

THE ROLE OF SURFACE IN HYDRIDE FORMATION PROCESSES[†]

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Several LaNi₅-based hydrogen storage alloys were studied using secondary ion mass spectrometry (SIMS) technique. Ar⁺ ions with the energy of 10 - 18 keV were used as primary ions. The study of the initial stages of the processes of LaNi₅-based alloys interaction with hydrogen under the experimental conditions showed that on the areas of clean surface, hydrogen formed chemical compounds with the both of the main components of the alloy: nickel and lanthanum. As hydrogen accumulates on the surface and in the near-surface region, a hydrogen-containing structure is formed, which is characterized by a certain stoichiometric ratio of components. Nickel in this structure has strong chemical bonds with two hydrogen atoms, and lanthanum – with two or more hydrogen atoms. Along with such compounds, some structures with lower hydrogen content are also formed. The formed hydrogen-containing structure includes both main alloy components, La and Ni for all the studied samples, even though only lanthanum is generally accepted to be the hydride-forming element in such alloys. The SIMS studies of the chemical composition of the surface monolayers of the intermetallic alloy LaNi₅, in the process of its interaction with oxygen, showed the following. As a result of the oxygen interaction with the alloy, a complex chemical structure including oxygen, lanthanum and nickel is formed on the surface and in the near-surface region of LaNi₅. Oxygen in such a structure, similarly to hydrogen, forms strong chemical bonds with both components of the alloy. This is indicated by the presence in the mass spectra of a large set of oxygen-containing emissions of positive and negative secondary ions with lanthanum and nickel, as well as oxygen-containing lanthanum-nickel cluster secondary ions. The formed oxide compounds have a three-dimensional structure and occupy tens of monolayers. Oxygen poisoning of the surface of the hydride-forming alloy LaNi₅ can occur regardless of whether the surface of the alloy was clean from the very beginning or it was covered with a layer of hydrogen-containing chemical compounds.

Keywords: SIMS; surface; intermetallic alloy; lanthanum alloy; LaNi₅; hydrogen; metal hydride; oxygen; oxides

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INTRODUCTION

The energy supply independence is currently an integral part of the sovereignty of every state. One of the promising directions for solving the problem of the energy supply independence and ensuring sustainable development is the development of the field of hydrogen energy, that is, the field of energy, which is based on the use of hydrogen as a means for the energy production, accumulation, transportation and consumption. Hydrogen energy has turned into a direction, along with some other ones, with which the leading countries of the world associate the prospects of their national economics. The needs of various branches of hydrogen energy, which are necessary for the production and utilization of hydrogen as a renewable, ecological and safe energy carrier, require the introduction and development of various types of metal hydride technologies, that is, the technologies, based on the ability of a number of hydride-forming intermetallic alloys reversibly react with gaseous hydrogen to form metal hydrides.

The ability of a number of metals and alloys to reversibly absorb significant amount of hydrogen with the formation of metal hydrides has given rise to a number of technical solutions for the practical use of this phenomenon. The basis for this is the unique combination of the metal-hydrogen systems properties, namely, the possibility to achieve extremely high volumetric densities of hydrogen atoms in metal lattices (up to 0.09-0.1 g cm⁻³), a wide range of operating temperatures and pressures, selectivity of the hydrogen absorption process, significant changes in the physical properties of the metal, when it is saturated with hydrogen, catalytic activity and a number of other features [1-4].

The reversible reaction of metal hydride formation can occur either as a result of direct interaction of the hydride-forming metal (or alloy) with gaseous hydrogen, or as a result of an electrochemical process. The process of direct interaction includes the following stages: transport of hydrogen molecules to the metal surface; physical adsorption, dissociation of adsorbed H₂ molecules and the transfer of hydrogen atoms into the material volume with the formation of an interstitial solid solution (α -phase) and then – hydride (β -phase). The concentration of hydrogen atoms in the α -phase is small; they are statistically distributed in the interstitial voids of the metal matrix, which retains the original structure with a small (up to 5%) increase in the volume. On the contrary, the hydride is characterized by a high content of hydrogen atoms and their ordered arrangement.

The reaction of interaction with hydrogen takes place with the release of heat during the formation of the hydride and the absorption of heat during hydride dissociation. The reaction is reversible, the process can be turned to one direction or the other and its speed can be controlled by changing only the temperature and (or) pressure. An increase in the pressure of gaseous hydrogen and a decrease in temperature shift the equilibrium of the reaction to the side of hydride formation, while a decrease in pressure and an increase in temperature cause decomposition of the hydride [5,6].

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Among the large number of metal hydrides known to date, the hydrides of intermetallic compounds occupy a special place. Such hydrides are represented by the general formula $A_mB_nH_x$, where A_mB_n is an intermetallic compound of two or more metals, at least one component (A) of which has a high affinity for hydrogen, i.e. forms a highly stable binary hydride, and the other one (B) does not interact directly with hydrogen under normal conditions. It is customary to classify the hydride-forming intermetallics according to the ratio of hydride-forming (A) and non-hydride-forming (B) components. Among the large number of types of hydride-forming intermetallics, such compounds as AB_5 , AB_2 , AB and A_2B are of the greatest practical importance. In the compounds AB_5 , rare earth elements and/or calcium are used as the component A; in the compounds AB_2 and AB , the elements of the titanium subgroup are used; in the compounds A_2B , mainly magnesium is used. The component B in all the intermetallics mainly includes transition metals (Fe, Co, Ni, V, Mn, Cr, etc.). The formation of hydrides of intermetallic compounds is accompanied by the expansion of crystal lattices. Typical values of the increase in the volume of the unit cell vary from 10 - 15 to 20 - 25%. In this case, the symmetry of the original metal matrix is usually preserved.

The technologies based on the use of metal hydrides, the so-called metal hydride technologies, include the accumulation, compact and safe storage and transportation of hydrogen, thermosorption compression, separation of hydrogen from gas mixtures, its purification, distribution of isotopes, as well as ensuring the operation of various physical and technical devices, such as injectors of thermonuclear facilities, ion sources of accelerators, gas supply systems of vacuum-plasma facilities, etc. [2, 7, 8].

Accumulation, compact and safe storage, and transportation of hydrogen

The reversible storage of hydrogen in the form of intermetallic hydride has a number of advantages as compared to the conventional storage methods using gas cylinders or cryogenic equipment. The intermetallic hydrides have clearly defined volumetric advantages as compared to the compressed or liquefied gas. In fact, the density of hydrogen in hydrides approaches that of liquid hydrogen, since the packing density of H in the hydride crystal lattice is usually much higher than that of liquid hydrogen. This method of storage can be implemented at relatively low temperatures and pressures, which provides a high degree of fire and explosion safety, without the use of cryogenic technology and expensive and highly insulated containers, which are necessary to minimize the losses caused by liquid hydrogen evaporation. Furthermore, the method is characterized by compactness and low energy costs for the hydrides formation as compared to the liquefaction and compression of hydrogen [6].

Thermosorption compression

The concept of hydrogen compression by using intermetallic hydrides is based on the fact that the process of hydrogen absorption, accompanied by the formation of a metal hydride, occurs with the release of heat (exothermic reaction); in the course of the hydride decomposition with the hydrogen release, the heat absorption occurs (an endothermic process). The absorption occurs at a rather low pressure of hydrogen, and the release – at high pressure, similar to the processes of suction and discharge in a mechanical compressor. This makes it possible to carry out the process of low-pressure hydrogen absorbing at a lower temperature, and to desorb higher-pressure hydrogen when the appropriate heat is delivered to the metal hydride. This method is called thermosorption (or thermochemical) hydrogen compression, and the devices implementing it are the metal hydride thermosorption compressors (MH TSC) [9]. The metal hydride thermosorption compressor has a number of advantages as compared to traditional mechanical compressors. Such a compressor has no moving parts, pistons, membranes, or bellows. This provides a simplified design and high reliability, thus reducing the probability of explosive hydrogen leakage.

By applying the thermosorption compressors, it is possible to solve the problem of utilization of low-potential (unusable) heat in various industries, converting it into highly organized energy of compressed gas.

Hydrogen purification, hydrogen separation from gas mixtures

The selectivity of the intermetallics reaction with hydrogen allows for the realization of the processes of hydrogen purification from gaseous impurities, as long as the reactive species, such as O_2 , H_2O , CO , etc., tend to be absorbed by hydride, and the inert species, such as N_2 , CH_4 , etc., can be removed at the initial stages of the dehydrogenation process. Thus, the devices based on the intermetallic hydrides are often used in specialized applications, where H_2 "ultra-high purity" is required (for example, as a gas-carrier of gas chromatograph). The selectivity of the reaction also allows using the devices based on intermetallic hydrides to extract hydrogen from the gas mixtures without application of expensive devices, such as palladium filters.

The intermetallic hydrides can also be used to separate different isotopes of hydrogen: protium (H), deuterium (D), and tritium (T), for example, the separation of D from natural hydrogen (0.016% of D, residual H), or the removal of radioactive T from non-radioactive D and/or H. For example, zirconium-based getter alloys are used in a number of nuclear energy technologies, as well as in the fuel cycle research and development of thermonuclear reactors. Zirconium-based (Zr_2Fe) non-evaporable getters are used to solve the rather urgent task of purifying gas streams from hydrogen tritium isotope [10-12]. The advantage of using Zr_2Fe (SAES Getters ST198) instead of traditional methods of tritium collection and removal [13] is simplicity and possibility to avoid the production of tritium water, which makes a greater biological hazard. The gas absorption method is a non-oxidation process, in which the tritium water vapor is

never produced in the process line. In getters, tritium is stored more safely than in derivative products of the conventional oxidation-adsorption process. Also, the hydrogen isotopes, captured by the metal hydride getters, can be later extracted in their elemental form.

Ensuring the operation of various physical and technical devices.

The ability to control the pressure of desorbed hydrogen by means of a directed thermal effect on the metal hydride allows using the metal hydrides for high-precision regulated supply of hydrogen to the consumer. Some metal hydrides with fast dynamics of low-pressure hydrogen absorption (hydrogen getters) formed the basis of efficient hydrogen removal systems and systems of regulated supply of low-pressure hydrogen to the vacuum-plasma installations.

A distinctive feature of getter hydride-forming intermetallics is the low equilibrium pressure of hydrogen sorption-desorption at the temperatures close to the room ones. This feature allows using them in various devices operating at sub-atmospheric pressures, in particular, to ensure the operation of various physical and technical devices, such as injectors of thermonuclear installations, ion sources of accelerators, gas power systems of vacuum-plasma installations, gas lasers and other devices using hydrogen as a working medium [[14], **Error! Reference source not found.**].

THE ROLE OF IMPURITY GASES IN HYDROGEN IN THE PROCESSES OF INTERACTION WITH HYDRIDE-FORMING ALLOYS

The impurity gases that are present in hydrogen have different effects on the absorption capacity of hydride-forming alloys, in some cases, they can significantly change the kinetic parameters of the sorption-desorption processes and the hydrogen capacity of the alloy [16]. The impurity gases can be conventionally divided into four groups according to the nature of their influence on the alloy and its hydrogen-sorption characteristics [17, 18].

The first group is the impurities that lead to surface poisoning. The impurity gas molecules, contacting the surface, form a strong chemical bond with the surface metal atoms, which cease participating in the processes of dissociative chemisorption of hydrogen. In general, a monolayer coating is sufficient for complete deactivation of the material. Such a deactivated surface efficiently blocks the area of the underlying material from interaction with hydrogen. Thus, the surface poisoning lies in the formation of a surface structure that prevents the rapid dissociation of hydrogen on the surface $H_2 \rightarrow 2H$ and/or the penetration of hydrogen into the volume, what is equally necessary for the practical use of reversible hydrides. In the process of cycling, the poisoning causes a rapid decrease in hydrogen capacity. However, as long as the impurity molecules are localized only on the surface, the poisoned samples can often be reactivated (for example, by cycling and/or heating in pure H_2). An example of poisoning is exposure to the surface (at certain temperatures) of CO carbon monoxide, which forms a chemisorbed monolayer on the surface of $LaNi_5$ with a heat of adsorption comparable to the heat of nickel carbonyl formation. This makes the nickel atoms, on which the catalytic dissociation of hydrogen takes place, inactive. CH_3SH (methyl mercaptan) and H_2S produce a similar effect.

The second group are the impurities that slow down the processes of interaction with hydrogen, in particular, lead to some decrease of the hydrogen absorption kinetics, but not to the detriment of the hydrogen capacity. This group includes the impurities that are characterized by much softer and more homogeneous form of interaction with hydride-forming materials, than the interactions categorized as poisoning. The influence of CO_2 , NH_3 is an example.

The third group are the impurities that have a reactive effect, i.e., initiate a chemical reaction causing the alloy volume corrosion and, as a result, an irreversible decrease in hydrogen capacity. This situation occurs when hydrogen is contaminated with oxygen (in some situations, oxygen has a poisonous effect). In the case with the lanthanum-nickel alloys, the effect of oxygen lies in the formation of compounds with lanthanum: La_2O_3 or various hydrates or hydroxides. Some oxygen compounds with nickel atoms are also formed. At the room temperature, this process is quite slow. H_2O has a similar effect. In this case, the H_2O molecule dissociates on the surface, thus resulting in the surface efficient oxidizing (hydrolysis). The rate of the oxidation reaction can be slightly slowed down by the presence of a certain amount of physisorbed H_2O molecules on the surface. The reaction usually causes the formation of very stable chemical compounds that are hydrogenated irreversibly and cannot be easily regenerated to the original state.

And the fourth group are the impurities chemically inert to the alloys, which do not form chemical compounds with the alloy material and do not transform the surface, but slow down the kinetics of sorption due to the formation of an inert layer of the impurity components on the surface. This effect is caused by CH_4 , C_2H_4 or N_2 .

It should be noted that the nature of the impurities influence can change significantly with temperature, time and, possibly, concentration.

THE SURFACE ROLE IN HYDRIDE FORMATION PROCESSES

As a result of the researchers' serious efforts, a large number of hydride-forming alloys for the application in various fields have been synthesized. At the same time, for a long period, the properties of such alloys had been optimized mainly by changing their component composition or the method of their preparation. A large number of publications have been devoted to these problems over the past ten to twenty years. Much less attention was paid to the study of the role of the materials surface in the processes of their interaction with hydrogen, as well as the role of gaseous impurities in hydrogen during interaction with the surface. Such processes can play a decisive role in the processes of hydride formation. Therefore, the progress of the practical development of metal hydride technologies requires careful research at the monolayer level of both the actual elementary processes of hydrogen interaction with the

surface of materials that form hydrides, and the influence of gas impurities. Such studies will allow solving a number of problems related to the dynamics of sorption - desorption and surface poisoning.

It is generally accepted that the surface of a solid body contains not only the upper atomic layer, but also several upper monolayers, which differ in composition from the bulk. In the case of a pure single-crystal sample, there may be three or four such monolayers. For the polycrystalline metals or multiphase alloys, the surface or surface layer can be as thick as 10 nm. The formation of the surface layer of chemical compounds is caused by interaction with the gas phase. The composition of such compounds, in addition to the bulk impurities, includes the elements: C, O, H, and N. This surface layer is formed naturally on an initially clean and reactive metal surface. In some cases, it completely passivates the metal surface. The passivation is quite desirable in some respects, for example for corrosion protection, but plays a negative role in cases, where the surface must remain reactive, for example for catalysts, getters or hydride-forming metals and alloys. The surface properties are especially important in the absorption of hydrogen by intermetallic hydride-forming compounds, since the first stage of absorption is physical adsorption followed by dissociation (atomization) of the adsorbed hydrogen molecules on the transition metal atoms.

Among the intermetallic compounds of the system, such as AB, AB₂, AB₅ and A₂B (where A is a metal forming a stable hydride, B is, mainly, a transition metal that does not interact with hydrogen under normal conditions) have gained interest as potential materials for technological applications. So, AB₅ alloys, based on lanthanum, attract considerable attention due to their ability to store large amount of hydrogen, ease of activation, and ability to react quickly and reversibly at ambient temperature and moderate pressures [19]. The alloys such as TiFe and Mg₂Ni, have been recognized as H₂ carriers for vehicles, mainly due to their convenient pressure-composition-temperature (PCT) relations, high H₂ content, favorable kinetics, and lower cost as compared to some other suitable alloys. However, a serious problem for all these materials in technological applications is their poor resistance to poisoning by gaseous impurities such as O₂, H₂O vapor, CO, CO₂, etc., which are present in the supplied H₂ gas and in atmospheric sources [18]. As a result, the alloys frequently require activation procedures before they accept hydrogen. Applicability of intermetallics for storage, transportation, purification of hydrogen, its separation from gas mixtures, etc. depends mainly on their cyclic stability, H-capacity, absorption and desorption kinetics.

While the cyclic stability and hydrogen capacity are determined by the volumetric properties of intermetallic compounds, namely: parameters of the crystal lattice, electronic band structure, the kinetics of sorption-desorption largely depends on the properties of the surface. Despite numerous studies of bulk characteristics, the nature and properties of the surface of these materials have so far attracted little attention, although the activated intermetallics, which disperse during hydrogenation, are a fine powder, and therefore their surface is an important factor in the hydrogenation process [20, 21].

The studies of surface properties in relation to the kinetics of sorption-desorption processes, as well as in relation to the activation, deactivation and reactivation of materials, are absolutely necessary, especially given the urgency of developing activation procedures, as well as to improve the properties of metal hydride systems in terms of hydrogenation using commercial H₂ sources, for example, hydrogen from steam reforming of hydrocarbons, etc.

The knowledge of the chemical composition of the surface outer monolayers is quite important when studying the kinetics of hydrogen sorption-desorption processes, since the surface of any metal material, subject to the experimental conditions, is always covered with a greater or lesser amount of chemical compounds, what is due to the interaction with the gas phase [22]. Such compounds largely determine the parameters of further interaction with the gas phase. A clean surface can be obtained only due to some special measures, which are often difficult to implement.

Although there are many studies in the literature on the interaction of hydrogen with metals, not all the publications consider the influence of the material surface on the characteristics of the hydrogen sorption-desorption process. There are few experimental studies (e.g. [23, 24]) of the influence of the surface coatings chemical composition on the processes kinetics. The nature of such studies is fragmentary, as they do not provide an opportunity to form a general idea of the patterns of such influence. One of the reasons for this is that the detection of hydrogen using the most common analytical methods of surface investigation is very problematic. The electronic spectral methods (such as AES and XPS) cannot always detect hydrogen and its compounds. One of the unique features of the mass spectrometric methods SIMS (secondary ion mass spectrometry) and SNMS (secondary neutral mass spectrometry) is the ability to detect hydrogen.

Thus, the study of the composition of chemical compounds on the surface is of great importance. The studies of this kind are very important for understanding the initial stages of the processes that develop on the surface, such as the initial accumulation of hydrogen, poisoning of the reaction due to the presence of impurities in the gas phase, activation or passivation of hydrogenation, etc. [25]. Such studies attract considerable attention of scientists engaged in various disciplines from both fundamental and applied viewpoint.

