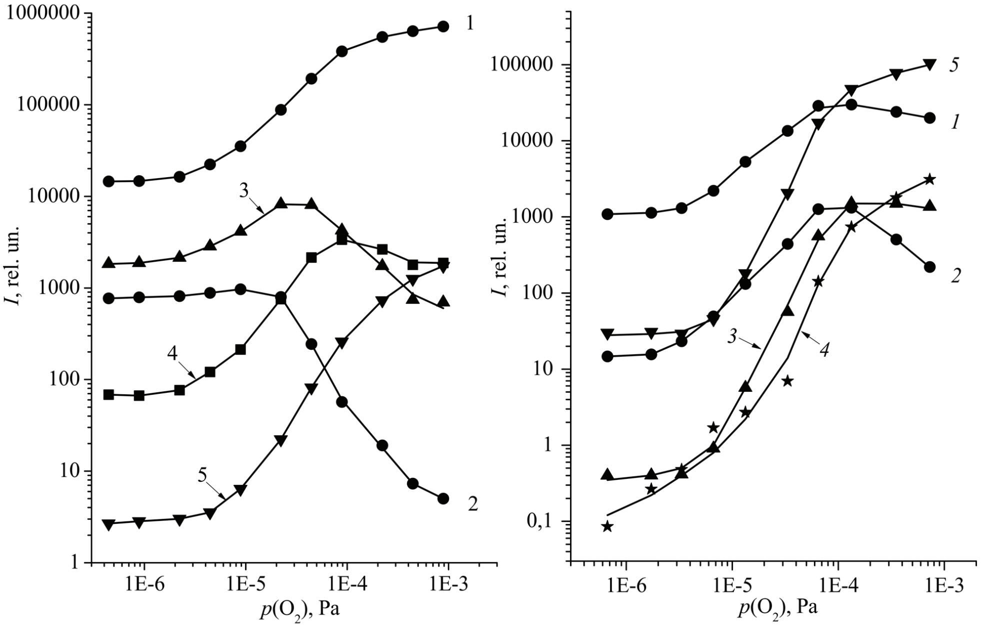

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Fig. 1. Dependences of the emission intensity of secondary ions with lanthanum and nickel sputtered from the $LaNi_5$ surface at room temperature on the partial pressure of hydrogen: (panel *a*) LaH^+ (*1*), La_2H^+ (*2*), LaH_2^+ (3), and $LaOH^+$ (*4*); (panel *b*) $^{58}NiH^-$ (*1*), $^{58}Ni_2H^-$ (*2*), Ni_3H^- (*3*, $m/z = 175$), Ni_4H^- (*4*, $m/z = 233$), $^{58}NiH_2^-$ (*5*), $^{58}Ni_2H_2^-$ (*6*), and H^- (*7*)

hydrogen flow to the surface indicates an increase in the amount of hydrogen-containing chemical compounds, containing both nickel and lanthanum, on the surface. A hydrogen-containing structure with a certain stoichiometric ratio of components is formed on the surface and in the near-surface region of the specimen. In the case of SIMS experiments, such a structure is characterized by both the set of hydrogen-containing secondary ions (positive and negative) and their emission intensity ratios. For the prevailing majority of positive and negative hydrogen-containing secondary ions, the dependences of the emission intensity on the partial hydrogen pressure within the indicated interval of hydrogen pressures can be approximated by a power function with a power exponent both larger and smaller than unity.

Some examples illustrating the dependences of the emission intensity of positive and negative hydrogen-containing secondary ions on the partial hydrogen pressure measured at residual (about 1×10^{-8} Pa) partial pressure of oxygen are depicted in Fig. 1. The appearance of hydrogen-containing chemical compounds on the surface – in particular, hydrides of alloy components with various compositions – and the increase of their amount with the hydrogen pressure indicate to the dissociative character of the hydrogen chemisorption. In essence, the latter is a necessary condition for the hydrogenation process to start, and it can be considered as one of its stages.

In order to study the interaction of $LaNi_5$ with oxygen, the mass spectra of positive and negative secondary ions sputtered from the surface were measured at room temperature within the interval of $(6.6 \div 8.8) \times 10^{-7}$ Pa for the partial oxygen pressure and at a residual partial hydrogen pressure of $(5 \div 8) \times 10^{-7}$ Pa. The growth of the partial oxygen pressure led to the appearance of a large set of oxygen-containing emissions corresponding to positive and negative secondary ions of the alloy components $La_nO_m^\pm$ and $Ni_nO_m^\pm$ (here, n and m vary from 1 to 4, being different for positive and negative ions) in the mass spectra. There are also a large number of oxygen-containing emissions of complex secondary ions of the type $La_nNi_mO_k^\pm$, which are composed of lanthanum, nickel, and oxygen atoms in various ratios. Together with the emissions of oxide ions, the spectra also contain the corresponding emissions of hydroxide and hydride ions.