APPLICATION OF SECONDARY ION MASS SPECTROMETRY (SIMS) METHOD FOR STUDYING THE SURFACE OF SOLIDS AND THEIR OUTER ATOMIC LAYERS

The SIMS method is based on the analysis of the characteristics of the ionic component of the products of solids sputtering with a beam of accelerated primary ions (or atoms). When interacting with the surface of a solid, the primary ion can undergo elastic or inelastic scattering, be recharged, adsorbed, or penetrate deep into the solid. In the latter case, as a result of the repeated collisions with atoms of a solid (cascade of collisions), the ion losses energy, is

neutralized and can either be implanted into the lattice or fly-off into vacuum as a result of scattering. At the same time, a part of the atoms located on the surface and near the surface receive the energy exceeding that of the interatomic bond in the lattice, and when moving towards the surface, this part of the atoms can leave the surface, thus resulting in the “cathode sputtering” (emission of neutral atoms) and in the secondary ion emission (emission of secondary positive and negative ions) [22, 26-29].

Among the distinguishing features of the SIMS method are: the possibility of analyzing any solid substances without any special preparation (metals and alloys, semiconductors, dielectrics); possibility of detection of all the elements from hydrogen to transuranic elements; high sensitivity of the analysis corresponding to the trace atoms concentration: $\sim 10^{-4}$ - 10^{-7} % (or corresponding to the substance consumption: $\sim 10^{-6}$ of a monolayer); the possibility of performing depth profiling analysis of materials with high depth resolution: ~ 30 - 100 Å; the possibility of identifying not only individual elements and isotopes, but also their chemical compounds.

When conducting the surface analysis, SIMS method is mainly used for the identification of surface atoms and molecules, as well as for studying the dynamics of the surface phenomena, various physical and chemical processes at the interface between a solid and a gas. Such surface phenomena as catalysis, corrosion, adsorption, and diffusion are investigated by the SIMS method.

The information about the elemental and isotopic composition, about the composition of chemical compounds on the surface is usually provided by the mass spectra of sputtered positive and negative secondary ions. The information about the physical and chemical processes on the surface of solids under different experimental conditions can be obtained by analyzing the dependences of the emission intensity of characteristic secondary ions on the temperature of the sample, the partial pressure of the gas in the target chamber, the current density of primary ions, and kinetic dependences.

Along with high sensitivity, the SIMS method has a unique ability not only to detect hydrogen, but also to determine the presence of hydrogen chemical compounds on the surface and in the near-surface layer, as well as to detect changes in the composition of such compounds, subject to the experimental conditions. This makes the method quite an effective tool for studying the characteristics of hydrogen sorption-desorption processes by materials used in metal hydride technologies [30].

The following content of this article is an overview of the works studying the metal hydrides surface by the SIMS method.

SIMS INVESTIGATION OF THE LaNi_5 ALLOY SURFACE AND A NUMBER OF LANTHANUM-BASED ALLOYS DURING THEIR INTERACTION WITH HYDROGEN

In 1970, when studying the intermetallic compounds AB_5 (where A is a rare earth metal, B is nickel or cobalt), it was found that the intermetallic LaNi_5 is capable to absorb and release a large amount of hydrogen at temperatures close to the room one and at relatively low pressures [19]. Thus, as a result of hydrogen sorption at the room temperature and the pressure of 0.2-0.5 MPa, the $\text{LaNi}_5\text{H}_{6,7}$ hydride was formed, in this case the volume of the crystal lattice unit cell increased by 25% with maintaining hexagonal symmetry. The hydrogen content in the hydride was 1.4 wt. %: If calculated per unit volume, this is one and a half times greater than the amount of hydrogen contained in liquid hydrogen.

The subsequent studies of AB_5 intermetallic compounds determined their main properties and parameters. The hydrides of AB_5H_x composition, where x, subject to the nature of A and B, varies from 3 to 8, are characterized by moderate dissociation pressures (from 0.01 to 1 MPa) at the room temperature and low enthalpy of hydrogen absorption ($30 - 40 \text{ kJ}\cdot\text{mol}^{-1}$). In practice, of greatest interest is the intermetallic LaNi_5 hydride, whose absorption capacity and kinetics of hydrogen absorption can be considered as a comparison standard for the preparation of other materials for hydrogen batteries operating at low temperatures. LaNi_5 alloy is a vivid example of hydride-forming materials used in metal hydride technologies. Due to high hydrogen capacity, high cyclic stability and ease of activation, the materials based on it occupy one of the central places in metal hydride energy technologies.

Fig. 1 shows the pressure-composition-temperature diagram for the LaNi_5/H system. The results of numerous studies on LaNi_5 are presented in a vast number of original works and reviews [1-3, 31, 32]. In general, according to the published data, the hydrogen sorption characteristics of the LaNi_5 alloy can be characterized as follows. The intermetallic has a hexagonal structure of the CaCu_5 type. The equilibrium saturation of LaNi_5 with hydrogen is achieved in ~ 10 minutes, and most of the hydrogen (up to 90%) is absorbed or desorbed in the first few minutes. The absorption rate depends weakly on the temperature and pressure, what indicates a low activation energy of this process. The desorption of hydrogen occurs with some hysteresis, that is, the pressure of hydrogen required for the formation of a hydride is greater than that at which the hydride decomposes (pressure hysteresis). The value of hysteresis decreases as the number of cycles of the absorption - desorption process increases.

The absorption capacity of the intermetallic LaNi_5 increases markedly with a decrease in temperature with an almost unchanged absorption rate. The LaNi_5 hydride formation enthalpy is $15.7 \text{ kJ mol}^{-1}\text{H}$, decomposition enthalpy is $15.1 \text{ kJ mol}^{-1}\text{H}$ [33].

As it was noted earlier, there is a large number of works studying hydrogen absorption in metals and alloys, especially in hydride-forming materials. At the same time, the number of works devoted to the influence of the surface itself on the initial stages of hydride formation is quite limited.

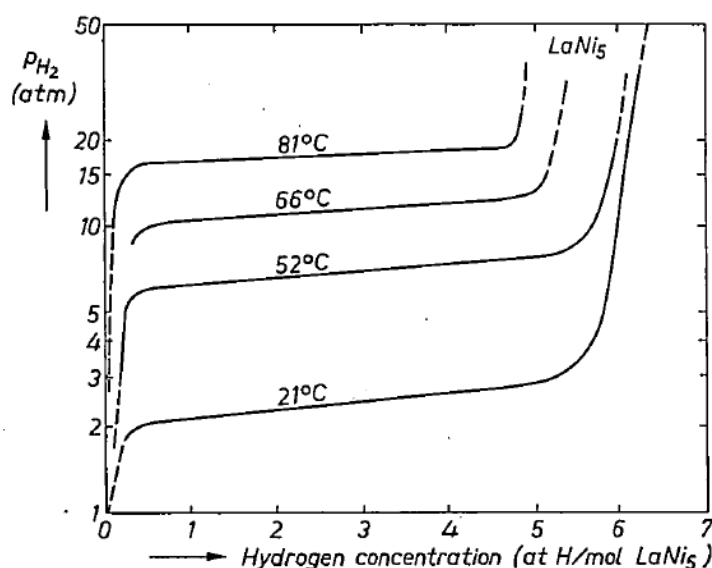


Figure 1. Pressure-composition isotherms for the LaNi₅/H system [19]

Among the works devoted to the study of the surface of hydrogen-storing alloys by the SIMS method, we should mention the works [34, 35], which present the results of studying the hydrogen-containing samples of the LaNi₅ alloy. In [36] the characteristics of chemical bonds in hydrogen (deuterium)-saturated LaNi₅ alloys, as well as in the alloy, in which nickel is partially replaced by Al or Ag, were investigated by SIMS and X-ray photoelectron spectroscopy. In addition to AB₅ hydrogen storage alloys based on La, the alloys based on Nd and Sm were also studied with SIMS. In [37], the characteristics of the components of Nd₂Co₁₄B and Nd₂Fe₁₄B alloys interaction with hydrogen and their function during hydrogenation were studied with SIMS. The information about the metal-hydrogen bonds in the SmCo₅D_n system was presented in [38].

Below are presented the results of studying with SIMS the initial stages of the interaction of hydrogen with the surface of the hydrogen-storing alloy LaNi₅, as well as a number of lanthanum-based alloys when interacting with hydrogen [39-41].

The measurements were carried out in the following way. The monolithic samples, or tablets, compressed from finely dispersed alloy material, were bombarded with a beam of Ar⁺ ions with the energy of 8 keV when analyzing the positive secondary ions, and 16 keV when analyzing the negative secondary ions. The residual vacuum in the target chamber was ~ 4 · 10⁻⁶ Pa, the current density of the primary beam was 1.2-12.0 μA cm⁻², what corresponded to the SIMS dynamic mode. The SIMS instrument was equipped with an energy filter, which allowed measuring the emission intensities of only low-energy (in a narrow range of energies) secondary ions, which largely characterize the presence and composition of chemical compounds on the surface under study [42]. The intensities of secondary ion emissions were measured in the dynamic range of at least 6 orders of magnitude. Before the measurements, the samples were annealed in the residual vacuum at the temperature of 750-1000 K in order to partially clean the surface from the chemical compounds that are either desorbed or dissolved in the volume of the material during the annealing process. After annealing, the surface was cleaned with a beam of primary ions until the composition of the mass spectra and intensity of secondary ion emissions were completely stabilized. The composition of the gas phase was monitored using a gas mass spectrometer. With the help of the same mass spectrometer, after the necessary calibrations, small partial pressures of gases in the vacuum chamber were measured. The studied alloy samples were the tablets pressed from finely dispersed material.

In the case, when the emissions of polyatomic secondary ions, which characterize the composition of chemical compounds on the surface, overlap in a complex manner by mass, their specific contributions were divided according to the usual procedure, utilizing the known natural distribution of isotopes.

Generally, the data of the SIMS experiments were analyzed to determine the functions of various components of the alloy in relation to its interaction with hydrogen, that is, adsorption on the surface and its subsequent binding in the alloy.

The mass spectra analysis of positive and negative secondary ions sputtered from the surface of the investigated LaNi₅ samples, measured before and during the annealing process, showed the presence of a vast number of various emissions related to the alloy material and its impurities, as well as the objects introduced from the gas phase. During the samples annealing, in addition to the emissions of positive and negative secondary ions, the emission of positive thermoions was observed (in the absence of the primary beam bombardment). Namely, emission of positive thermoions of alkali metals Na⁺, K⁺, Rb⁺, Cs⁺, which, in principle, are typical for metals and alloys of technical purity, as well as emission of thermoions La⁺, LaO⁺ were observed. The emission of such La-containing thermal ions is explained by the decomposition and desorption of oxides, which are on the surface from the very beginning and which, as a rule, must be removed to achieve high reactivity of the surface. The oxides removal is essentially the purpose of the samples activation.

As an example, Fig. 2 shows the dependence of the emission intensity of thermoions La^+ , LaO^+ on the sample temperature. Fig. 3 shows the time dependence of the emission intensity of the same thermoions at the temperature of 880 K. It is obvious that in a few minutes the intensity of the oxygen-containing lanthanum ions emission, and therefore the amount of oxygen-containing compounds of lanthanum on the surface, decreases several times.

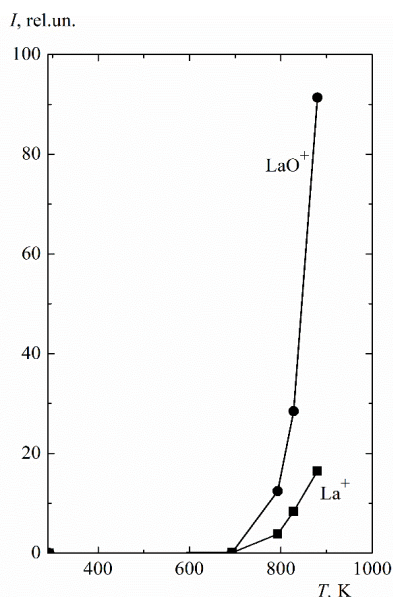


Figure 2. Temperature dependence of the emission intensity of thermoions La^+ , LaO^+ from the surface of the LaNi_5 sample

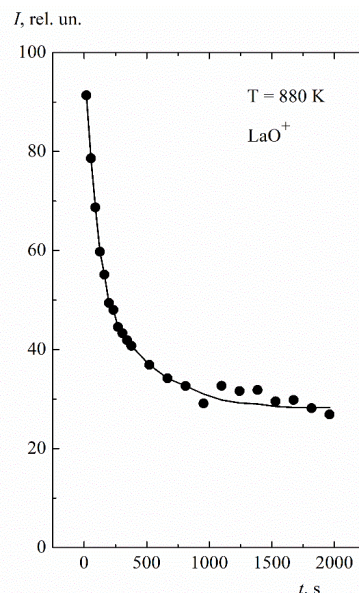
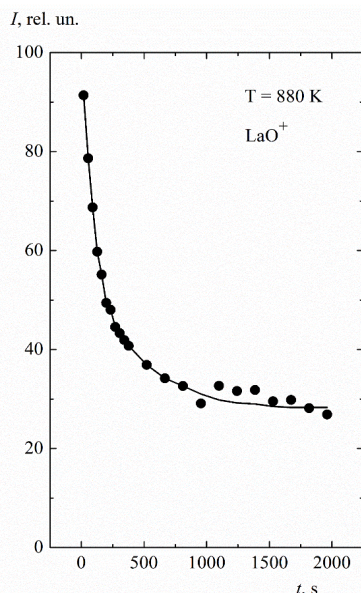


Figure 3. Time dependence of the emission intensity of La^+ , LaO^+ thermionic ions from the surface of the LaNi_5 sample at the temperature of 880 K

The mass spectra measured after annealing and cleaning of the surface with the primary beam are much cleaner. Figs. 4, 5 are the examples of such a spectra. The spectra of positive secondary ions contain emissions of atomic and cluster ions of lanthanum and nickel, intermetallic ions of lanthanum and nickel, the emissions, which are attributed to the compounds of these ions with hydrogen, oxygen, and carbon (what is typical for metals and alloys). Moreover, the emissions related to lanthanum predominate, and the most intense emission is the emission of lanthanum oxide ions, whereas the nickel oxide emission is almost absent. The spectra of negative secondary ions, in contrast to the positive ones, contain for the most part, nickel-related emissions, including nickel oxides.

This composition of mass spectra indicates that even after annealing and cleaning with the primary beam, the surface of the studied samples is, to a certain extent, covered with chemical compounds, which include hydrides, oxides, hydroxides, and carbides. In this case, judging by the presence in the emission spectra of cluster ions, such as Ni_4^+ or LaNi_2^+ , this coating is not continuous, that is, the surface of the samples has areas free of chemical compounds.

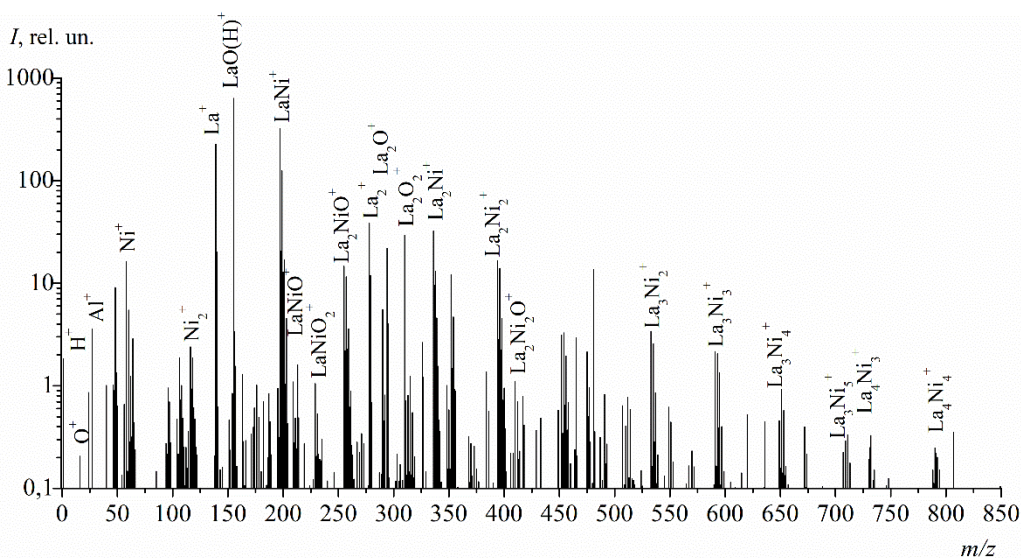


Figure 4. Section of the mass spectrum of positive secondary ions, sputtered from the surface of the LaNi_5 alloy sample at the room temperature, in a residual vacuum and with a primary ion current density of $j=4.5 \mu\text{A}\cdot\text{cm}^{-2}$

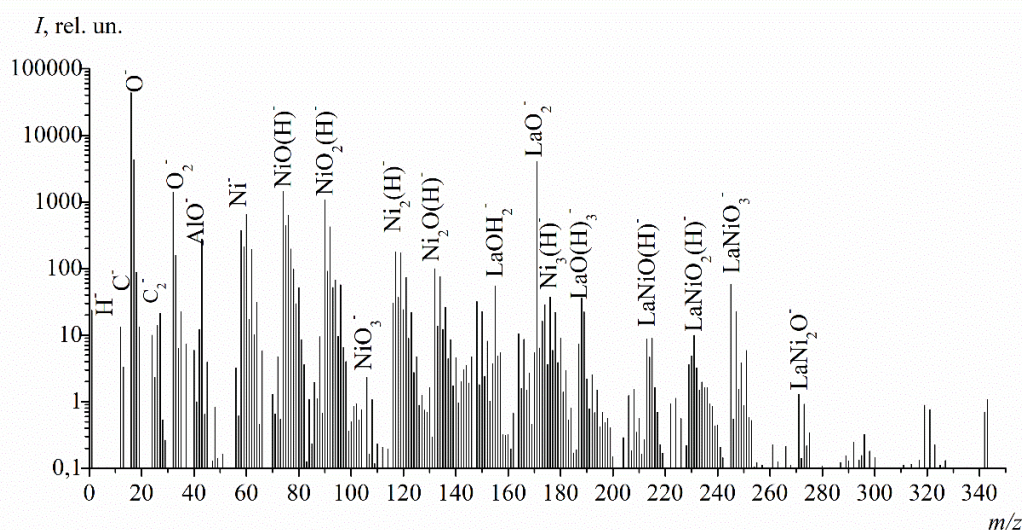


Figure 5. Section of the mass spectrum of negative secondary ions, sputtered from the surface of the LaNi₅ alloy sample at the room temperature, in a residual vacuum and with a primary ion current density of $j=4.5 \mu\text{A} \cdot \text{cm}^{-2}$

It is known that the equilibrium pressure of the processes of hydride formation (and hydride decomposition) at the temperatures $>300\text{K}$ for the LaNi₅ alloy is much higher (close to atmospheric) than that in the vacuum chamber during SIMS experiments. The hydrogen-saturated samples placed in the chamber are degassed as a result of vacuum pumping, here not only the β -phase, in which the hydrogen in the alloy is in the form of a hydride, decomposes, but also little remains of the α -phase, i.e. of the solid solution of hydrogen in the lattice, especially since the samples are annealed before the measurements. Under the indicated conditions of the experiment, the hydrogen molecules colliding with the surface, as in the case with a number of other metals and alloys, interact only with the surface atoms and, in the best case, hydrogen saturates only the near-surface region, without diffusing in a noticeable amount into the volume. Such a situation does not allow carrying out the SIMS study of the LaNi₅ samples surface whose volume concentrations of hydrogen are substantial.