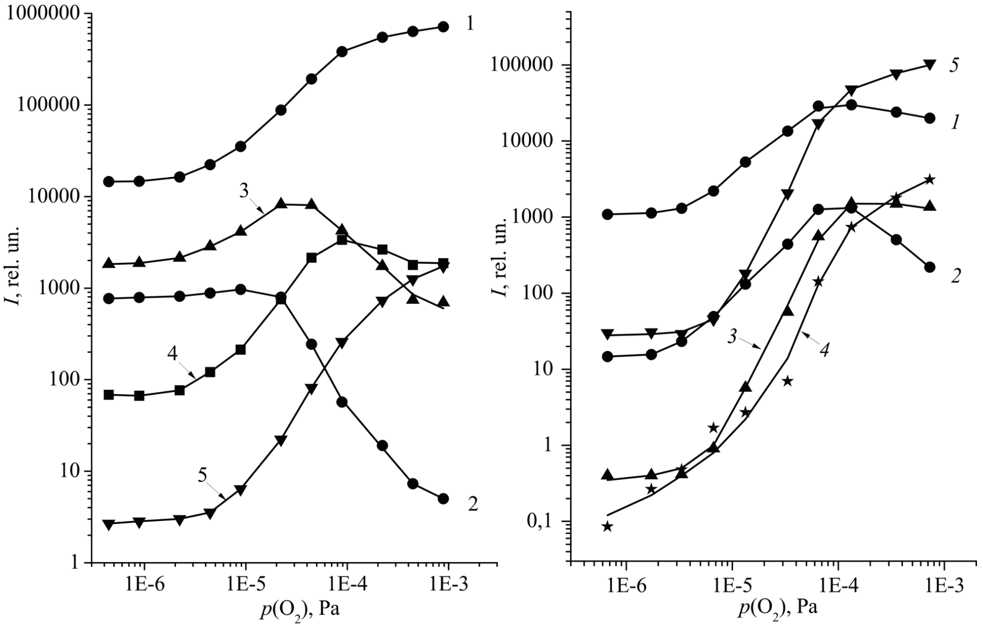

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Fig. 2. Dependences of the emission intensity of secondary ions with lanthanum and nickel sputtered from the LaNi$_5$ surface at room temperature on the partial pressure of oxygen: (panel *a*) LaO$^+$ (*1*), La$_2$O$^+$ (*2*), La$_2$O$_2^+$ (3), La$_2$O$_3^+$ (*4*), and LaO$_2^+$ (*5*); (panel *b*) ^{58}NiO$^-$ (*1*), ^{58}Ni$_2$O$^-$ (*2*), ^{58}Ni$_2$O$_2^-$ (*3*), ^{58}Ni$_2$O$_3^-$ (*4*), and ^{58}NiO$_2^-$ (*5*)

On the basis of the measurements, the dependences of the emission intensity on the partial pressure of oxygen in he specimen chamber at the residual partial pressure of hydrogen were plotted for the group of oxygen-containing emissions. As an example, some of those dependences are shown in Fig. 2. The analysis of the measured dependences showed that the emission intensities of oxygen-containing secondary ions have a maximum. Furthermore, the more the oxygen atoms per metal atom are in the secondary ion, the higher the oxygen pressure at which the maximum is observed. There are also secondary ions, the emission intensity of which only tends to the saturation with the growth of the partial oxygen pressure. Thus, the results of our experiments give grounds to assert that, owing to the influence of oxygen, a complex chemical structure composed of oxygen, lanthanum, and nickel is formed on the surface and in the near-surface region of LaNi$_5$. The behavior of the dependences shown in Fig. 2 reflects an increase in the number of oxygen atoms per matrix atom in the formed oxygen-containing structure with the growth of the partial oxygen pressure.

We also measured the emission intensities of the positive and negative hydrogen-containing secondary ions sputtered from the LaNi$_5$ surface as functions of the partial hydrogen pressure at elevated values of the partial oxygen pressure, i.e. under conditions, when hydrogen contained various fractions of oxygen as an impurity, so the surface was simultaneously affected not only by hydrogen, but also by oxygen. In so doing, we assumed that the emission intensities of hydrogen-containing secondary ions and their change objectively reflect the process occurring at the initial stages of the hydride formation.

The oxygen pressure in the specimen chamber during the measurement of the indicated dependences was monitored with the help of a gas mass spectrometer. The measurements were performed as follows. At the residual oxygen and hydrogen partial pressures, the specimen surface was cleaned by the primary beam. Then, the selected value of the partial oxygen pressure was established. After the emission intensities of the observed secondary ions had been stabilized, the mass spectra were measured at some partial hydrogen pressure values. The procedure was repeated for the next value of the partial oxy-