In order to verify the assumption that, under the specified experimental conditions, the hydrogen, upon reaching the surface, interacts only with the surface and near-surface metal atoms, without diffusing in significant quantities into the volume, the following experiment was conducted. The surface of the LaNi₅ sample was cleaned with the primary beam with the density of $6 \mu\text{A} \text{cm}^{-2}$ in a residual vacuum, then the primary beam was turned off and hydrogen was supplied into the chamber settling within few seconds to a partial pressure of $\sim 3.5 \cdot 10^{-3} \text{ Pa}$. At this pressure, the sample was exposed for a certain period, then the hydrogen was pumped out (the major mass of hydrogen was pumped out in a few seconds), the primary beam was turned on (with the current density of $0.3 \mu\text{A} \text{cm}^{-2}$), and the dependence of the emission intensity of the secondary ions Ni₂H⁻ (Ni₂H⁻ are characteristic of the hydrogen compounds), on the time of sputtering was measured. That is the depth profiling analysis was carried out. However, the exact calculation of the number of sputtered monolayers is not possible, since the sputtering coefficient of the material under study is unknown, so only an estimate of the number of sputtered monolayers was calculated for the sputtering coefficient equal to 4 (bombardment of the sample at the angle of 60° to the normal). The measurements were made for several hydrogen exposure duration values. The results of the measurements are shown in Fig. 6.

The analysis shows that about 12 monolayers are sputtered in $\sim 300 \text{ s}$, while the emission intensity of Ni₂H⁻ ions decreases several times, which indicates to a decrease in the amount of hydrogen-containing chemical compounds. This fully agrees with the assumption that the processes of interaction with hydrogen for this sample are limited only to the near-surface region at the given experimental conditions. At the same time, of course, one should not forget about the effects introduced by the primary beam, namely, the implantation of recoil atoms (hydrogen atoms located on the surface) and ion mixing. As a result of such influence, the hydrogen can be detected even at the depth of several tens of monolayers, but such hydrogen is not an object that characterizes the actual processes of interaction with the alloy surface.

Thus, under the specified experimental conditions, it is indeed possible to study only the initial stages of hydrogen accumulation (hydrogenation), namely, the interaction of hydrogen with the surface of the specified alloys, without taking into account its diffusion into the volume, as one of the channels for changing the surface composition. In this case, of course, the influence of the primary beam must be taken into account. Taking this in mind, the studies of changes in the quantitative and qualitative composition of the mass spectra of secondary ions, sputtered from the surface of the samples, subject to the partial pressure of hydrogen in the sample chamber, were conducted. Figs. 7,8 show the examples of such dependences for hydrogen-related emissions of positive and negative secondary ions, sputtered from the surface of the LaNi₅ sample. Fig. 9 also shows the dependence for the hydrogen-containing complex lanthanum nickel ions.

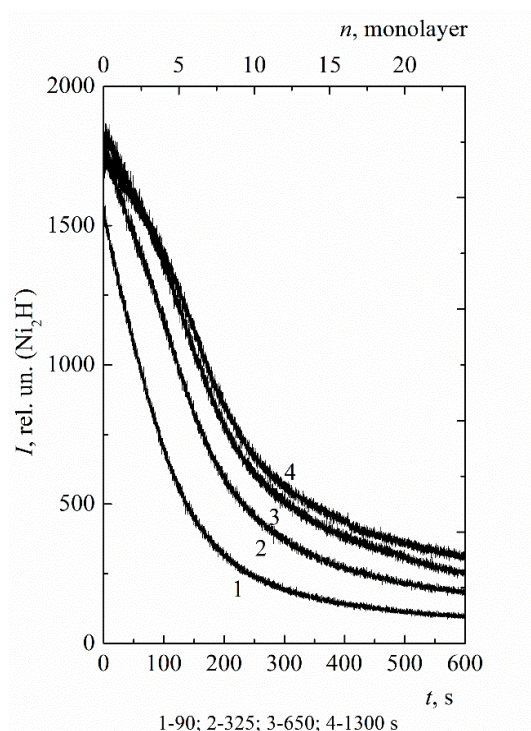


Figure 6. Time dependence of the emission intensity of negative secondary Ni_2H^- ions, sputtered from the surface of LaNi_5 at the room temperature, for different exposure doses at a hydrogen partial pressure of $3.5 \cdot 10^{-3}$ Pa

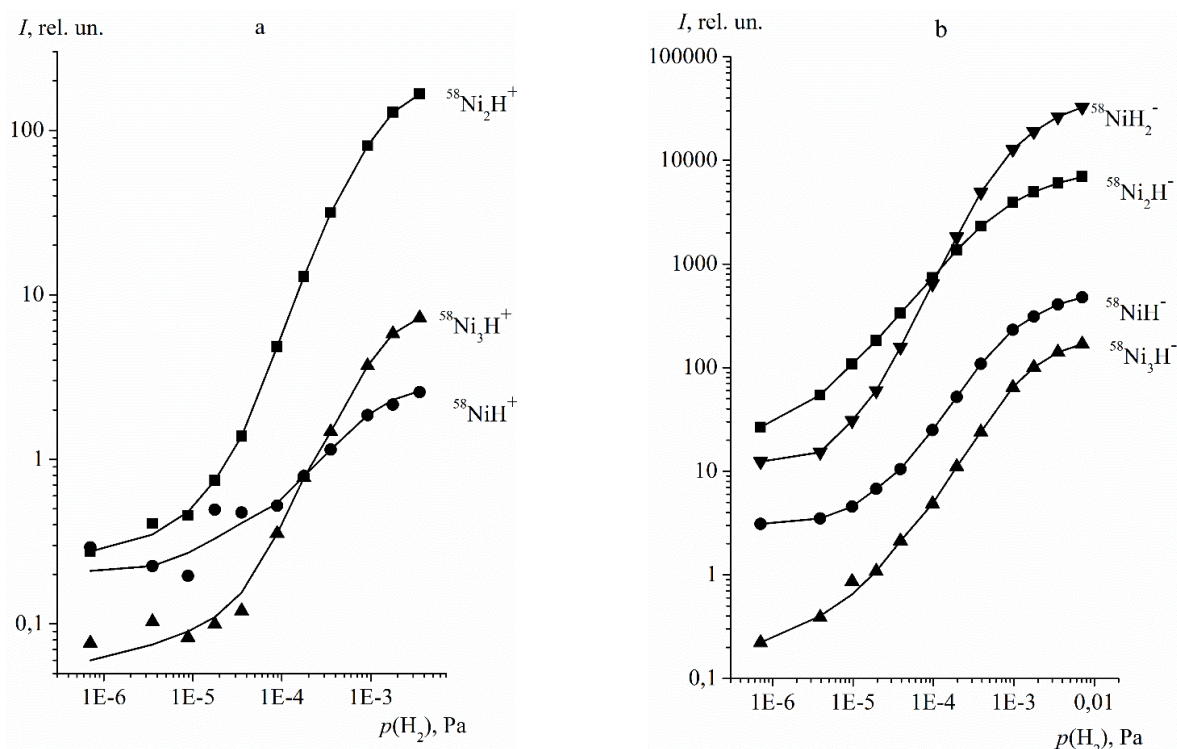


Figure 7. Dependence of the emission intensity of positive (a) and negative (b) hydrogen-containing secondary ions with nickel, sputtered from the surface of LaNi_5 at the room temperature, on the partial pressure of hydrogen.

As the analysis shows, when the partial pressure of hydrogen increases from residual $\sim 7 \cdot 10^{-7}$ to $\sim 3 \cdot 7 \cdot 10^{-3}$ Pa, the intensity of both positive and negative hydrogen-containing secondary ions, which are observed, increases by two orders of magnitude. In the spectrum of positive ions, the hydrogen-containing ions with lanthanum are the most intensive, in the spectrum of negative ions the most intensive are those with nickel (what is explained by the different electron affinity energy of 0.5 eV for lanthanum and 1.15 eV for nickel).

The presence of the emissions of hydrogen-containing ions with lanthanum and with nickel and complex lanthanum-nickel ions (LaNi^- , LaNi_2H^-), as well as the increase in the intensity of such emissions, indicates that

hydrogen, impacting the surface, forms chemical bonds with both components of the alloy. The increase in the intensity of these emissions with the increase in the flow of hydrogen on the surface indicates an increase in the number of hydrogen-containing chemical compounds, which include nickel and lanthanum, on the surface.

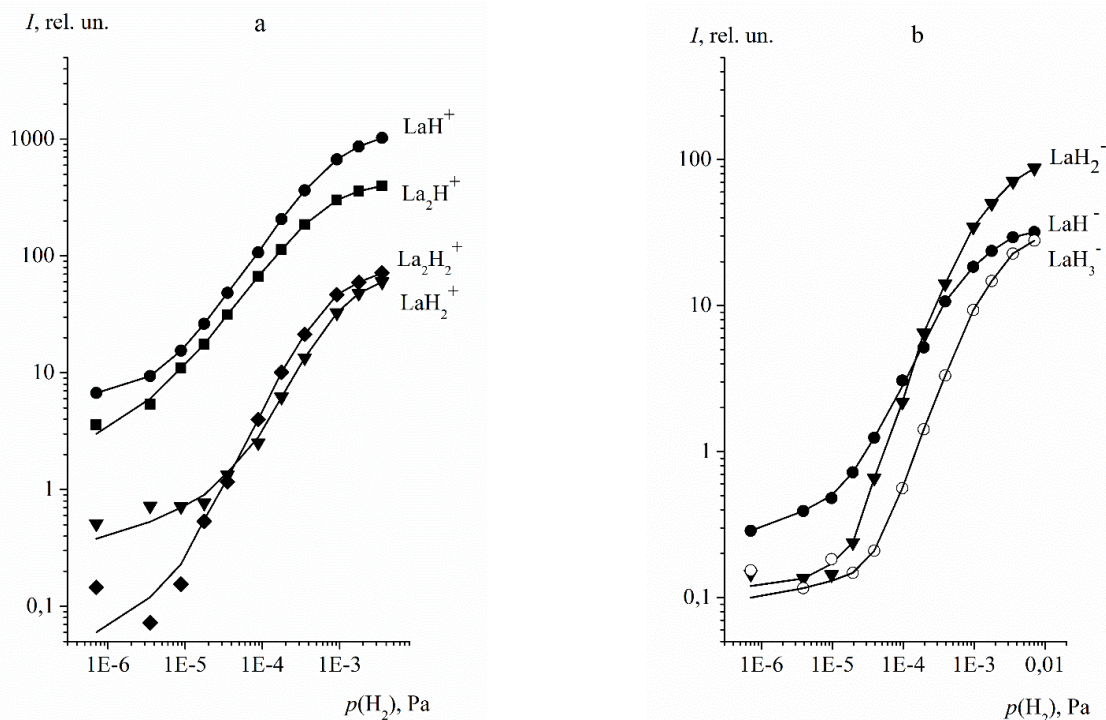


Figure 8. Dependence of the emission intensity of positive (a) and negative (b) hydrogen-containing secondary ions with lanthanum, sputtered from the surface of LaNi_5 at the room temperature, on the partial pressure of hydrogen

Regarding the kind of compounds which are formed on the surface, the following can be said. The emission of some ions stands out slightly from the general picture of the growth of the hydrogen-containing ions intensity. The emission intensity of NiH_2^- ions increases more rapidly with the increase of the hydrogen partial pressure, than that for the other hydrogen-containing secondary ions, and increases by more than three orders of magnitude. For the maximum pressure values, the emission of NiH_2^- ions becomes predominant. It is logical to assume that at the partial pressures higher than $\sim 10^{-5}$ Pa, a hydrogen-containing structure begins to form actively on the surface, the characteristic fragment of which is the NiH_2^- ion. As long as nickel is divalent in most chemical compounds, it is also logical to assume that as the partial pressure of hydrogen increases, nickel hydride NiH_2 is formed on the surface and in the near-surface region, and NiH_2^- ions are the fragments of this compound. A similar picture occurs with the emission of LaH_2^- and LaH_3^- ions. The emission intensity of these ions also increases at a faster rate, and it also increases by more than two orders of magnitude (for LaH_2^- – by three orders of magnitude). It can be assumed that lanthanum hydride LaH_2 and LaH_3 are formed on the surface along with nickel hydride NiH_2 , and the ions LaH_2^- , LaH_3^- , LaH_2^+ and La_2H_2^+ are characteristic fragments of these chemical compounds.

The tendency of the curves in Figs. 7-9 to reach the plateau is, apparently, due to the fact that at hydrogen partial pressures greater than $\sim 7 \cdot 10^{-3}$ Pa (at the room temperature) on the surface and in the near-surface region a hydride structure is completely formed, whose composition does not undergo qualitative or quantitative changes at further hydrogen pressure increase.

The dependences of the emission intensity of the oxygen-containing secondary ions on the partial pressure of hydrogen were also measured. The examples of such dependencies are shown in Fig. 10.

As Fig. 10 shows, an increase in the partial pressure of hydrogen leads to an increase in the intensity of the emission of hydroxide ions (both lanthanum and nickel) and practically does not affect the emission of oxide ions. The lack of influence of oxide ions on the emission can be explained by the fact that the oxide structure (which includes both lanthanum and nickel atoms), from which the oxygen-containing ions are sputtered, does not undergo significant changes, neither quantitative nor qualitative, as the hydrogen pressure increases. Earlier, a number of arguments were proposed in favor of a certain picture of hydride formation; however, such a picture makes sense only for a relatively clean surface. It is difficult to assume that the same processes of hydride formation take place on the surface covered with oxides; at least, the obtained experimental data do not support such an interpretation. A logical explanation of such a situation can be the assumption that the surface is only partially covered with oxides; along with islands of oxides, there is also a clean surface, on which the interaction with hydrogen actually takes place. The oxides on the surface have an island structure, whose size is hardly affected by hydrogen. The effect of hydrogen on oxides lies only in the formation of a certain amount of hydroxides.

The analysis of the results shows that a group of ions, containing more than one hydrogen atom, stands out from an overall large number of hydrogen-containing secondary ions that are sputtered. For NiH_2^- , La_2H_2^+ , LaH_2^+ , LaH_2^- , LaH_3^- , LaNiH_2^- , LaNiH_3^- , the dependence of the emission intensity on the partial pressure of hydrogen within the pressure range from $\sim 10^{-5}$ to $\sim 10^{-3}$ Pa allows for approximation by a power function with the exponent greater than one. For the other numerous group of hydrogen-containing ions, such as La_2H^+ , LaH^+ , Ni_nH^- ($n = 1, 2, 3, 4$), as well as complex ions LaNiH^+ , LaNi_2H^+ such an approximation is also possible, however, in all the cases with different exponents that are smaller than one.

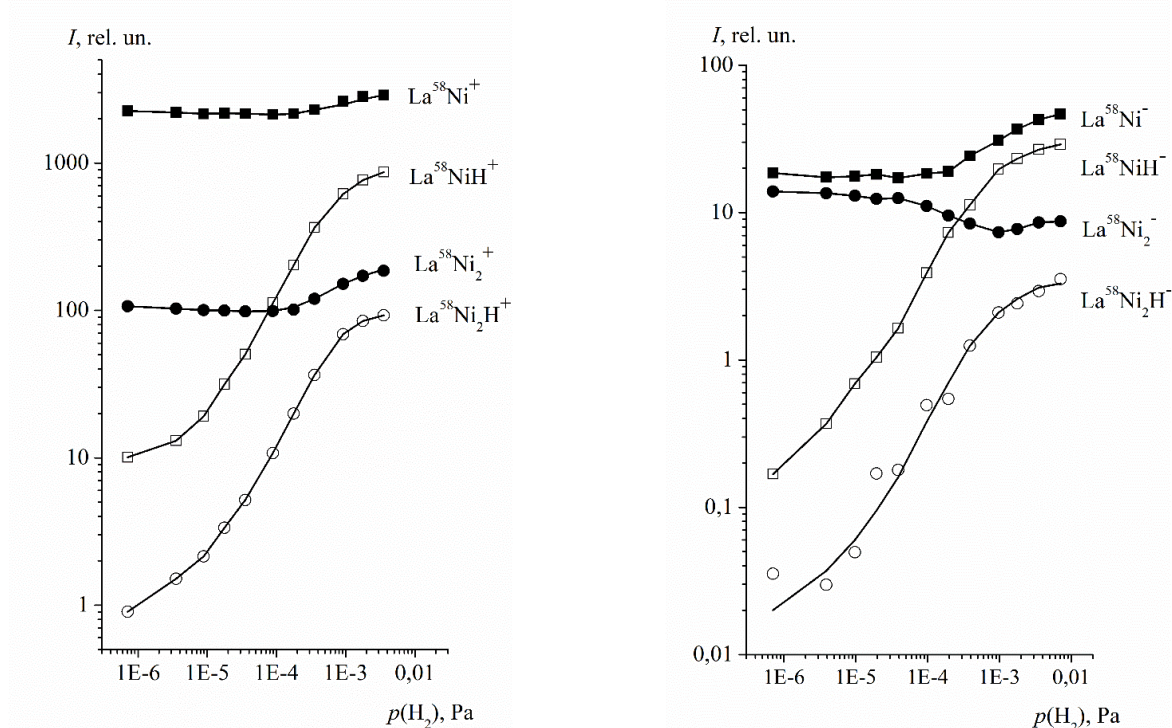


Figure 9. Dependence of the emission intensity of hydrogen-containing complex secondary ions (with lanthanum and nickel), sputtered from the surface of LaNi_5 , on the partial pressure of hydrogen, at the room temperature