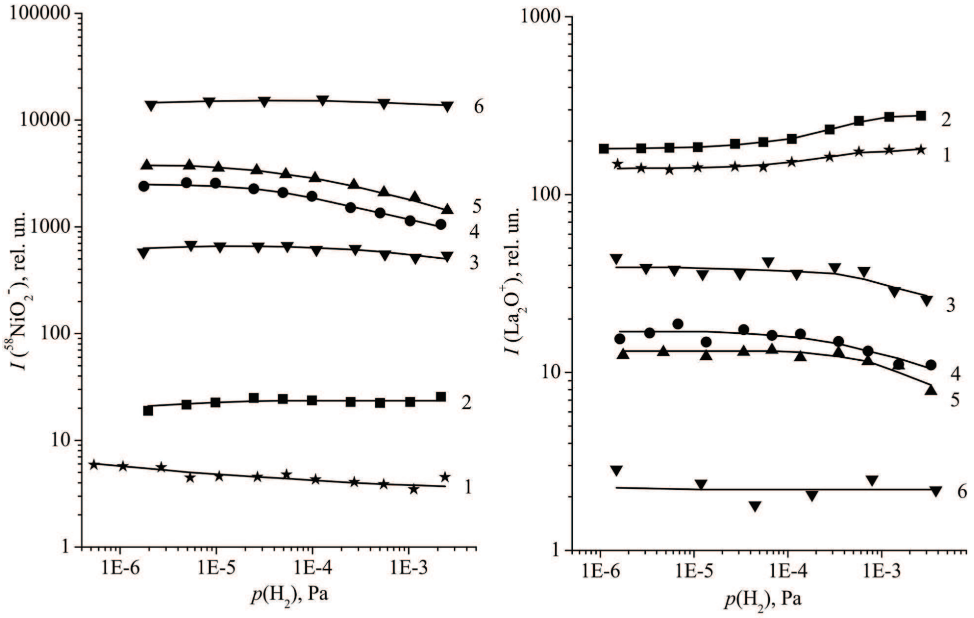

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Fig. 3. Dependences of the emission intensity of secondary oxide ions sputtered from the $LaNi_5$ surface at room temperature on the partial pressure of hydrogen for various partial oxygen pressures $p(O_2) = 1.3\times10^{-8}$ (*1*), 1×10^{-5} (*2*), 4×10^{-5} (*3*), 7×10^{-5} (*4*), 1×10^{-4} (*5*), and 5×10^{-4} Pa (*6*)

gen pressure. In other words, a certain equilibrium oxide coating was created on the surface, and the processes of interaction with hydrogen were considered against this background. By analyzing the measured mass spectra, the dependences of the emission intensities of the positive and negative secondary ions of the oxides, hydroxides, hydrides, *etc.*, of the alloy components that were present in the mass spectra on the partial hydrogen pressure were plotted for various values the partial oxygen pressure. It should be emphasized that the amount and the composition of chemical compounds on the examined surface are a result of the simultaneous action of several processes: chemisorption of gas phase components, diffusion into the bulk, desorption from the surface, and sputtering by the primary beam.

The analysis of the measured dependences showed the following. If the partial oxygen pressure was fixed, the emission intensities of positive and negative secondary oxide ions with lanthanum and nickel changed weakly (no more than by a factor of 2–3) when the hydrogen pressure increased from a residual one to about $(2\div2.5)\times10^{-3}$ Pa. The growth of the partial oxygen pressure shifted the curves describing the emission intensity dependences on the partial hydrogen pressure toward the region of higher or lower intensities. For the secondary oxide ions with lanthanum and nickel, this shift occurred, generally speaking, differently. A common feature for the lanthanum and nickel oxide ions is that, for the ions with large ratios between the number of oxygen atoms and the number of metal atoms in a sputtered ion ("oxygen-enriched" ions), the curves of the emission intensity dependences on the partial hydrogen pressure became shifted to the region of higher intensities. For the ions with lower ratios between the number of oxygen atoms and the number of metal atoms in an ion ("oxygen-depleted" ions), the curves of the emission intensity dependences on the partial hydrogen pressure became shifted, at first, toward the region of higher intensities and, afterward, to the region of lower intensities, thus passing through a kind of maximum. The latter took place at different oxygen pressures for different ions. For the displacement of the curves obtained for the oxide ions with lanthanum and nickel, there exists a qualitative correspondence between the results of measurements of the emission intensity dependences on the partial oxygen pressure obtained for those ions (Fig. 2). In Fig. 3, the emission intensity dependences on the partial hydrogen

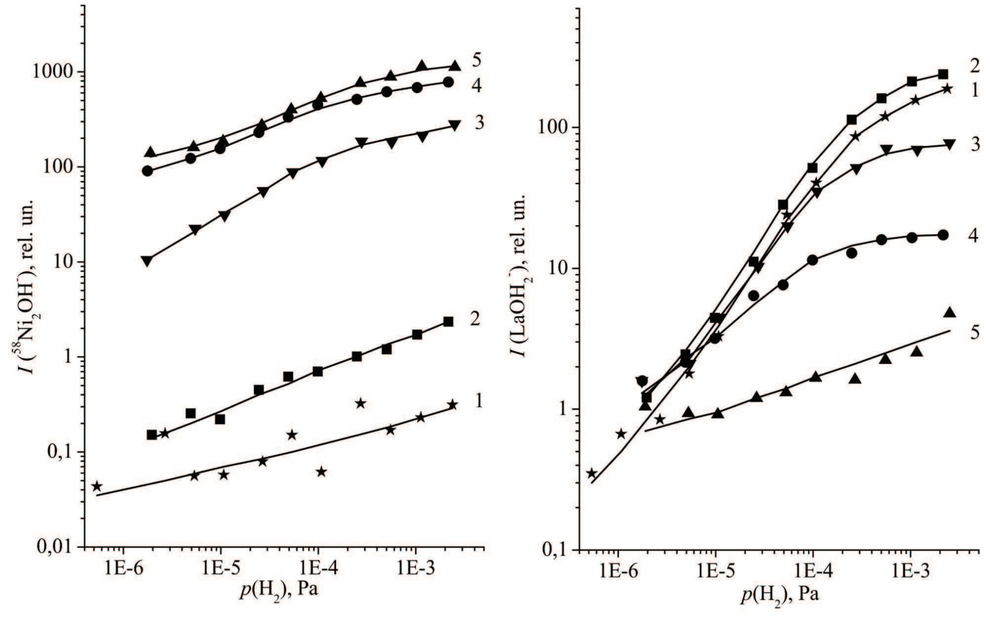

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Fig. 4. Dependences of the emission intensity of secondary hydroxide ions sputtered from the $LaNi_5$ surface at room temperature on the partial pressure of hydrogen for various partial oxygen pressures $p(O_2) = 1.3 \times 10^{-8}$ (*1*), 1×10^{-5} (*2*), 4×10^{-5} (*3*), 7×10^{-5} (*4*), and 1×10^{-4} Pa (*5*)

pressure measured for the secondary ions of oxides from the first and second groups, i.e. "oxygen-enriched" ($^{58}NiO_2^-$) and "oxygen-depleted" (La_2O^+), are presented as an example.

The emission intensities of the secondary hydroxide ions with lanthanum and nickel, unlike those of oxide ions, increase with the partial hydrogen pressure at a fixed partial pressure of oxygen. When the partial oxygen pressure increases from residual one to 1×10^{-4} Pa, such increasing dependences of emission intensities of hydroxide ions on the partial hydrogen pressure become either shifted toward the region of higher intensities or, at first, shifted toward the region of higher intensities and, afterward, toward the region of lower values, thus passing through a kind of maximum. This situation is similar to that observed in the case of oxide ions. This fact gives grounds to consider that hydroxides are formed at the surface regions occupied by oxides and their amount corresponds to the amount of oxides and, of course, increases with the growth of the partial hydrogen pressure.

For nickel hydroxides – e.g., NiO_2H^-, NiO_3H^-, and $Ni_2O_3H^-$ – the emission intensity dependences on the partial hydrogen pressure are shifted to higher intensity values as a rule. Such a behavior corresponds to the emission intensity dependences on the partial oxygen pressure for the secondary ions of nickel oxides within the same interval of partial oxygen pressures. Being shifted, the curves remain approximately similar to one another. Some examples are shown in Fig. 4, *a*.

For lanthanum hydroxide ions, the situation is somewhat different. In some cases, as it was for the ions of nickel hydroxides, the curves for the oxygen-enriched $LaO_2H^\pm$, LaO_3H^-, $LaNiO_2H^-$, and LaO_3H^+ ions shifted to the region of higher intensity values but remained similar to one another. At the same time, for oxygen-depleted emissions – e.g., $LaOH^-$, $LaOH_2^-$, $LaNiOH^-$, La_2OH^+, and La_2NiOH^+ – the curves mainly shifted either, at first, toward the high-intensity region and, afterward, toward the low-intensity region, or shifted to the lower-intensity region and their slopes decrease (Fig. 4, *b*). Such a behavior also corresponds to the dependences of the emission intensity of the lanthanum oxide secondary ions on the partial oxygen pressure.

The increase in the emission intensity of the hydroxide secondary ions with the growth of the partial hydrogen pressure within the examined pressure interval indicates the increase of the amount of hydrox-

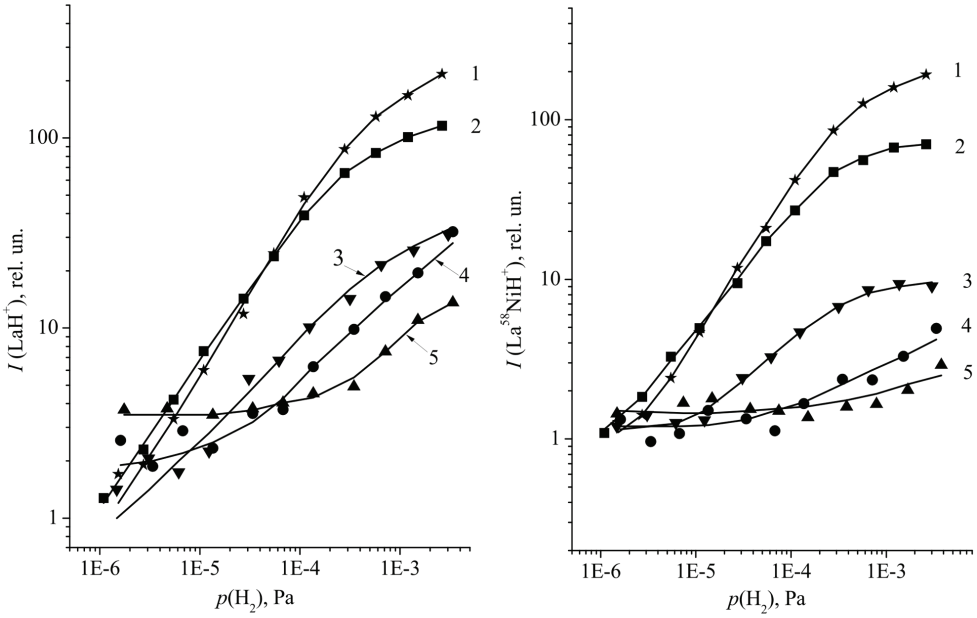

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Fig. 5. Dependences of the emission intensity of secondary hydride ions sputtered from the $LaNi_5$ surface at room temperature on the partial pressure of hydrogen for various partial oxygen pressures $p(O_2) = 1.3 \times 10^{-8}$ (*1*), 1×10^{-5} (*2*), 4×10^{-5} (*3*), 7×10^{-5} (*4*), and 1×10^{-4} Pa (*5*)

ides with a certain composition, i.e. the hydroxides which fragmentation at the sputtering led to the formation of indicated ions. The decrease in the slope of the curves describing the emission intensity dependence on the partial hydrogen pressure shows that, as the oxygen content in the gas mixture increased, the growth of the hydrogen partial pressure exerted a weaker and weaker effect on the composition and the amount of hydroxides on the surface and in the near-surface region.