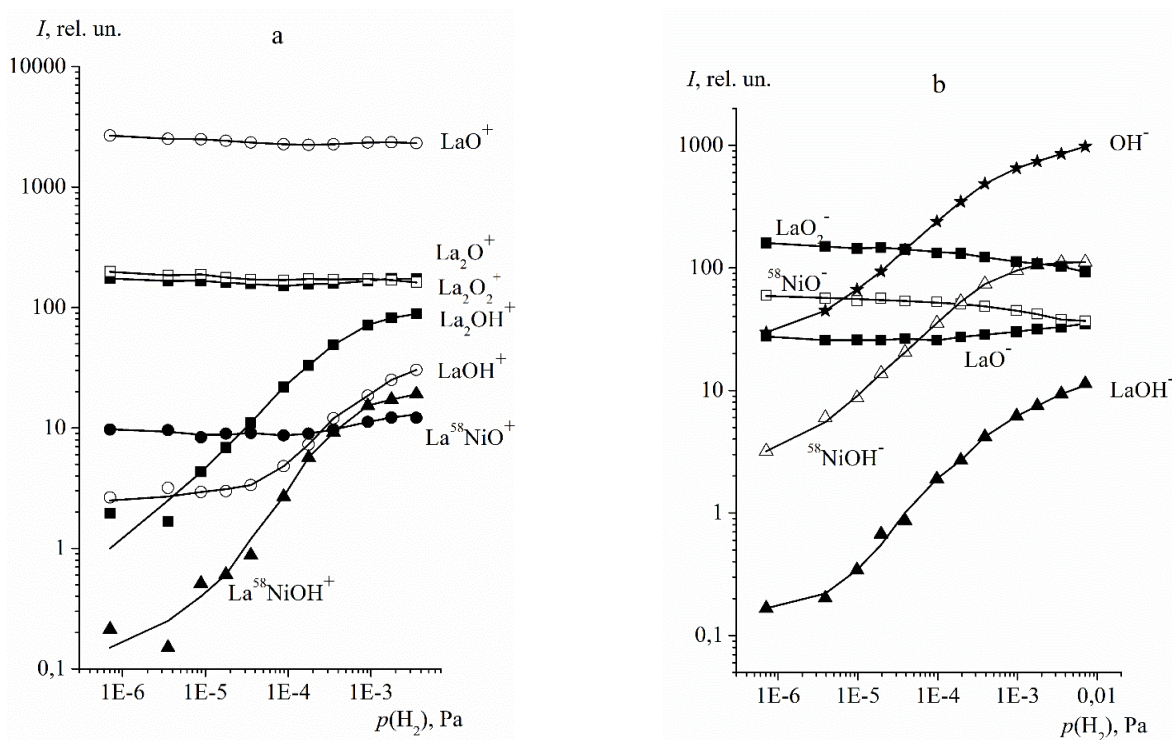


Figure 10. Dependence of the emission intensity of oxygen-containing positive (a) and negative (b) secondary ions, sputtered from the surface of LaNi_5 at the room temperature, on the partial pressure of hydrogen

The presence of the group of secondary ions containing more than one hydrogen atom and differing in the value of the exponent of the degree of the power function, which approximates the dependence of the emission intensity on the partial pressure of hydrogen, gives reason to assume the following. As hydrogen accumulates on the surface and in the near-surface region of the samples, a parent hydrogen-containing structure, whose characteristic fragments are secondary ions containing more than one hydrogen atom, is formed. This compound is characterized by the fact that nickel, which is divalent in most chemical compounds, has strong bonds with two hydrogen atoms, and trivalent lanthanum has such bonds with more than two hydrogen atoms. The fact that the set of characteristic ions for this compound includes the complex LaNiH_2^- ion indicates that the formed hydrogen-containing structure includes the both main components of the alloy. Thus, it can be assumed that under the specified conditions of the experiment, a hydrogen-containing intermetallic compound, characterized by a certain stoichiometric ratio, is formed on the surface and in the near-surface region. Such a compound cannot be identified with the bulk hydride phase of the alloy (β -phase), which is formed in the volume of the sample at significantly higher pressures and is characterized by a number of thermodynamic and crystallographic parameters.

The emission of the secondary ions, containing less than two hydrogen atoms, is the result of the fragmentation of the hydrogen-containing surface-structures, in which the alloy components do not exhibit their valence limits. The increase in the intensity of such emissions represents only an increase in the number of such structures or, in fact, an increase in the amount of hydrogen, which formed a bond with the alloy components, in various atomic combinations.

In the processes of intermetallic alloys hydrogenation, the temperature is an equally important parameter as the hydrogen pressure, therefore, when carrying out the work, the dependence of the emission intensity of hydrogen-containing secondary ions on the samples temperature was measured. The measurements were carried out at the residual pressure and, for a greater clarity, at an increased partial pressure of hydrogen $p_{\text{H}_2}=3.54 \cdot 10^{-4}$ Pa. As it was in the case of dependences on the partial pressure of hydrogen, the temperature dependences for the secondary ions, which include the alloys main components, that is, lanthanum and nickel, are similar. As an example, Fig. 11 shows a series of such dependencies for the secondary ions sputtered from the surface of the LaNi_5 sample.

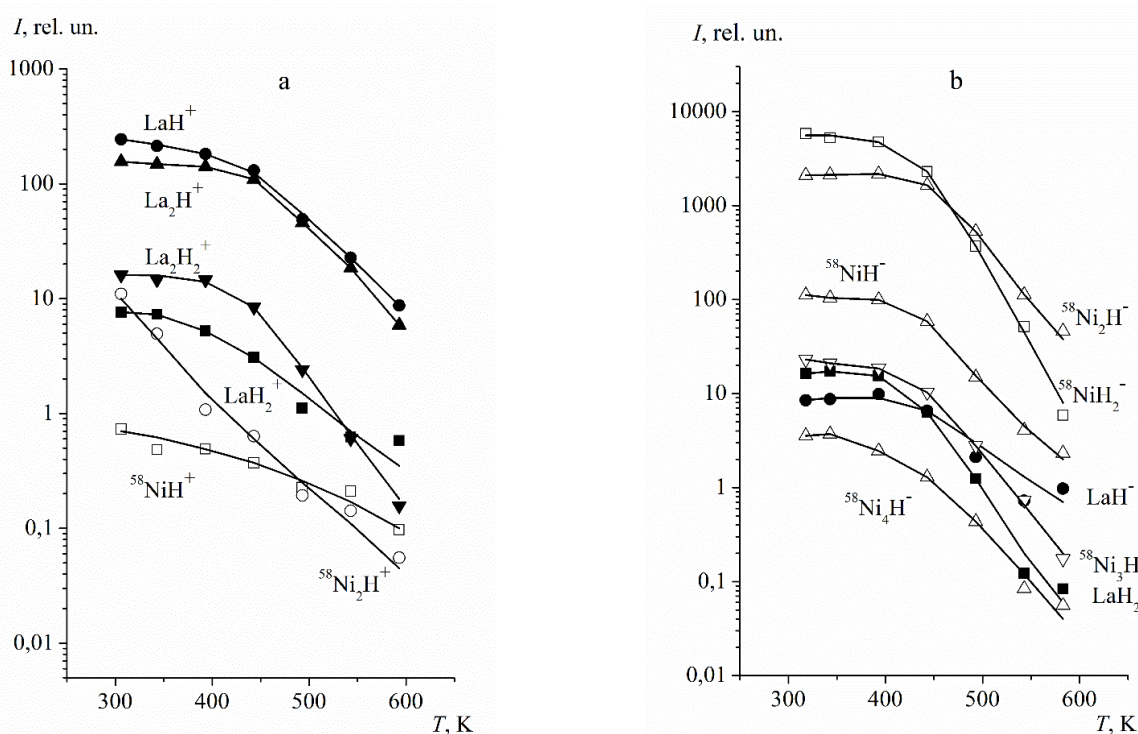


Figure 11. Dependence of the emission intensity of positive (a) and negative (b) hydrogen-containing secondary ions, sputtered from the surface of LaNi_5 , on the temperature at the hydrogen pressure increased to $p(\text{H}_2)=3.54 \cdot 10^{-4}$ Pa, and at the current density of primary ions $j=4, 5 \mu\text{A} \cdot \text{cm}^{-2}$

The main characteristic feature of the temperature dependences, measured at an increased hydrogen partial pressure, is a significant decrease in the emission intensity of almost all the positive and negative hydrogen-containing ions as the temperature increases. The emission intensity of such ions correlates with the amount of hydrogen-containing compounds on the surface; therefore, a decrease in the intensity of these emissions indicates a decrease in the amount of hydrogen-containing chemical compounds.

The steady state coverage of the surface by the adsorbed particles and the products of chemical reactions of these particles with the surface atoms of a solid is determined by the dynamic balance between several processes. These are the adsorption-desorption processes, since the steady state coverage is realized at adsorption-desorption equilibrium

between the gas phase and the surface, as well as the processes of sputtering by the primary beam and diffusion processes of adsorbed particles into the volume. The parameters of sputtering processes, in the first approximation, do not change with temperature in the studied temperature range and, therefore, sputtering affects the steady state coverage in the same way at different temperatures. The parameters of the diffusion processes, as a rule, can significantly depend on the temperature, especially for hydride-forming alloys. In order to find out the role of the diffusion processes in our experimental conditions, the following experiment was conducted.

The surface of the sample (LaNi₅) was pre-cleaned with the high-density primary beam. Then hydrogen was supplied into the chamber, settling within 1-2 seconds to a pressure of $1.8 \cdot 10^{-4}$ Pa, simultaneously, the time dependence of the emission intensity of the Ni₂H⁻ ions, which is characteristic of hydrogen-containing compounds, was measured. During this measurement the primary current density was reduced to $j=1.13 \mu\text{A cm}^{-2}$. A lower density, than that at measuring the temperature dependences, was used to reduce the sputtering effect of the primary beam. The exposure duration at the increased hydrogen pressure was 150 seconds. The results of measuring the time dependence of the characteristic ion emission intensity during the exposure are presented in Fig. 12. After the exposure for 150 c, the hydrogen was pumped out within ~ 1 s. The density of the primary beam was increased to $j=4.5 \mu\text{A cm}^{-2}$, and the time dependence of the emission intensity was measured, i.e. in the process of sputtering of the formed layer of hydrogen-containing compounds. This procedure was repeated for various sample temperatures. These data are presented in Fig. 13.

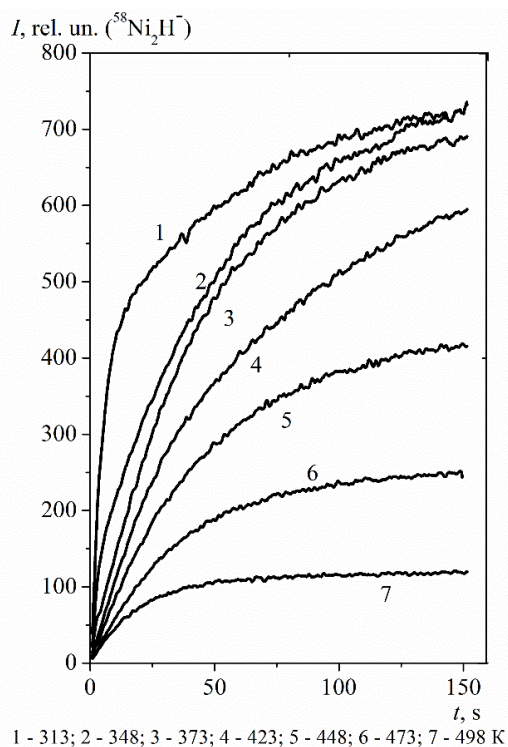


Figure 12. Time dependence of the emission intensity of secondary ions Ni₂H⁻, sputtered from the LaNi₅ surface, for different temperatures of the sample at the current density of primary ions $j=1.13 \mu\text{A cm}^{-2}$ and the partial pressure of hydrogen $p(\text{H}_2)=1.8 \cdot 10^{-4}$ Pa

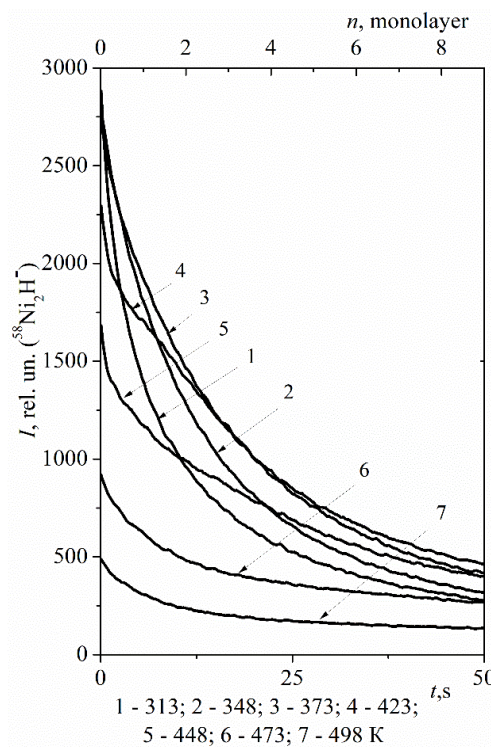


Figure 13. Dependence of the emission intensity of secondary ions Ni₂H⁻ on the time of sputtering after exposure at hydrogen partial pressure $p(\text{H}_2)=1.8 \cdot 10^{-4}$ Pa at different temperatures and primary ion current density $j=4.5 \mu\text{A cm}^{-2}$

From the data shown in Fig. 12 the following is evident. First, the emission intensity of secondary ions, characteristic of the hydrogen-containing compounds, increases with time, what is quite natural. All the curves tend to reach the plateau. Since the registered ions are sputtered from the upper monolayers, the increase of their emission intensity indicates an increase in the amount of hydrogen-containing compounds on the surface, the fragment of which is Ni₂H⁻ ion. Secondly, the emission intensity of the characteristic ions decreases with an increase of the temperature, at which the exposure was realized. Such a decrease, by the same logic, can be explained by the fact that at a fixed partial pressure of hydrogen, an increase in the temperature of the sample leads to the formation of a smaller number of hydrogen-containing compounds on the surface. In this case, the dynamic equilibrium between the processes of adsorption, desorption, diffusion and sputtering is realized faster; the curves reach the plateau faster.

An approximate estimate of the number of sputtered monolayers was made as a function of time for the sputtering coefficient equal to 4. The analysis of the data (Fig. 13) allows concluding that during the exposure at the specified partial pressure in the studied temperature range, the hydrogen diffuses with the formation of chemical bonds in noticeable quantities only to the depth of ~ 10 monolayers.

In addition to the above, the following should be noted. In the process of sputtering, the amount of the hydrogen-containing compounds for different stages of sputtering changes in a complex manner. Considering that in this case the sputtering itself is the process that determines the composition of the surface compounds, that is, without taking into account the hydrogen diffusion in the process of measurements, then it can be assumed that the data, obtained in the sputtering process, actually represent the results of the depth profiling analysis. This allows tracing the dependence of the amount of hydrogen-containing compounds on the temperature, at which the exposure was realized, for different stages of sputtering. Fig. 14 presents the following data.

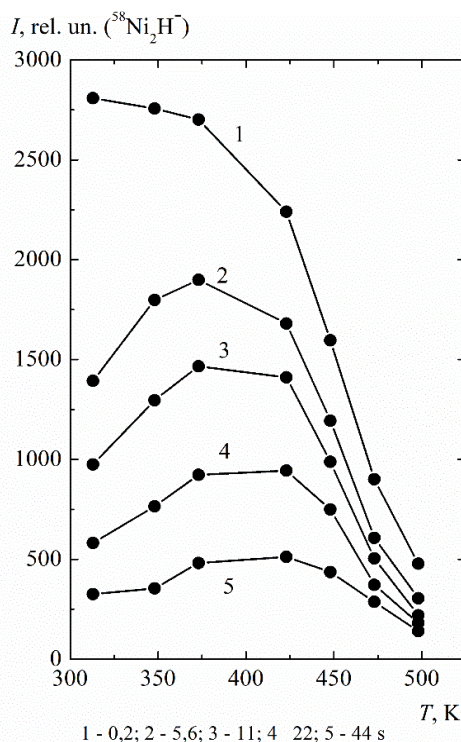


Figure 14. Dependence of the emission intensity of secondary ions Ni_2H^+ , sputtered from the surface of LaNi_5 , on the exposure temperature for different stages of sputtering

The analysis of the dependences presented in Fig. 14 shows, that in the first monolayer at the beginning of sputtering for ~ 0.2 s, the number of hydrogen-containing compounds decreases monotonically with the increase of the exposure temperature, i.e., the curve monotonically decreases. For the subsequent monolayers, there is a tendency for reaching the maximum emission intensity at the temperatures higher than the initial one. Thus, in the second monolayer (after ~ 5.6 s of sputtering) and, similarly, in the third and fourth monolayers (after ~ 11 and 17 s of sputtering), the amount of hydrogen-containing compounds increases with the increase of the exposure temperature from 313 K to 373 K. In the fifth and deeper monolayers, the number of hydrogen-containing compounds increases with the increase of the exposure temperature up to 423 K. At the higher exposure temperatures, the number of compounds decreases for all the monolayers. Thus, in the region from the fifth monolayer and deeper, the maximum emission intensity, and therefore the amount of hydrogen-containing compounds, is in the temperature range of 373 - 423 K. At the same time, a general decrease in the emission intensity is observed for each subsequent monolayer.

The given results allow for the following conclusions. After the exposure for 150 s, at the hydrogen partial pressure of $\sim 10^{-4}$ Pa, the number of chemical compounds on the surface monotonically decreases several times as the exposure temperature increases \sim to 500 K. In the deeper monolayers, the amount of hydrogen-containing compounds increases at the beginning with the increase in the temperature, at which the exposure is realized, and only after reaching ~ 423 K it begins to decrease. The maximum number of compounds at the depth of more than ~ 5 monolayers is formed in the temperature range of 373 - 423 K.

Thus, there are additional reasons to believe that under experimental conditions, realized in this study, the processes of hydrogen interaction with the investigated alloys take place only, mainly, on the surface and in the nearest near-surface region. This, in turn, allows to interpret the obtained results as the initial stages of hydrogen accumulation (hydrogenation) processes, namely, as the interaction of hydrogen with the surface of these alloys, without taking into account its significant diffusion into the volume, as one of the channels for changing the surface composition.

In addition to the temperature dependences of the emission intensity of hydrogen-containing secondary ions the temperature dependences of the oxygen-containing ions of the main components of the alloys under investigation and carbon-containing ones, were measured. As an example, Figs. 15, 16 show the temperature dependences for such secondary ions, sputtered from the LaNi_5 surface, which were measured at the residual partial pressure of hydrogen.