As for the emissions of the secondary hydride ions, the emission intensities of such ions increased with the partial hydrogen pressure, as it was for the hydroxide ions. However, with the growth of the oxygen content in the gas mixture, this increase became less and less considerable. This is a common feature of the measured dependences for the hydrides ions with lanthanum and nickel. In Figs. 5 and 6, some examples of the measured dependences for the secondary ions with lanthanum and nickel are depicted.

The analysis of the dependences shown in Fig. 5 allows us to draw a conclusion that lanthanum hydrides, the fragments of which are nothing else but the corresponding secondary ions, are formed on the surface free of oxides (hydroxides). As the area of such a free surface decreases, the amount of lanthanum hydrides also decreases, which leads to a reduction in the emission intensity of the corresponding ions (Fig. 5, *a*). This situation is also typical of complex hydrides including lanthanum and nickel (Fig. 5, *b*). Of course, one cannot exclude that the fragmentation of the corresponding hydroxides may also make a certain contribution to the emission of lanthanum hydride ions.

The analysis of the dependences obtained for the ions of nickel hydrides (Fig. 6) allows the same interpretation. Some nickel hydrides, like lanthanum ones, are formed on the surface free of oxides and hydroxides, and their amount decreases with the reduction of oxygen-free surface area. This is evidenced by the dependences of the emission intensity of secondary ions on the partial hydrogen pressure obtained for some secondary ions of nickel hydrides and for lanthanum hydride ions. Those dependences are shifted toward the lower-intensity region, and their slope gradually diminishes within the whole interval of partial oxygen pressures (Ni_2H^-, Ni_3H^-) (Fig. 6, *a*). For the emissions of hydrogen-enriched nickel hydride ions NiH^- and NiH_2^-, the transformation of the dependences occurs quite drastically when changing from the oxygen

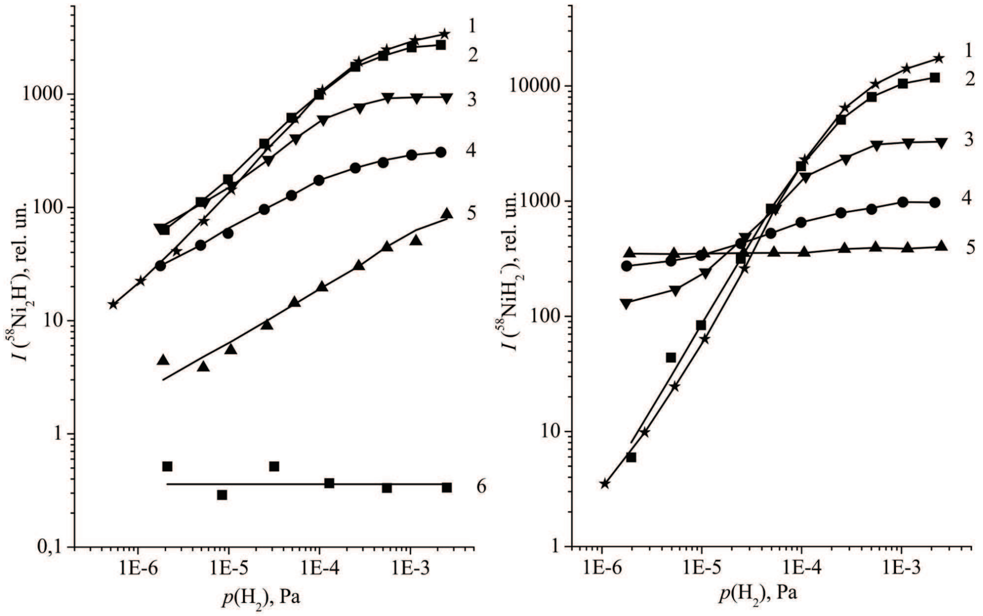

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Fig. 6. Dependences of the emission intensity of secondary hydride ions sputtered from the $LaNi_5$ surface at room temperature on the partial pressure of hydrogen for various partial oxygen pressures $p(O_2) = 1.3\times10^{-8}$ (*1*), 1×10^{-5} (*2*), 4×10^{-5} (*3*), 7×10^{-5} (*4*), 1×10^{-4} (*5*) , and 5×10^{-4} Pa (*6*)

pressure of 1×10^{-5} Pa to the pressure of 4×10^{-5} Pa (Fig. 6, *b*). Here, the secondary ions with a mass of 60 amu are interpreted as NiH_2^-, although if the partial oxygen pressure is sufficiently high, a contribution from, e.g., AlO_2H^- ions is possible, because the specimen contains a small amount of aluminum as an impurity.

As one can see from Fig. 6, *b*, if the partial hydrogen pressure is relatively low ($1\times10^{-6}\div1\times10^{-5}$ Pa), an increase of the partial oxygen pressure leads to an increase of the emission intensity of the $^{58}NiH_2^-$ hydride ions by one or two orders of magnitude. At the same time, at high partial hydrogen pressures ($1\times10^{-4}\div5\times10^{-3}$ Pa), the growth of the partial oxygen pressure results in a decrease of the emission intensity of hydride ions. It is difficult to explain such a behavior in the framework of the speculations presented above that the contribution of various secondary ions of nickel hydrides to the emission is made only by the surface areas free of oxides and hydroxides. In this model, there are no mechanisms for the emission intensity of nickel hydride ions to grow. As the partial pressure of oxygen increases, the surface becomes more and more covered with oxides, and the area of the relatively clean surface suitable for the formation of nickel hydrides becomes smaller. Therefore, the experimental data obtained for the emission of some nickel hydride ions has to be interpreted in a different way.

As was indicated above, there are studies according to which the appearance of oxygen on the $LaNi_5$ surface gives rise to a substantial reconstruction of the surface with the formation of large clusters of nickel atoms. Such clusters have a high catalytic activity and provide the dissociative chemisorption of hydrogen, which is required at the hydrogenation, thus preventing the surface blocking by reactive impurities (oxygen). The formation of nickel clusters is confirmed by experimental data on the $LaNi_5$ magnetic properties. According to those data, the oxidation leads to the manifestation of high ferromagnetic properties of the alloy, which is interpreted as the formation of nickel clusters [9–13].

In the secondary ion emission, one of the indicators that the sputtered surface consists of identical atoms is the presence of polyatomic secondary ions that include only matrix atoms (cluster secondary ions) in the mass spectrum. In other words, according

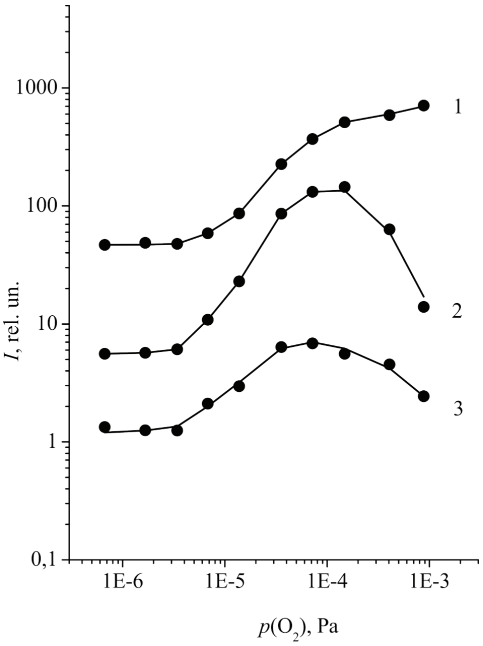

Fig. 7. Dependences of the emission intensity of various secondary polyatomic ions with nickel sputtered from the LaNi$_5$ surface at room temperature on the partial pressure of oxygen: ^{58}Ni$_2^+$ (*1*), Ni$_3^+$ (*2*, $m/z = 176$), and Ni$_4^+$ (*3*, $m/z = 234$)

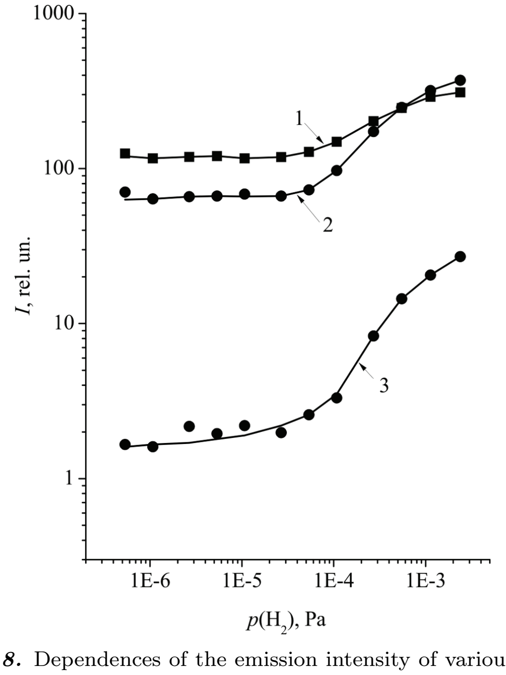

Fig. 8. Dependences of the emission intensity of various secondary polyatomic ions with nickel sputtered from the LaNi$_5$ surface at room temperature on the partial pressure of hydrogen: ^{58}Ni$_2^-$ (*1*), Ni$_3^-$ (*2*, $m/z = 174$), and Ni$_4^-$ (*3*, $m/z = 234$)

to the sputtering model of such ions [19], it is necessary that the atoms forming a secondary ion should be initially adjacent both on the surface and in the nearest-to-the-surface monolayers, whereas no other atoms should be located in the immediate vicinity. In our case, the growth of the emission intensity of polyatomic secondary nickel ions Ni$_n^{\pm}$ and, to some extent, their analogs with oxygen and hydrogen can serve as an indicator that the areas of metallic nickel are formed on the surface and in the near-surface region under certain experimental conditions.