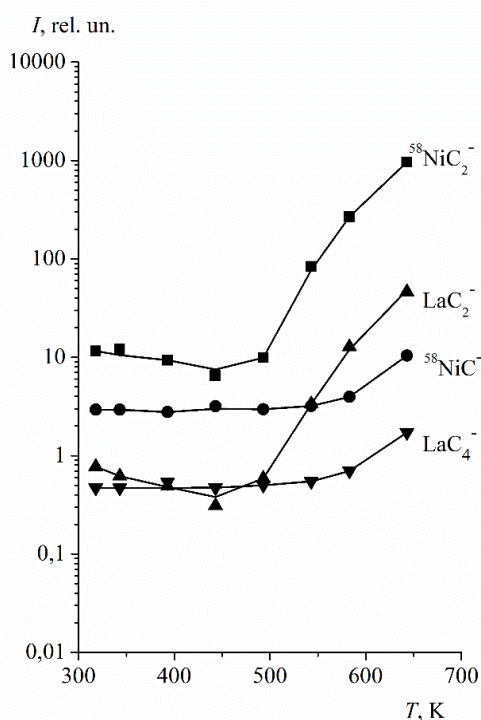


Figure 15. Temperature dependence of the emission intensity of carbon-containing negative secondary ions, sputtered from the surface of LaNi₅, at the residual partial pressure of hydrogen, and the current density of primary ions $j=4.5 \mu\text{A}\cdot\text{cm}^{-2}$

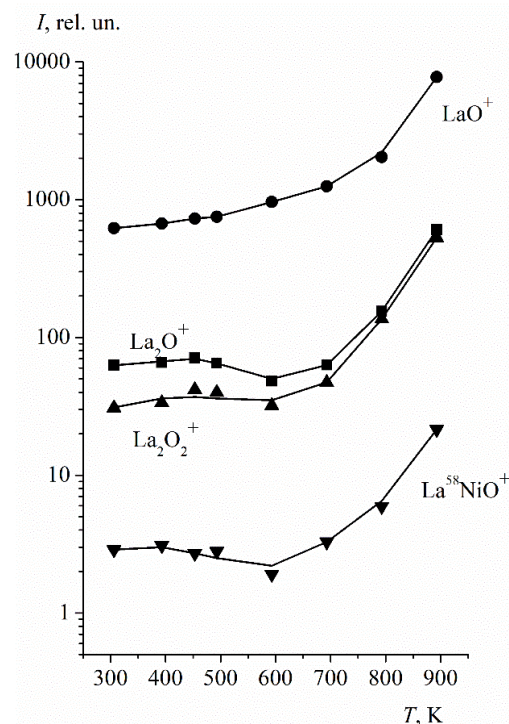


Figure 16. Temperature dependence of the emission intensity of positive secondary ions containing oxygen, which are sputtered from the surface of LaNi₅ at the residual partial pressure of hydrogen and the current density of primary ions $j = 4.5 \mu\text{A}\cdot\text{cm}^{-2}$

The presence of the emissions of carbon-containing ions is due to the fact that carbon is present in the volume of polycrystalline samples as an impurity. A common feature of all the temperature dependences of carbon-containing ions emissions is a greater or lesser increase in the emission intensities at an increase of the temperature (Fig. 15). Especially intensive growth is observed at the temperatures above ~ 450 K ($^{58}\text{NiC}_2^-$, LaC_2^-). This, most likely, is due to the fact, that at these temperatures carbon begins to diffuse from the volume to the surface, where it forms chemical bonds with the alloy components.

The presence of oxygen-containing ions in the mass spectra of secondary ion emissions is a consequence of both the presence of oxides in the samples volume as a bulk impurity, and, to a lesser extent, the result of oxygen sorption from the gas phase. As Fig. 16 shows, the emission intensity of oxide ions at the temperatures above ~ 600 K has a general tendency to increase with the temperature rise. The observed increase in the emission intensities of oxygen-containing ions is logically to be associated with the intensification of the oxide formation processes at these temperatures.

Next, the results of the investigation of the surface of intermetallic alloys $\text{LaNi}_{4.75}\text{Al}_{0.25}$ and $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ by SIMS are presented. That is, the LaNi₅-based alloys, in which a part of the nickel atoms were replaced by aluminum or manganese atoms, were studied [41].

It is known, that the properties of the intermetallic LaNi₅ can be changed within wide range by replacing lanthanum or nickel completely or partially with some other metals. As long as lanthanum has a rather high cost, it is replaced by the mixed metal Mm, which contains La, Ce, Pr, Nd, Sm Gd in different percentage ratios. This significantly reduces the cost of the intermetallic without significant change in its properties. In order to change the hydrogen sorption characteristics of alloys of the LaNi₅ (MmNi₅) type, reduce the number of activation cycles, increase the stability of characteristics in the process of operation, and reduce the cost, they are alloyed by replacing the nickel atoms by various elements (Mg, Al, Ti, Zr, Mn, Mo, Cr, V, Fe, Co, Si, Zn, Sn). [4, 5, 43, 44]. Different options of Mm(Ni, Co, Mn, Al)₅ alloys are the basis of most up-to-date commercial anodes of nickel-metal hydride (NiMH) batteries.

Various hydrogen sorption characteristics of such doped alloys have been extensively studied experimentally. However, despite the considerable efforts by experimentalists, the mechanisms causing doping effects still remain insufficiently determined.

Summarizing the results of a large number of works devoted to the study of the influence of alloying with aluminum and manganese, the following conclusions can be drawn. Partial replacement of Ni atoms in the intermetallic LaNi₅ by Al or Mn atoms causes significant reduction of the equilibrium pressure in the plateau region, reducing the absorption/desorption pressure hysteresis with a slight decrease in the hydrogen capacity. The kinetics of sorption processes also does not change significantly, although the data on the kinetics are contradictory [5, 45-48].

It was established that the alloy with aluminum has a higher cyclic stability than LaNi_5 , and is also characterized by a greater resistance to the presence of an oxygen admixture in hydrogen. The partial replacement of nickel atoms by aluminum increases the resistance to both internal and external degradation of the material [49-52].

The study of Al influence on the hydrogen diffusion in the alloy hydride doped with aluminum showed a significant increase of the activation energy of hydrogen diffusion at the room temperature, and, accordingly, a decrease in the rate of diffusion by more than two orders of magnitude as compared to the base alloy hydride [53, 54].

When discussing the reasons for the decrease in equilibrium pressure, corresponding to the plateau on the sorption/desorption isotherm, when nickel is replaced by aluminum or manganese, many authors, for example, in [47, 55, 56] agree that the main reason is an increase in the size of the elementary crystal cell of the alloy, since the atomic radius of Al and Mn exceeds that of Ni. In [55] it is shown that the plateau pressure on the pressure-composition-temperature diagram is inversely proportional to the interstitial hole size in the crystal lattice, in which the hydrogen is accommodated. As a result of the increase of interstitial hole size, the hydrogen atoms are more easily embedded in the crystal lattices, forming thermodynamically more stable hydrides, which leads to an increase in the enthalpy of hydride decomposition and a decrease in the equilibrium potential of hydride formation.

Therefore, the replacement of nickel atoms in LaNi_5 by larger atoms stabilizes the hydride phase of these materials and leads to the formation of more stable hydrides. From the technological point of view, this replacement is a convenient option for expanding the working temperature range of these materials. Unfortunately, the replacement of nickel with larger atoms is usually accompanied by a slight decrease in the hydrogen capacity [57, 58].

Generally, the data of SIMS experiments were analyzed in order to determine the functions of different components of the alloy related to the interaction with hydrogen, that is, the adsorption on the surface and its subsequent binding in the alloy.

The analysis of the mass spectra of positive and negative secondary ions, sputtered from the surface of the investigated samples $\text{LaNi}_{4.75}\text{Al}_{0.25}$ and $\text{LaNi}_{4.5}\text{Mn}_{0.5}$, which were measured before and in the process of annealing, as in the case with LaNi_5 , showed the presence of a vast number of various emissions. These emissions are atomic and cluster ions of lanthanum, nickel, aluminum, manganese and also ions which combine the alloy components and the impurities that are present in the samples. In the mass spectra, there are also emissions caused by interaction with the gas phase, that is, the emissions corresponding to the compounds with hydrogen and oxygen. The spectra of positive secondary ions are dominated by the emissions related to lanthanum. The most intensive emission in the spectra of positive ions for all the samples was the emission of lanthanum oxide ions. The spectra of negative secondary ions contain intensive emissions related to nickel, including nickel oxides.

Besides, at the temperatures of more than 700 K, the emission of La^+ and LaO^+ thermionic ions was observed for all the samples; for the samples $\text{LaNi}_{4.75}\text{Al}_{0.25}$ and $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ the emission of Al^+ and Mn^+ thermionic ions, respectively, was observed. The emission of such thermoions can be the result of the decomposition and desorption of the oxides that are on the surface from the very beginning.

The mass spectra measured after annealing and cleaning with the primary beam is much cleaner. In Figs. 17, 18 the examples of spectra of positive ions for $\text{LaNi}_{4.75}\text{Al}_{0.25}$ and $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ are presented. Like with LaNi_5 , the spectra of positive secondary ions contain emissions of atomic and cluster ions of lanthanum and nickel, intermetallic ions of lanthanum and nickel, emissions related to the compounds of these ions with hydrogen, oxygen, carbon (which, in general, is typical for metals and alloys). Moreover, the emissions related to lanthanum predominate, and the most intensive emission was that of lanthanum oxide ions, but the emission of nickel oxide was virtually absent. The spectra of negative secondary ions, in contrast to the positive ones, contain mostly nickel-related emissions, including nickel oxides.

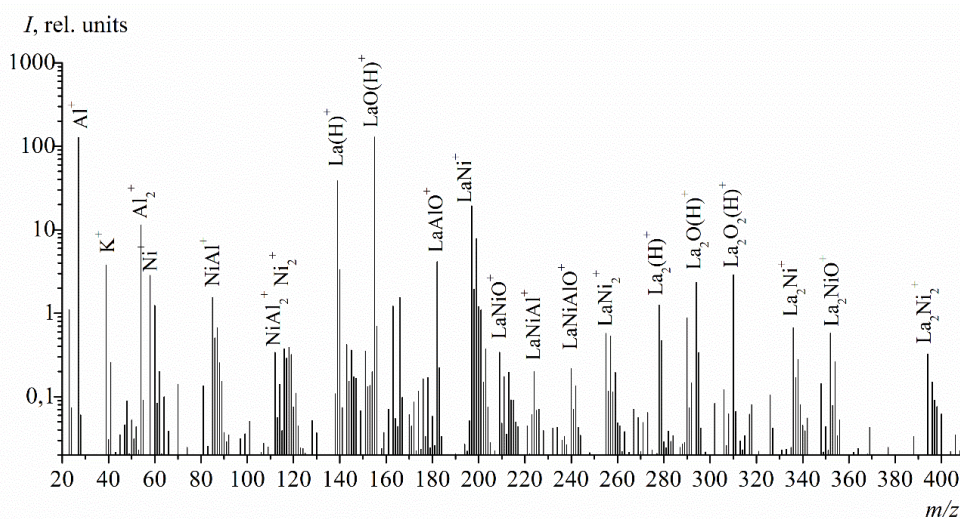


Figure 17. Section of the mass spectrum of positive secondary ions, sputtered from the surface of the $\text{LaNi}_{4.75}\text{Al}_{0.25}$ alloy sample at the room temperature, in the residual vacuum

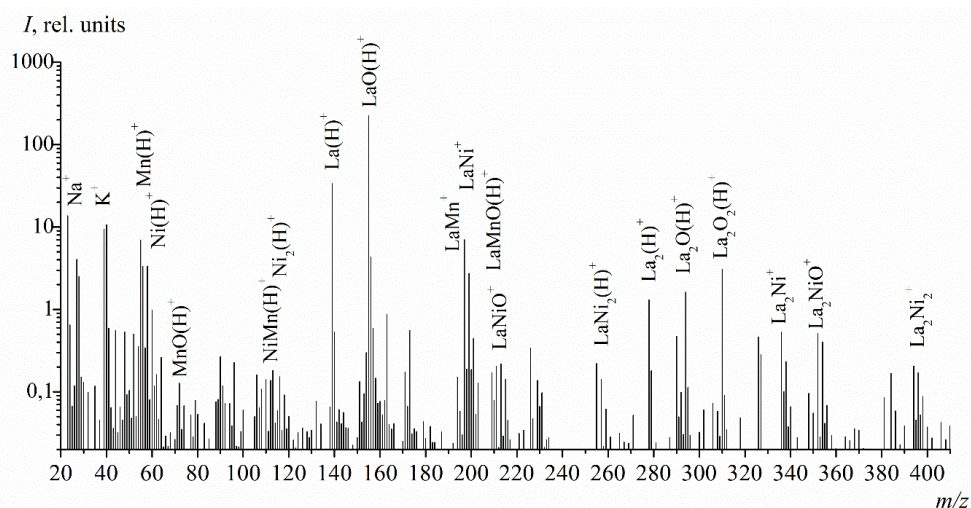


Figure 18. Section of the mass spectrum of positive secondary ions, sputtered from the surface of the $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ alloy sample at the room temperature, in the residual vacuum

As long as the alloys under study are of main interest concerning the interaction with hydrogen, the dependences of the emission intensity of various hydrogen-containing secondary ions, which were sputtered from the surface of the samples, on the partial pressure of hydrogen in the sample chamber, were measured first of all. It is such emissions that allow drawing a conclusion about the presence and composition of chemical compounds containing hydrogen on the surface. The mass spectra obtained at the increased hydrogen partial pressures, as in the case with LaNi_5 , contain a large set of hydrogen-containing emissions of both positive and negative secondary ions. In the spectra of positive ions, the emissions of hydrogen-containing ions containing lanthanum atoms are the most intensive. In the spectra of negative ions, there are ions containing nickel atoms. The electron affinity energy for lanthanum is 0.5 eV, for nickel it is 1.15 eV [59].

The analysis of the results has shown that for all the samples under study, as in the case of LaNi_5 , the composition of the mass spectra and the dependence of the emission intensity of the secondary ions, containing lanthanum and nickel, on the partial pressure of hydrogen, are similar. The mass spectra contain emissions of hydrogen-containing positive ions LaH_n^+ , La_2H_n^+ ($n=1, 2$), Ni_mH^+ ($m=1, 2, 3$), negative ions LaH_n^- , ($n=1, 2, 3, 4$), NiH_m^- ($m=1, 2$), Ni_nH^- ($n=2, 3, 4$) and a number of other ions with low intensity.

The specific character of the Mn/Al-doped alloys is the presence of a number of additional emissions related to manganese or aluminum. In the mass spectra of the secondary ions, sputtered from the surface of the $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ alloy, in addition to the ions comprising the main components of the alloy, there is an emission of secondary ions containing Mn. These are positive ions Mn_n^+ , Mn_nH^+ ($n=1, 2$), NiMn^+ , NiMnH^+ , LaMn^+ , LaMnH^+ and negative ions MnH^- , MnH_2^- , MnNiH^- , MnNiH_2^- . Besides, the emission of manganese ions with oxygen MnO^- , MnOH^- is also observed. This indicates that the composition of chemical compounds on the surface of this sample, including oxygen-containing ones, under the specified conditions of the experiment includes all the components of the alloy, including manganese.

In the mass spectra of secondary ions, sputtered from the surface of the alloy doped with aluminum $\text{LaNi}_{4.75}\text{Al}_{0.25}$, additional emissions of Al^+ , NiAl^+ , LaAl^+ , LaAlO^+ , Ni_2Al^+ , as well as hydrogen-containing emissions of complex nickel-aluminum and lanthanum-aluminum ions NiAlH^+ , LaAlH^+ , LaAlOH^+ , NiAlH^- , NiAlH_2^- , Ni_2AlH^- , are observed. At the same time, there are no emissions corresponding to compounds of aluminum directly with hydrogen (namely $\text{Al}_n\text{H}_m^{\pm}$), at least in the amount that allows for their unambiguous interpretation in the mass spectra. Since the complex hydrogen-containing ions of aluminum with nickel or with lanthanum are the fragments of the surface chemical compounds, the absence of $\text{Al}_n\text{H}_m^{\pm}$ ions allows to conclude that at the increased pressures, the hydrogen on the surface is not bound to aluminum, but bound to nickel or lanthanum atoms. This is a notable difference from the alloy with manganese, where the presence of emissions of secondary manganese ions directly with hydrogen ($\text{Mn}_n\text{H}^{\pm}$) gives reason to believe that manganese, along with nickel and lanthanum, takes a direct part in the processes of hydride formation. Fig. 19 presents the examples of the dependence of the emission intensity of hydrogen-containing ions with manganese and with aluminum on the partial pressure of hydrogen.

The measured dependences of the emission intensities on the partial pressure of hydrogen for all the alloys under study show the following. As the partial pressure of hydrogen increases, the intensity of most of the observed positive and negative hydrogen-containing secondary ions increases substantially. The growing nature of these dependences indicates an increase in the number of hydrogen-containing compounds on the surface and in the near-surface region of the samples, which include all the alloy components. The specific feature of the alloy doped with aluminum, as noted earlier, is that under the given experimental conditions, hydrogen does not form chemical bonds directly with aluminum, unlike with nickel, lanthanum, and manganese.

The temperature dependences for the hydrogen-containing secondary ions, which include the dopant atoms sputtered from $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ and $\text{LaNi}_{4.75}\text{Al}_{0.25}$ alloys, have mainly the same decreasing character.

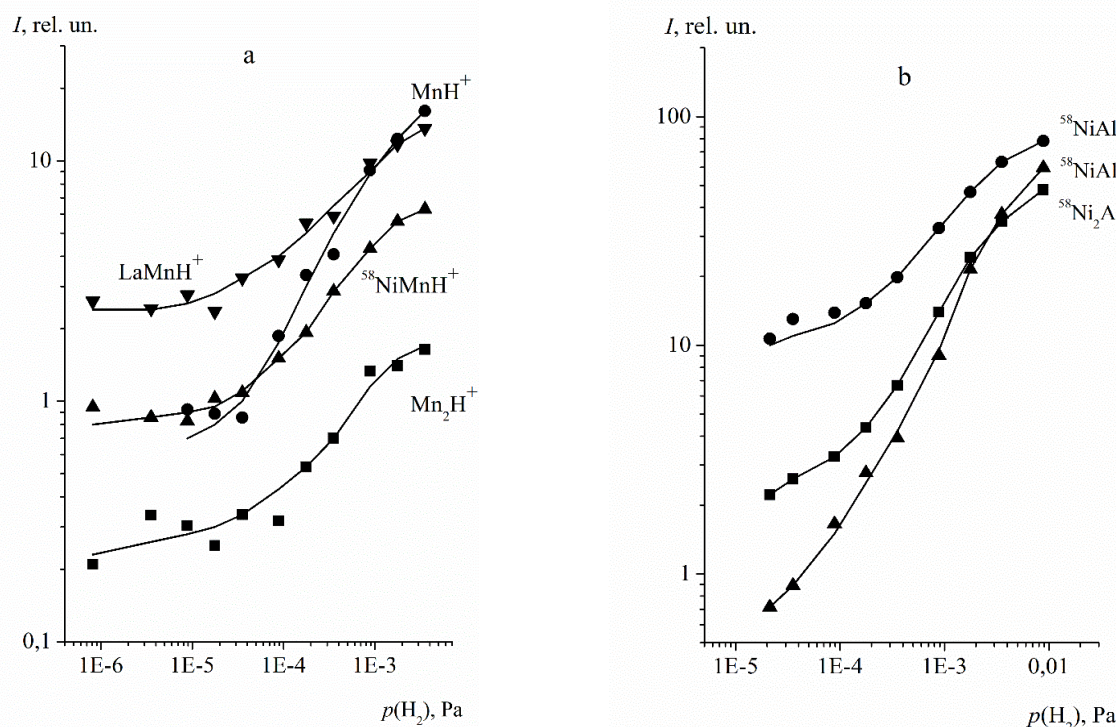


Figure 19. Dependence of the emission intensity of the positive hydrogen-containing secondary ions with manganese, sputtered from the surface of $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ (a), and negative hydrogen-containing secondary ions with aluminum, sputtered from the surface of $\text{LaNi}_{4.75}\text{Al}_{0.25}$ (b), on the partial pressure of hydrogen at the room temperature and current density of primary ions $j=4.5 \mu\text{A}\cdot\text{cm}^{-2}$

SIMS INVESTIGATION OF CHEMICAL COMPOSITION OF THE COMPOUNDS ON THE SURFACE OF LaNi_5 ALLOY DURING ITS INTERACTION WITH OXYGEN

In the following section we present the results of the SIMS studies of the surface monolayers chemical composition of the intermetallic alloy LaNi_5 in the process of its interaction with oxygen [60, 61].