As was mentioned earlier, we measured the dependences of the emission intensity of various secondary ions, including the secondary nickel ions Ni$_n^+$, on the partial oxygen pressure at the residual partial pressure of hydrogen (Fig. 7). From the presented dependences, one can see that, at hydrogen pressures close to residual one, the increase of the partial oxygen pressure within an interval from 5×10^{-6} to 8×10^{-5} Pa led to a substantial increase of the emission intensity of the Ni$_2^+$, Ni$_3^+$, and Ni$_4^+$ ions. The emission of nickel oxide ions Ni$_n$O$^+$ also increased. Those facts clearly testify that, in the indicated interval of oxygen pressures, the areas with three, four, or more adjacent nickel atoms arose and grew on the sputtered surface and in the near-surface region. In essence, this conclusion allows us to interpret the results obtained as the grouping of nickel atoms on the surface and in the near-surface region [20]. At partial oxygen pressures higher than 8×10^{-5} Pa, the emission intensity of nickel ions Ni$_3^+$ and Ni$_4^+$ decreased. Probably, this occurred, because a substantial number of the grouped nickel atoms became covered with oxides at such oxygen pressures.

It is of interest that the dependences of the emission intensities of the polyatomic secondary nickel ions on the partial hydrogen pressure which were measured in this work at a partial oxygen pressure close to the residual one (see Fig. 8) turned out qualitatively similar to the results described above. It was found that the appearance of chemisorbed hydrogen on the surface also leads to the grouping of nickel atoms. This is evidenced by the growth of the emission intensity of the Ni$_2^-$, Ni$_3^-$, and Ni$_4^-$ ions, as well as the Ni$_3^+$ and Ni$_4^+$ ones, with the increase of the partial hydrogen pressure. This result means the following. Despite that the enthalpy of the lanthanum hydride (LaH$_2$) formation is substantially lower than the enthalpy of the lanthanum oxide (La$_2$O$_3$) formation [21, 22], the hydrogen chemisorption, as well as oxygen chemisorption, on $LaNi_5$, can stimulate the surface segregation and grouping of nickel atoms, though to a less extent than the oxygen chemisorption does. Hence, the surface segregation and grouping of nickel atoms comprise a general reaction of the surface and near-surface monolayers in the LaNi alloy to the common chemisorption of hydrogen and oxygen.

The involvement of the nickel clustering process into consideration makes it possible to explain the features of the dependences shown in Fig. 6, *b*. At first, hydrogen-enriched $^{58}NiH_2^-$ ions are sputtered from the relatively clean surface areas, where the space nearby nickel atoms is enough for the chemisorption of two hydrogen atoms. An increase in the partial oxygen pressure initiates the surface segregation and the formation of nickel clusters that occupy some areas on the surface. The surface of such nickel clusters can be oxidized to NiO or Ni_2O_3. If hydrogen, including residual one, is also present, the oxides are transformed into hydroxides: $Ni(OH)_2$ or $Ni(OH)_3$ [14, 15]. In this case, various sections of the surface contribute to the emission of nickel hydride ions. As it was at the residual oxygen pressure, the contribution is made by the surface sections that are not occupied by nickel clusters. Again, this process continues as long as there is the enough space nearby the nickel atoms for the chemisorption of two hydrogen atoms. Sections occupied by nickel clusters also contribute. As a result of the reaction with residual hydrogen, nickel hydrides are formed on the surface of the clusters and, up to certain oxygen pressures, there are always sites for the chemisorption of two or more hydrogen atoms. Furthermore, a contribution is given by the fragmentation of nickel hydroxides with a certain stoichiometric ratio that were formed on the sections both free from nickel clusters and occupied by them.

As the partial oxygen pressure increases, owing to the oxidation and the formation of lanthanum and nickel hydroxides, the possibility for several hydrogen atoms to be chemisorbed near nickel atoms on a surface section not occupied by clusters decreases. Therefore, the contribution of this surface section to the emission of corresponding ions as a result of the nickel hydride fragmentation also diminishes. The formation of oxides and hydroxides, now only of nickel, also takes place on the surface of nickel clusters. Hence, the contribution of this part of the surface to the emission of the corresponding ions as a result of the fragmentation of nickel hydrides also gets smaller. Ultimately, the emission of hydrogen-enriched nickel hydride ions, which is associated with the fragmentation of nickel hydrides, becomes low. In this case, only the fragmentation of nickel hydroxides is responsible for the emission of nickel hydride ions.

Thus, the obtained experimental data allow the initial stages of the interaction between a hydrogen-oxygen gas mixture and a $LaNi_5$ alloy surface to be described as follows. If there is not enough oxygen in the gas phase, the influence of hydrogen on $LaNi_5$ results in the formation of a hydrogen-containing (hydride) structure consisting of nickel, lanthanum and hydrogen in certain stoichiometric ratios on the alloy surface. As the partial pressure of hydrogen grows, the amount of hydrides with various compositions increases. The presence of hydrides indicates the dissociative character of the hydrogen chemisorption.