The practical use of the intermetallic alloys in various areas of hydrogen energy, such as compact and safe storage of hydrogen, purification, its separation from gas mixtures, and ensuring the operation of various devices using hydrogen as a working medium, requires the solution of a number of problems, one of the main of which is the problem of resistance to gaseous impurities. The impurity gases, which are present in hydrogen, as was indicated earlier, can significantly affect the absorption capacity of intermetallic alloys. In some cases, they can significantly change the kinetic parameters of the sorption-desorption processes and the hydrogen capacity of the alloy [16-18].

The impurity gases, adsorbed on the intermetallic alloy surface, can form a strong chemical bond with the surface metal atoms, as a result these atoms cease participating in the processes of dissociative chemisorption of hydrogen. Such a deactivated surface effectively blocks the underlying region of the material from interacting with hydrogen. If the impurity gas is oxygen, then the high activation energy between the physisorbed and chemisorbed states of hydrogen on the oxidized surface prevents dissociative chemisorption and associative desorption, since most metal oxides do not have valence electronic states for hydrogen chemisorption. The sticking coefficient of hydrogen becomes practically zero. Molecular hydrogen cannot penetrate through the protective surface layer in order to dissociate on the metal surface under the oxide.

On the other hand, the hydrogen dissolved in the alloy cannot leave the surface because the associative desorption is prevented [58]. The removal of the surface oxides lowers the activation energy and causes an increase in the hydrogen sticking coefficient, as well as an increase in the rate of dissociative chemisorption and associative desorption.

The intermetallic alloy LaNi_5 has a set of parameters that are very attractive for the practical needs. The alloy is characterized by high hydrogen capacity, excellent sorption-desorption kinetics, relatively low sensitivity to impurities in gaseous hydrogen, and the ability to be easily reactivated after poisoning. At the same time, if the study of the specific character of the alloy bulk properties attracted and continues to attract the attention of many researchers, much less attention was paid to the analysis of the surface properties and its influence on the parameters of hydrogen sorption-desorption processes [62]. Based on this, studies of the surface properties of intermetallic alloys, in general, and the LaNi_5 alloy, in particular, remain relevant even nowadays. The study of the surface chemical composition, at the initial stages of interaction with reactive gases, can provide useful information that will allow not only to expand the general understanding of the processes of hydride formation, but also is of undoubted interest for the improvement of activation technologies applied in the processes of interaction with hydrogen, which has gaseous impurities.

A number of works investigated the influence of oxygen on the processes of the intermetallic alloy LaNi_5 interaction with hydrogen. At the same time, the published results show some contradictions regarding the nature of the compounds, which are present on the surface.

Thus, in papers [17, 20, 21, 49, 58, 64-66] dedicated to the study of the influence of impurities in gaseous hydrogen and the state of the metal surface on the sorption characteristics of intermetallic alloys, it is considered that the oxygen influence on the properties of the intermetallic alloy LaNi_5 involves the processes of the components segregation on the surface. In these works, a model of surface segregation of LaNi_5 is proposed. This model is based on the analysis with X-ray photoelectron spectroscopy, low-energy electron diffraction and Auger electron spectroscopy, as well as the magnetic susceptibility measurements.

The essence of the model is as follows. On a freshly prepared LaNi_5 sample, the component composition of the surface is the same as in the volume. As long as the surface energy of lanthanum is lower than that of nickel, when reaching the state of thermodynamic equilibrium, the surface is enriched with lanthanum. Selective oxidation of lanthanum on the surface additionally lowers its surface energy. Since the surface segregation is usually driven by the difference in the surface energy of the alloy components, the oxidation of lanthanum promotes the prerequisites for its segregation. Lanthanum diffuses to the surface and binds with oxygen. In the presence of hydrogen, the surface of the alloy is largely covered with La_2O_3 or $\text{La}(\text{OH})_3$. The surface oxide is formed as a result of the reaction with oxygen from the gas phase and with the bulk oxygen diffused to the surface.

The authors of these works believe that, as lanthanum segregates and oxidizes, the nickel atoms group together, forming large clusters, which in some cases cross the surface, resulting in a mixture of Ni and La_2O_3 on the surface. Dissociative chemisorption and associative desorption of hydrogen in this case can occur on metallic nickel particles or on the lower LaNi_5 metallic layer. The lanthanum oxide and nickel form a protective coating over LaNi_5 , and therefore, this alloy is rather little affected by impurities such as CO_2 , H_2O or O_2 , which are present in hydrogen.

In [67], at the investigation of LaNi_5 using X-ray photoelectron spectroscopy, it was shown that, when it was exposed to oxygen, the lanthanum atoms, but not nickel ones, were oxidized. The nickel segregation occurs in each hydrogen sorption-desorption cycle. Lanthanum in this model actually serves as a gas absorber, thus ensuring the formation of pure nickel clusters. This process is a mechanism of self-regeneration of the LaNi_5 alloy active surface. A similar model was proposed in [68].

Thus, an essential feature of the considered model is the oxygen-induced separation of the alloy components into lanthanum oxidation products (oxides or hydroxides) and nickel clusters. The nickel clusters provide the necessary active centers for dissociative chemisorption of hydrogen before its penetration into the metal lattice.

In contrast to the model described above, in works [69, 70], on the bases of the photoelectron studies, the effect of oxygen is believed to be more complex than that assumed in the above model. Although the rare earth components (lanthanum) are oxidized rather quickly when being exposed to oxygen, however, the experiments have shown that nickel oxide is present in the first few surface monolayers along with the lanthanum oxide. Moreover, the magnetic susceptibility measurements show that primary clustering of nickel occurs during hydrogen desorption but not during its absorption. Thus, it appears that the lanthanum-rich oxide layer is important not because it provides large clusters of nickel on the surface, but rather because it protects the underlying material. In the course of hydrogen sorption-desorption processes, nickel remains unoxidized not due to the self-regeneration mechanism, but, most likely, due to the reducing hydrogen atmosphere [68].

In [62, 71, 72], in the frame of the discussion of the processes of intermetallic alloys activation, in particular LaNi_5 , the following is proposed. The metal surface, under the influence of air, is enriched with lanthanum and is completely oxidized, mainly to La_2O_3 . Actually, oxides, hydroxides and carbides are present on the surface. The nickel, which is on the surface, is completely oxidized. It consists of NiO , $\text{Ni}(\text{OH})_2$, and Ni_2O_3 , but the latter two components exist only in the upper few monolayers. The La_2O_3 layer extends to a greater depth as compared to NiO , the latter being present only in the form of thin oxide layers. Thus, it is believed that NiO oxide is distributed over the surface of La_2O_3 and, in fact, behaves as a system on a metal carrier, which has a higher catalytic activity as to hydrogen. The NiO , formed on the surface, can be easily reduced by hydrogen even at the room temperature to form active nickel clusters. In other words, after activation, NiO is reduced to the metallic state and forms the $\text{Ni}/\text{La}_2\text{O}_3$ system. This, in turn, intensifies the hydrogen adsorption and increases the reaction rate.

From the overview of the processes models of the of LaNi_5 interaction with the components of the gaseous medium it follows, that until now there is no doubt that the chemical composition of the surface of intermetallic alloys is one of the most important parameters, which controls many surface phenomena, including the processes of hydrogen sorption-desorption, heterogeneous catalysis, etc. At the same time, there is no consensus on what the surface actually represents, and what chemical compounds are present on it, when impurities are present in hydrogen, in particular, oxygen. This circumstance provides grounds for further research.

Next we present the experimental results of the SIMS study of the surface monolayers chemical composition of the intermetallic alloy LaNi_5 in the process of its interaction with oxygen. The studied samples were tablets pressed from the fine-grained LaNi_5 alloy. Before the measurements, the samples were annealed in a residual vacuum at the temperature of ~ 1000 K. After annealing, the surface was cleaned with the beam of primary ions until the composition of the mass spectrum and the emission intensity of various secondary ions were fully stabilized.

As mentioned earlier, after annealing and cleaning the sample with the primary beam, the measured mass spectra of both positive and negative secondary ions contain numerous emissions of atomic and cluster ions of the alloy components, as well as the emissions caused by interaction with the gas phase and bulk impurities, i.e. the emissions related to the compounds of lanthanum and nickel with hydrogen, oxygen, and carbon.

The mass spectra of positive and negative secondary ions, sputtered from the surface of the alloy, were measured in the range of oxygen partial pressures $6.6 \cdot 10^{-7}$ – $8.8 \cdot 10^{-4}$ Pa and the residual hydrogen partial pressure. The mass spectra contain a large set of oxygen-containing emissions of both positive and negative secondary ions. In the spectra of positive ions, the emissions of oxygen-containing ions, which include lanthanum atoms, turned out to be most intensive. This is, obviously, due to the electropositive nature of lanthanum.

In the spectra of negative ions, there is a large set of oxygen-containing ion emissions, which include nickel atoms. There are also a vast number of oxygen-containing emissions of the complex secondary ions, which include atoms of lanthanum, nickel and oxygen in various combinations. Despite the fact that in the operating mode the residual partial pressure of hydrogen is $4.5 \cdot 10^{-6}$ Pa, the spectra along with the emission of the oxide ions have corresponding emissions of hydroxide ions.

The dependences of the intensities of a number of oxygen-containing emissions on the partial pressure of oxygen in the sample chamber at the residual partial pressure of hydrogen and the room temperature were measured. The spectra of positive secondary ions were measured at the current density of the primary beam of $9 \mu\text{A cm}^{-2}$, and the spectra of secondary negative ions were measured at the current density of the primary beam of $17 \mu\text{A cm}^{-2}$. Figs 20-22 present the examples of the measured most specific dependences of the intensities for some positive and negative secondary ions with lanthanum, nickel and intermetallic lanthanum-nickel ions.

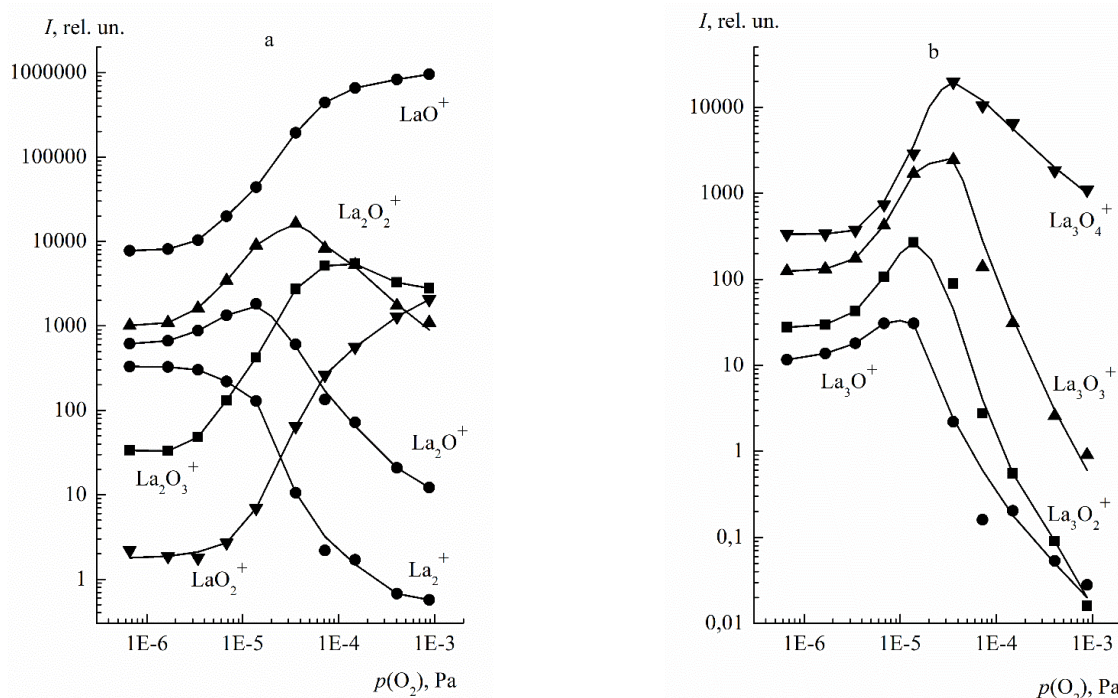


Figure 20. Dependence of the emission intensities of positive secondary ions with lanthanum, sputtered from the surface of LaNi_5 , on the partial pressure of the oxygen at the room temperature and primary ion current density of $9.0 \mu\text{A cm}^{-2}$

The sputtering of the surface of a solid, as is known, occurs when a sufficiently energetic cascade (initiated by primary ions) of paired collisions of target atoms approaches the surface [73]. In the sputtering process, along with monatomic or diatomic particles, the polyatomic complexes, as a part of the surface and near-surface region, are sputtered. Such complexes can escape from the surface if the binding energy of the atoms in it is greater or just under the binding energy of the corresponding complex with the surface. At the stage of separation from the surface, the fragmentation processes of these complexes can continue, as a result of which only stable fragments or only atomic particles remain. Also, at the stage of escape, as a result of electron exchange processes between the escaping complex and the surface, as well as between the complex fragments, a charge state and an excited state of stable fragments are formed. This is the basis of the secondary ion emission and SIMS method, and that, ultimately, allows drawing a conclusion about the state of the surface based on the analysis of the measured mass spectra.

It should be noted that, in contrast to the above mechanism, a model of the polyatomic secondary ions formation due to the recombination of atoms and molecules, sputtered independently in the same cascade of collisions from non-adjacent sites, as a result of interaction in the region near the surface, is also considered [74-77]. If such a model is correct, then the sputtered polyatomic ions will certainly not completely depict the composition of chemical compounds on the surface.

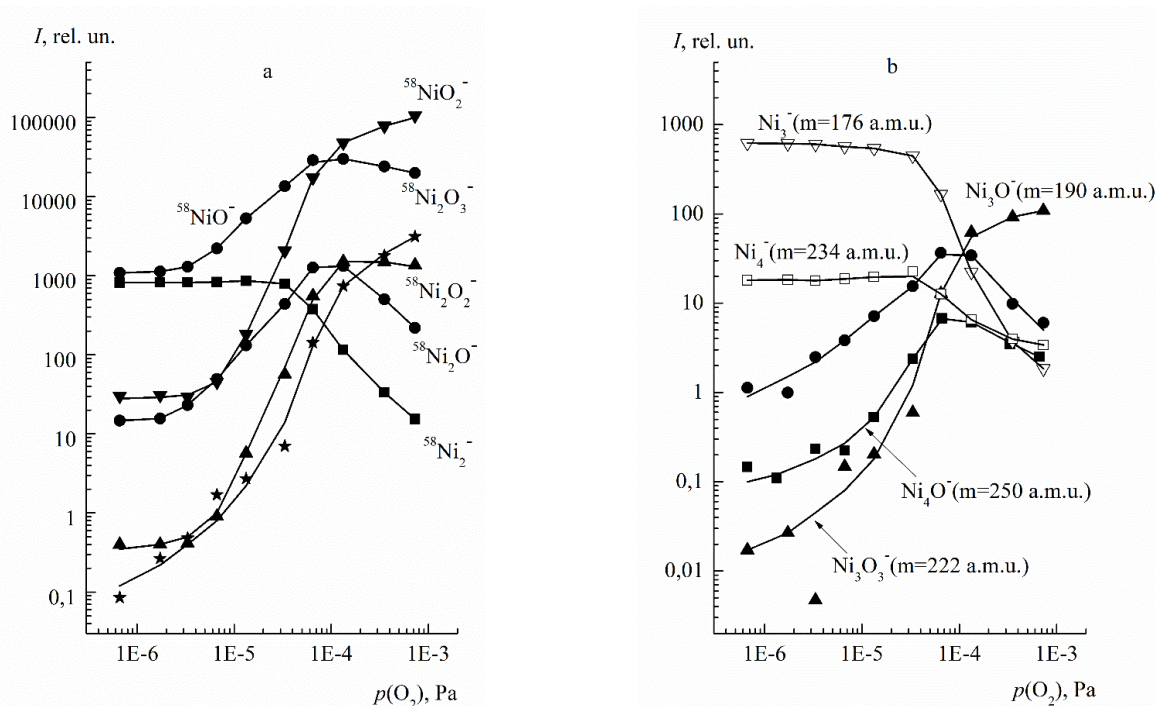


Figure 21. Dependence of the emission intensities of negative secondary ions with nickel, sputtered from the surface of LaNi₅, on the partial pressure of oxygen at the room temperature and primary ion current density of 17.0 μA cm⁻²

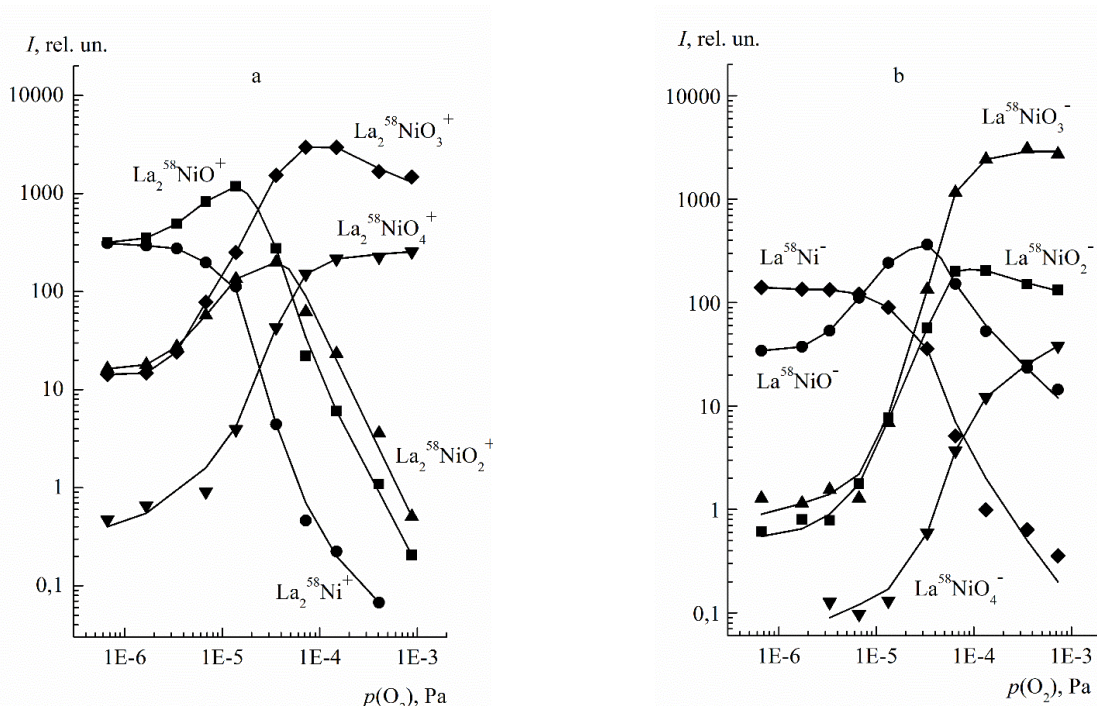


Figure 22. Dependences of the emission intensities of complex secondary ions with lanthanum and nickel, sputtered from the surface of LaNi₅, on the partial pressure of oxygen at the room temperature

First, such a model is proposed on the basis of theoretical calculations and has a very limited comparison with the experiment. Secondly, even if in some cases the model is valid for diatomic clusters, it is difficult to assume that up to 6-8 atoms, sputtered in one cascade from non-adjacent sites, recombine above the surface. But in our experiments, the emissions of such secondary ions (for example, Ni₄O₄⁻, LaNi₃O⁺, La₃Ni₂O⁺) are observed, although with low intensity.