If there is oxygen in the gas phase (up to a certain fraction), the influence of such a gas mixture on $LaNi_5$ leads, together with the formation of hydrides, to the formation of oxides and hydroxides of both components of the lanthanum–nickel alloy, although lanthanum is characterized by a higher chemical affinity to oxygen. As a result, there emerges a chemical structure consisting of hydrides, hydroxides, and oxides of lanthanum and nickel on the surface. Our experimental results do not give grounds to conclude that those hydrides, hydroxides, and oxides of lanthanum and nickel are somehow spatially separated, i.e. they form phase inclusions. As the oxygen pressure increases, the amount of oxides and hydroxides increases. The stoichiometric ratios in the oxide compounds, as was marked above, change toward the larger number of oxygen atoms per matrix atom. If the hydrogen pressure increases, the amount of oxides does not change, because oxygen forms a stronger bond with the metal than hydrogen does, so hydrogen cannot replace it. The amount of hydroxides increases with the growing amount of oxides.

At the same time, chemisorption of oxygen on the alloy surface initiates the surface segregation and grouping of nickel atoms with the formation of large nickel clusters. Under those conditions, there are areas on the surface of the LaNi alloy that are covered with hydrides, hydroxides, and oxides of lanthanum and nickel, as well as areas occupied by nickel clusters. Nickel hydrides, oxides, and hydroxides are formed on the surface of nickel clusters. Until there exist oxide- or hydroxide-free areas on the surface of nickel clusters, they can serve as catalytically active centers for the dissociative chemisorption of hydrogen molecules from the gas phase, even if there is no oxygen in the gas phase, thus promoting hydrogenation processes. Hydrogen located on the surface of nickel clusters can also reduce nickel oxide to the metallic state, thus being competing with oxygen to some extent. As a result, the rate of hydrogenation reaction increases.

The described processes, as was mentioned above, are active up to certain values of the partial oxygen pressure, i.e. as long as there still exist free places nearby metal atom (in particular, nickel) for the hydrogen chemisorption. As the oxygen content increases, probability that free places for the hydrogen chemisorption near a metal atom survive decreases. Those places become occupied by oxygen, which forms oxides. Therefore, the amount of hydrides of the alloy components also decreases, the presence of which indicates the dissociative character of the hydrogen chemisorption and is a necessary condition for the hydrogenation process initiation.

If there is a lot of oxygen in the gas mixture – in our case, at a partial pressure of oxygen higher than about 1×10^{-4} Pa – the surface becomes almost completely covered with a continuous layer of oxides and hydroxides. Hydrogen, when arriving at the surface, cannot form chemical bonds with the alloy components and, consequently, participate in hydrogenation processes.

4. Conclusions

Our research of the composition of chemical compounds appearing on the surface of the hydrogen storage alloy $LaNi_5$ at the initial stages of its interaction with hydrogen and oxygen has shown the following. The simultaneous influence of hydrogen and oxygen on the alloy surface leads to the formation of a complex surface chemical structure consisting of hydrides, hydroxides, and oxides of lanthanum and nickel. As the oxygen pressure increases, the amount of oxides and hydroxides of the alloy components grows. The stoichiometric ratios in the oxide and hydroxide compounds change toward the larger number of oxygen atoms per matrix atom. If the hydrogen pressure increases, the amount of oxides does not change, but the amount of hydroxides becomes larger.

In addition, the chemisorption of oxygen on the alloy surface initiates the surface segregation and grouping of nickel atoms with the formation of nickel clusters. Under those conditions, there exist surface sections of the $LaNi_5$ alloy that are covered with the hydrides, hydroxides, and oxides of lanthanum and nickel, as well as the sections occupied by nickel clusters that are covered with the hydrides, oxides, and hydroxides of nickel. Until there are oxide- and hydroxide-free areas on the surface of nickel clusters, they can serve as catalytically active centers for the dissociative chemisorption of hydrogen molecules, thus favoring the hydrogenation processes.

At high partial pressures of oxygen, the surface is completely covered with a continuous layer of oxides and hydroxides. Therefore, hydrogen, when arriving at the surface, cannot form chemical bonds with the alloy components and, consequently, participate in hydrogenation processes.

The results obtained in this work give grounds to conclude that the chemisorption of hydrogen, as well as oxygen, on $LaNi_5$ can stimulate, to some extent, the surface segregation and grouping of nickel atoms. Hence, the surface segregation and grouping of nickel atoms comprise a general reaction of the surface and near-surface monolayers of the LaNi alloy to the chemisorption of both oxygen and hydrogen.

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ДОСЛІДЖЕННЯ СИСТЕМИ $LaNi_5$-ВОДЕНЬ-КИСЕНЬ МЕТОДОМ ВТОРИННОЇ ІОННОЇ МАС-СПЕКТРОМЕТРІЇ

У роботі представлено результати дослідження поверхні сплаву $LaNi_5$ методом мас-спектрометрії вторинних іонів. Показано, що одночасний вплив водню і кисню на поверхню сплаву приводить до утворення складної поверхневої хімічної структури, що складається з гідридів, гідроксидів і оксидів лантану та нікелю. Стехіометричні співвідношення у цих сполуках визначаються долями водню і кисню у газовій суміші. Взаємодія кисню з поверхнею сплаву викликає поверхневу сегрегацію і угруповання атомів нікелю з утворенням великих нікелевих кластерів. Доки на поверхні таких кластерів є вільні від оксидів і гідроксидів ділянки, вони виступають каталітично активними центрами для дисоціативної хемосорбції молекул водню і, таким чином, сприяють процесам гідрування.

Ключові слова: вторинна іонна мас-спектрометрія (ВІМС), поверхня, сплави-накопичувачі водню, водень, кисень, гідриди.