Of course, matching of the composition of various secondary ions with specific chemical compounds on the surface must be approached with caution, since, to a much greater extent, the composition of the compounds on the surface corresponds to that of the neutral (not ionic) component of the sputter products. It should be kept in mind that the processes of a charge acquisition and preservation can affect the composition of the sputtered polyatomic ions.

The above said gives reasons to believe that the diversity of the composition of both positive and negative secondary ions, and even the behavior of the dependences of these ions emission intensity on the partial pressure of oxygen, observed in our experiments, are determined exclusively by the composition of the surface and near-surface monolayers, from which the sputtering takes place.

The analysis of the results allows concluding that oxygen forms strong chemical bonds with the both components of the alloy, when it impacts the surface of the LaNi₅ sample. This is evidenced by the presence of a large set of secondary ions of La_nO_m[±], Ni_nO_m[±] type, and the presence of secondary ions of La_nNi_mO_k[±] type (where n, m and k take different values in the case of positive and negative ions).

When discussing the mass spectra composition, the following must be kept in mind. Although all the sputtered ions are the fragments of the surface and near-surface monolayers of a solid, the emission of atomic and even diatomic secondary ions, as a rule, is not sufficiently informative. Such ions can be fragments of the chemical compounds having the most diverse composition. At the same time, the emission of complex ions, containing several atoms, largely characterizes the parent structure, from which its ionized fragments are knocked out.

The information about the composition and state of the surface, obtained on the basis of the analysis of such polyatomic emissions, can be more reliable. From this point of view, the most interesting are the emissions of La_nNi_mO_k[±] ions. The presence of such emissions in the spectrum gives reasons to believe that upon the oxygen sorption on the surface of LaNi₅, it not only forms strong chemical bonds with both components of the alloy, but forms a general structure of lanthanum, nickel, and oxygen. Moreover, judging by the diversity of the observed secondary ions composition, such an oxide structure in the investigated pressure range is not homogeneous, but is a superposition of structures with different stoichiometric ratios of the components.

With the increase of the oxygen pressure, the emission intensities of most oxygen-containing secondary ions (Figs. 20-22) pass through a maximum. Moreover, the more oxygen atoms in the composition of the secondary ion are per metal atom, the higher is the oxygen pressure, at which the maximum is observed. There are also secondary ions, the emission intensity of which with the increase of the oxygen partial pressure only tends to reach the plateau. Thus, the course of the observed oxygen dependences represents the process of increase in the number of oxygen atoms per number of metal atoms in the oxygen-containing structure, which is formed on the surface and in the near-surface region. As the partial pressure of oxygen increases, an oxide structure is realized on the surface of the LaNi₅ sample, in which the number of oxygen atoms per number of the matrix atoms increases.

As is noted above, the mass spectra contain a large number of the emissions of secondary hydroxide ions of the alloy components. In most cases, the intensity of these emissions is small as compared to that of the oxide ion emissions. The presence of such emissions is due to both the residual hydrogen in the sample volume and the interaction of the gas phase with the residual hydrogen. The dependences of the emission intensity of such ions on the partial pressure of oxygen generally correlate with those of the oxide ions. In most cases, the dependencies pass through a maximum or tend to reach the plateau. As an example, Fig. 23 shows the oxygen dependences for some secondary ions of hydroxides.

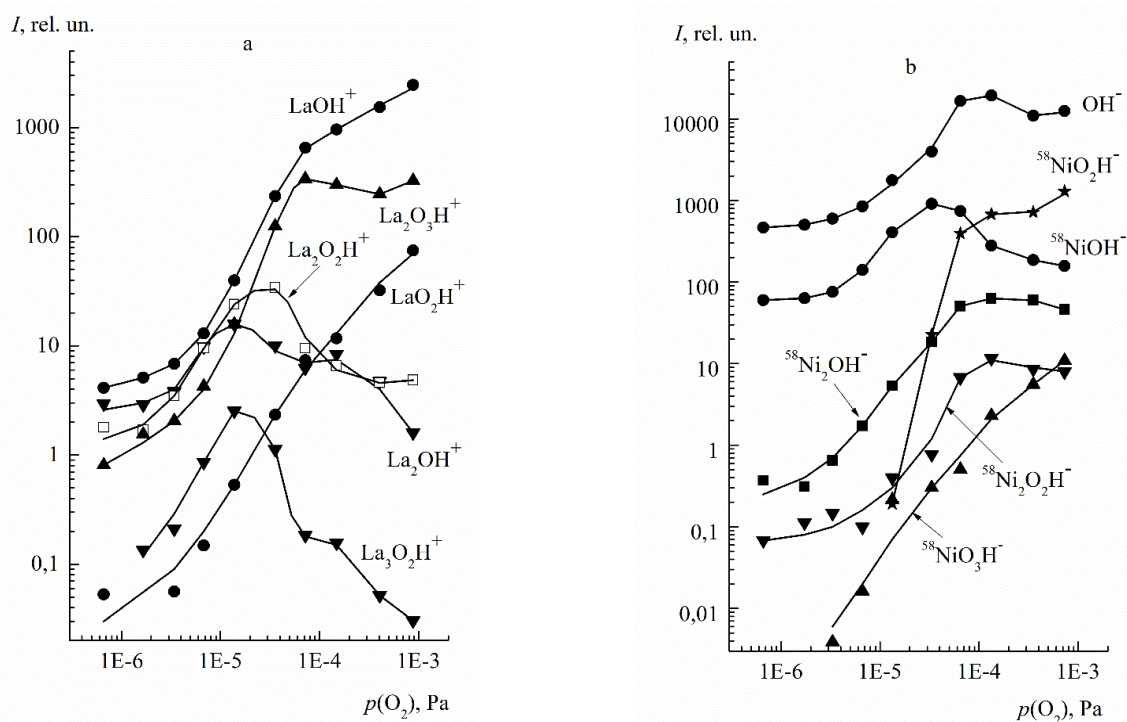


Figure 23. Dependence of the emission intensities of hydroxide secondary ions, sputtered from the surface of LaNi₅, at the room temperature, on the partial pressure of oxygen

It should be emphasized, that the concentration of oxygen on the surface, and therefore, the steady state coverage of the surface with oxygen-containing chemical compounds, under our experimental conditions at the room temperature, is determined by the dynamic equilibrium between the processes of oxygen adsorption from the gas phase and sputtering by the primary beam. Also, the effects of the ionic mixing should be taken into account.

Here the following should be noted. It cannot be excluded that under certain experimental conditions, the oxygen-containing secondary ions can be formed at the stage of the escape in the process of the escaping fragment interaction with the gas phase; in our case, as the result of association with oxygen. In this case, the composition of the sputtered ions will not completely characterize the surface structure. In order to check such a possibility, the following experiments were conducted.

After cleaning the surface of the sample with the primary beam at continuous recording of the emission intensity of the selected ion, oxygen was supplied into the sample chamber up to the pressure of $\sim 3.3 \cdot 10^{-4}$ Pa. After 44-46 seconds, the supply of the oxygen was shut off, and then the dependences of the intensity of secondary ion emission and the oxygen pressure in the sample chamber on time were measured. Fig. 24 presents the results of measurements at the sputtering stage after shutting off the supply of oxygen for the oxygen-containing positive ions with lanthanum La_2^+ , La_2O^+ , La_2O_3^+ , Fig. 24a, and for the negative ions with nickel NiO_2^- , Ni_2O_3^- , Ni_2O^- , Fig. 24b.

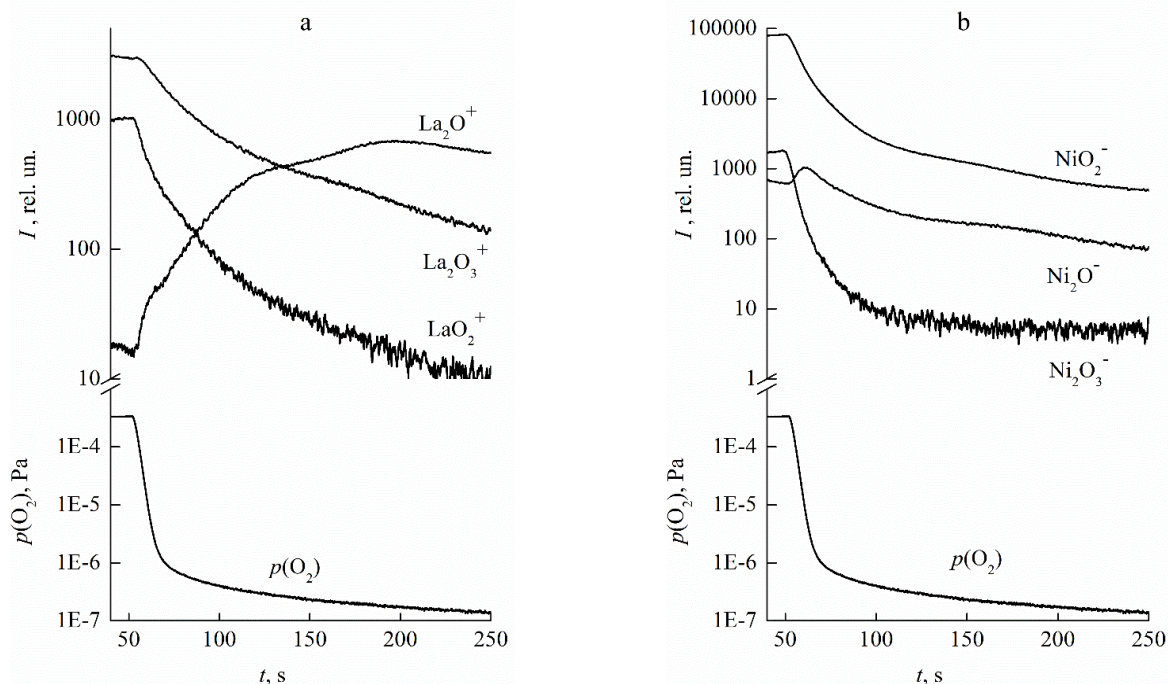


Figure 24. Time dependence of the emission intensities of the oxygen-containing secondary ions and of the partial pressure of oxygen in the sample chamber: a – positive ions, b – negative ions

The analysis of the obtained dependencies shows that the partial pressure of oxygen $p(\text{O}_2)$ in the sample chamber, after shutting off its supply, drops by two orders of magnitude in ~ 10 seconds. The emission intensity of secondary ions falls much more slowly. The emission intensity of La_2^+ ions during the same 10 seconds decreases only by 3.3 times, that of La_2O_3^+ ions by 1.4 times, in contrast, the emission intensity of La_2O_2^+ ions begin to grow and passes through a maximum. The situation with the emissions of oxygen-containing negative ions NiO_2^- , Ni_2O_3^- , Ni_2O^- , is similar. The emission intensity of NiO_2^- , Ni_2O_3^- ions decreases to a much lesser degree than the oxygen pressure, and the emission intensity of Ni_2O^- ions passes through a maximum.

Thus, the results of the experiments show that there is no direct correlation between the change in the partial pressure of oxygen and the change in the emission intensity of the secondary ions. This gives reasons to believe that the secondary ions are formed not as a result of association with oxygen of the gas phase, but as a result of sputtering of the oxides formed on the surface.

The behavior of the dependences of the emission intensity on time for the selected ions correlates well with the oxygen pressure dependences for these ions, which are shown in Fig. 20a, 22a. I.e. the curve for La_2O^+ (Fig. 20a) and the curve for Ni_2O^- (Fig. 21a) passes through a maximum as the oxygen partial pressure increases. The dependencies for these ions in Fig. 24a and Fig. 24b qualitatively repeat this trend but in the reverse order. The results, obtained for LaO_2^+ , La_2O_3^+ , NiO_2^- , Ni_2O_3^- , in this sense, also correlate with the oxygen dependencies for these ions: these dependencies are shown in Fig. 20a and Fig. 21a. The oxygen dependencies for these ions only tend to reach the plateau. The curves for LaO_2^+ , La_2O_3^+ , Ni_2O_3^- , NiO_2^- in Fig. 24, which correspond to sputtering, also qualitatively repeat this trend in the reverse order.

As a continuation of this type of experiments, a study of the dependences of the emission intensities of a wider range of secondary ions on the time of their sputtering after exposure of the sample to oxygen was carried out [78]. An oxide structure was created on the surface of the sample at an increased partial pressure of oxygen, what, as noted

above, is characterized by a set of oxygen-containing secondary ions and by the ratio of their emission intensities. Then this structure was sputtered with the primary beam. As the sputtering progressed, a change in the emission intensity of the observed secondary ions was recorded.

These experiments were carried out in the following way. After cleaning the surface of the sample with the primary beam in the residual vacuum, during the continuous recording of the emission intensity of the selected ion, oxygen was supplied into the chamber up to the pressure of $\sim 3.3 \cdot 10^{-4}$ Pa. After 46-48 seconds, the supply of the oxygen was shut off and the time-dependences of the secondary ion emission intensity and the oxygen pressure in the target chamber were further measured. The oxygen pressure was recorded using a gas mass spectrometer. The results of the measurements are presented in Figs. 25-28.

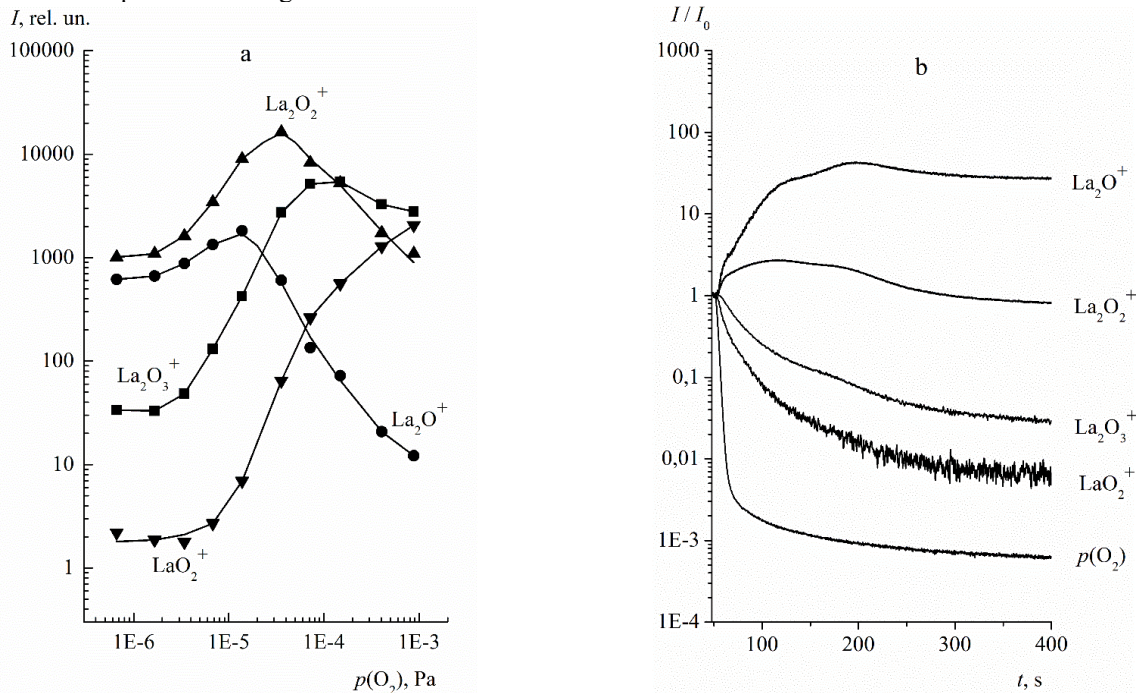


Figure 25. Dependences of the emission intensities of positive secondary ions with two lanthanum atoms on the oxygen partial pressure (a) and dependences of the emission intensities of positive secondary ions with lanthanum on the sputtering time after exposure to oxygen (b)

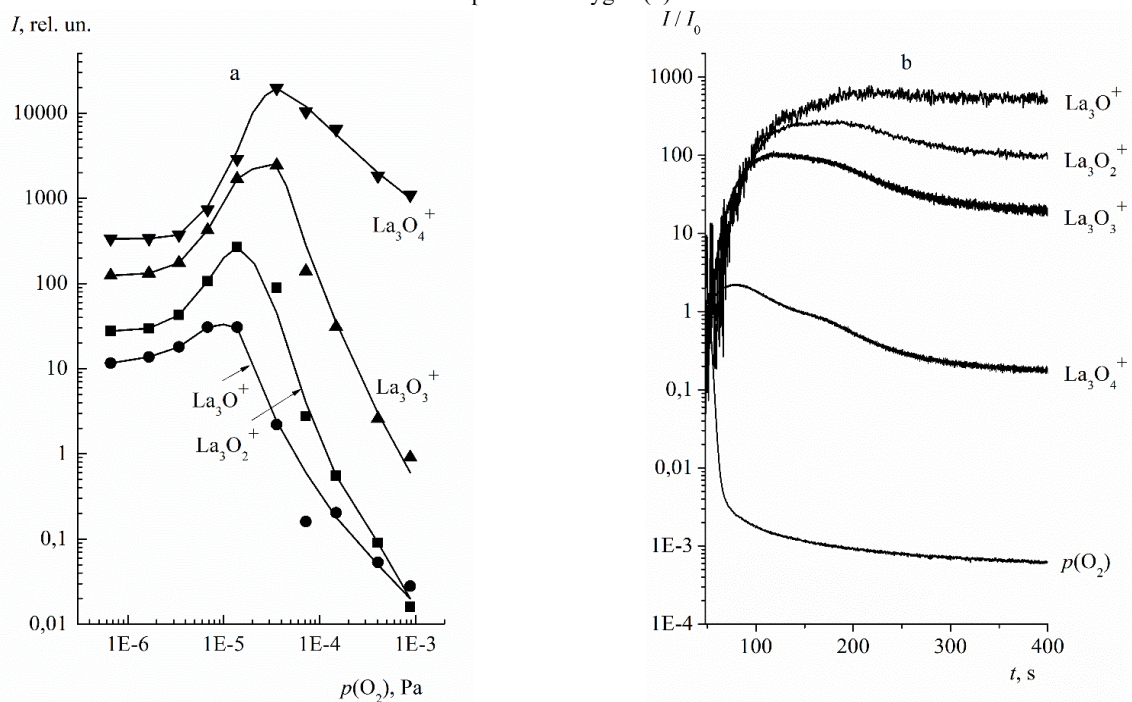


Figure 26. Dependences of the emission intensities of positive secondary ions with three lanthanum atoms on the oxygen partial pressure (a) and dependences of the emission intensities of positive secondary ions with lanthanum on the sputtering time after the exposure to oxygen (b)

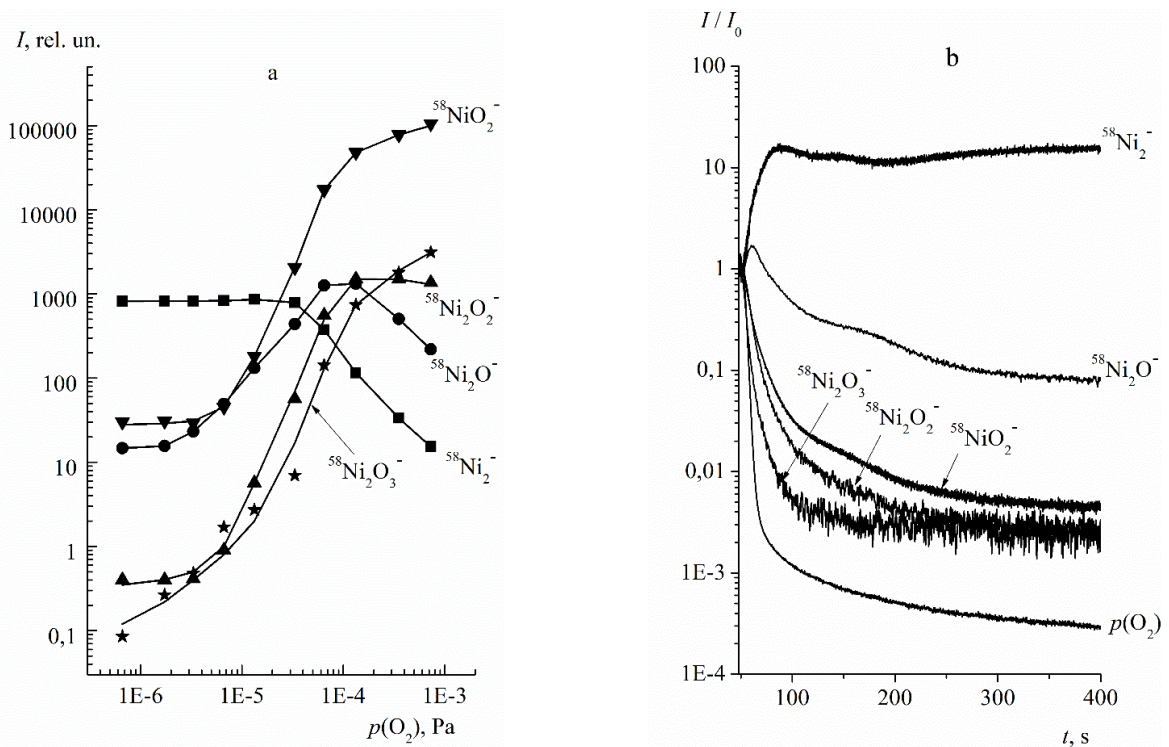


Figure 27. Dependences of the emission intensities of negative secondary ions with nickel on the oxygen partial pressure (a) and dependences of the emission intensities of negative secondary ions with nickel on the sputtering time after the exposure to oxygen (b)

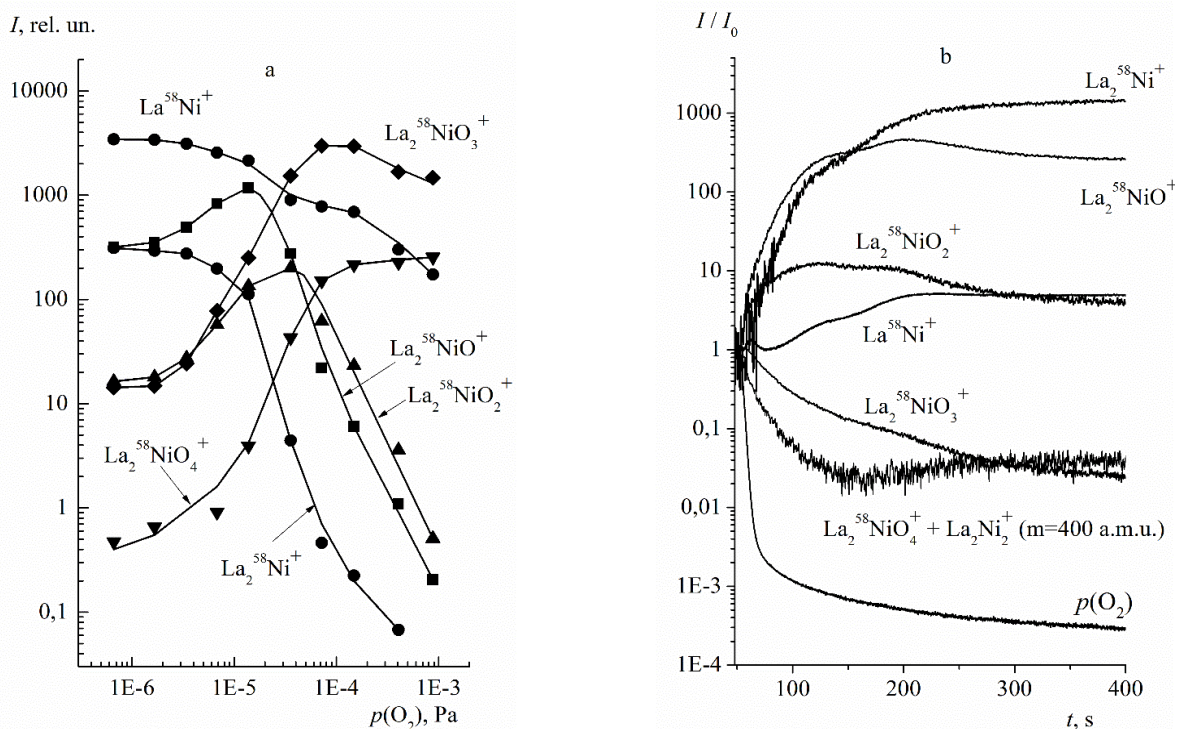


Figure 28. Dependences of the emission intensities of complex secondary ions with lanthanum and nickel on the partial pressure of oxygen (a) and dependences of the emission intensities of complex secondary ions with lanthanum and nickel on the sputtering time after the exposure to oxygen (b)

For clarity, these figures also present both the results of changes in the emission intensity of a number of oxygen-containing emissions (Figs. 25a, 26a, 27a, 28a), obtained at the increase in the partial pressure of oxygen, and the results of the measurements at the sputtering stage (Figs. 25b, 26b, 27b, 28b) after shutting off the supply of oxygen, for the oxygen-containing positive ions with lanthanum and for the negative ions with nickel. For the convenience of comparison, the actual emission intensities, shown in the figures concerning the sputtering, are normalized to their

intensity at the moment, which corresponds to the shutting off the supply of oxygen. Thus, the curves in Figs. 25b, 26b, 27b, 28b show how many times the emission intensity changes during the time of sputtering in relation to the starting point. The same figures present the dependences of the oxygen partial pressure in the chamber, also normalized to their initial value.

The curve marked in Fig. 28b as $\text{La}_2^{58}\text{NiO}_4^+ + \text{La}_2\text{Ni}_2^+$, represents the sum of the emissions of secondary ions $\text{La}_2^{58}\text{NiO}_4^+$ and La_2Ni_2^+ (400 a.m.u.), the separation of their specific contributions was not carried out, since the signal was recorded in a continuous mode (unlike the curve for $\text{La}_2^{58}\text{NiO}_4^+$ in Fig. 28a).

The analysis of the results obtained during the sputtering of oxides shows the following. The oxygen partial pressure $p(\text{O}_2)$ in the target chamber, after shutting off the supply, drops by two orders of magnitude in 10 seconds. At the same time, the intensity of the secondary ions emission changes much more slowly. For some secondary ions the emission intensity increases during the sputtering, for the others it decreases, and for a number of ions passes through a maximum. This applies both to the ions with lanthanum, and to those with nickel, as well as to the complex nickel-lanthanum ions (Figs. 24b-28b). Such a behavior of the emission intensity dependences on sputtering time for the selected ions correlates well with the oxygen dependences of these ions, shown in Figs. 24a-28a. The course of dependences of the ion emission intensity on the sputtering time qualitatively repeats in the reverse order the course of the corresponding dependences, obtained with the increase of the oxygen partial pressure.

Such a correlation allows to state that in the sputtering experiments, after the oxygen is pumped out of the sample chamber, as the oxides formed on the surface are sputtered, the situation is realized opposite to that, which occurs at the increase of the partial pressure of oxygen, when the number of oxygen atoms per atom of the matrix in the surface structure increases. That is, as the oxygen-containing structure (formed at the maximum oxygen partial pressures in these experiments) is sputtered, the number of oxygen atoms per number of matrix atoms decreases.

The data, presented in Figs. 24b-27b, indicate that the sputtering of the formed oxides continues during hundreds of seconds. This indicates that the formed oxide compounds have a three-dimensional structure and occupy dozens of monolayers. In such a three-dimensional oxide structure, the outer monolayers are characterized by the highest concentration of oxygen. The oxygen concentration decreases in the deeper lying monolayers.

The sputtering results, obtained during the sample exposure in oxygen under the action of the primary beam and the exposure with primary beam turned off (Fig. 27b) allow making a qualitative similar interpretation. This gives reasons to believe that the primary beam, while introducing the factor of sputtering and ion mixing, does not significantly affect the oxidation processes of LaNi_5 .

In addition to the above, the results of the sputtering experiments show that there is no direct correlation between the change with time in the partial pressure of oxygen and the change with time in the emission intensities of the secondary oxygen ions. This is a direct indication that the observed secondary ions are not a product of the association of the sputtered surface fragments with the oxygen of the gas phase at the fly-off stage, but are the products of the oxide compounds sputtering, and characterize the composition of the surface and near-surface regions.

SIMS INVESTIGATIONS OF THE OXYGEN EFFECT ON KINETICS OF HYDROGEN SORPTION-DESORPTION PROCESSES BY LaNi_5 HYDRIDE-FORMING ALLOY

Previously, the results of the study of the processes of hydrogen interaction with LaNi_5 alloy surface were presented. According to these data, as hydrogen accumulates on the surface (at an increase of hydrogen partial pressure), a hydrogen-containing structure, which is characterized by a certain stoichiometric ratio of components, is formed on the surface and in the near-surface region of the sample. For the SIMS experiments, this structure is characterized both by a certain set of hydrogen-containing secondary ions (positive and negative), sputtered from the surface by the primary beam, and also by the ratio of emission intensities of these ions. One of the secondary ions, which have one of the highest emission intensities at relatively low hydrogen partial pressures, is the Ni_2H^- secondary ion. The emission intensity of such ions depends almost linearly on the partial pressure of hydrogen and can be taken as a measure of the amount of hydrogen that has a chemical bond with the alloy components on the surface and near-surface region. The same applies to the secondary ion La_2H^+ . When analyzing the processes of hydrogen sorption-desorption on the surface of LaNi_5 , these secondary ions were chosen to monitor the amount of hydrogen on the surface.

When studying the effect of the composition of surface chemical compounds on the kinetics of hydrogen sorption processes, the experiments were carried out in the following way. The surface of the sample (LaNi_5) was cleaned with the high-density primary beam, next, oxygen was supplied into the chamber up to a certain pressure, so that a certain steady state coverage with oxygen-containing compounds was formed on the surface. Then, hydrogen was supplied into the chamber (within 2-3 seconds) up to a given pressure, and an increase in the number of hydrogen-containing compounds on the surface was observed; the number of compounds was monitored by the emission intensity of the specific secondary ions (Ni_2H^-). After the emission intensity reached the plateau, hydrogen was pumped out (within 2-3 seconds) from the sample chamber, and again, the process of sputtering of the hydrogen-containing compounds was observed by monitoring the emission intensity of the secondary ions Ni_2H^- . Next, the partial pressure of oxygen was increased stepwise, therefore increasing the steady state coverage with oxygen-containing compounds, and the procedure with hydrogen was repeated. Here, it is considered that the steady state surface coverage by adsorbed particles and the products of chemical reactions of these particles with the surface atoms of a solid (in our case, oxides

and hydrides), with the diffusion being not taken into account, is determined by the dynamic equilibrium between the processes of adsorption from the gas phase and the processes of sputtering by the primary beam. All the experiments were performed at the constant primary ion current density ($j=14 \mu\text{A cm}^{-2}$). In Figs. 29-31 the examples of the measured dependences for several values of the hydrogen partial pressure at different oxygen coatings are presented.

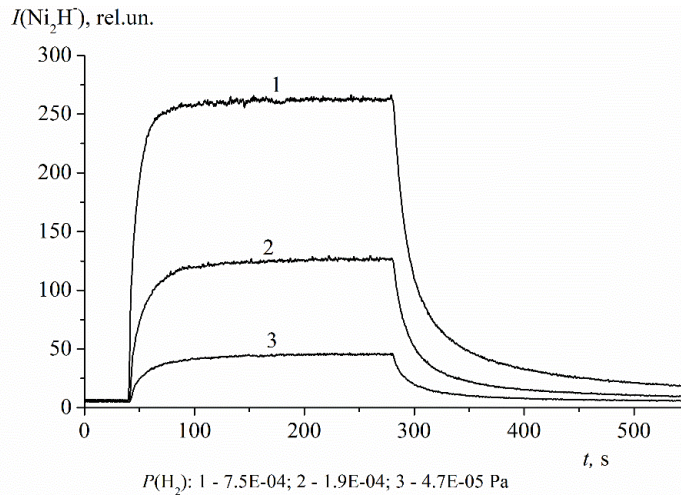


Figure 29. Time dependence of the emission intensity of Ni_2H^+ ions from the LaNi_5 surface at the residual surface pre-coverage with oxygen (at $P(\text{O}_2)$ residual) and at different values of hydrogen partial pressure

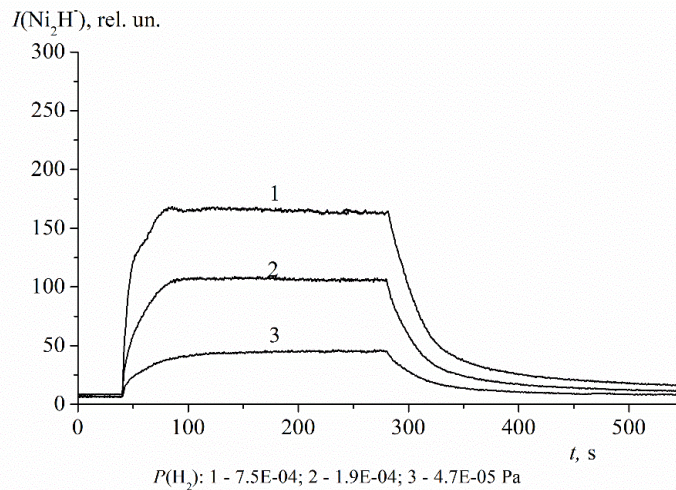


Figure 30. Time dependence of the emission intensity of Ni_2H^+ ions from the LaNi_5 surface for the surface pre-coverage with oxygen (at $P(\text{O}_2) 4 \cdot 10^{-5} \text{ Pa}$) and at different values of the hydrogen partial pressure

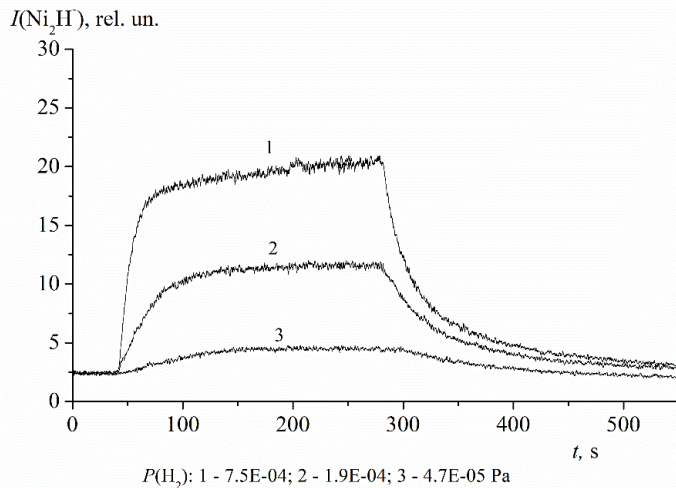


Figure 31. Time dependence of the emission intensity of Ni_2H^+ ions from the LaNi_5 surface for the surface pre-coverage with oxygen (at $P(\text{O}_2) 1 \cdot 10^{-4} \text{ Pa}$) and at different values of the hydrogen partial pressure

The analysis shows that the emission intensity of Ni_2H^+ ions and, therefore, the amount of hydrogen-containing compounds on the surface decreases as the partial pressure of oxygen increases, that is, as the surface oxidizes. An increase in oxygen pressure (above $\sim 4 \cdot 10^{-4}$ Pa) results in a decrease in the emission of Ni_2H^+ ions down to the background level, that is, with such oxygen coatings, the hydrogen ceases to interact with the surface. It is evident, that under such experimental conditions, the surface is completely covered by the layer of oxygen-containing chemical compounds, which prevent the hydrogen chemisorption. On the other hand, at the fixed oxygen pressure, the higher the pressure of hydrogen supplied to the chamber is, the greater is the number of hydrogen-containing compounds. Since at the sorption stage all the curves reach the plateau, this means that a steady state coverage of hydrogen-containing compounds is formed on the surface rather quickly, according to the balance between the processes of adsorption of hydrogen from the gas phase and the processes of sputtering. The lack of saturation of the emission intensity as to the hydrogen pressure indicates that all the hydrogen supplied to the chamber (in the applied pressure range) participates in the reaction and, potentially, the surface still has a sufficient resource for the formation of hydrogen-containing compounds either locally or stoichiometrically.

In order to present more clearly the kinetics of the hydrogen sorption process, the data obtained for the sorption stage were normalized to the maximum intensity; the results are given in Fig. 32.

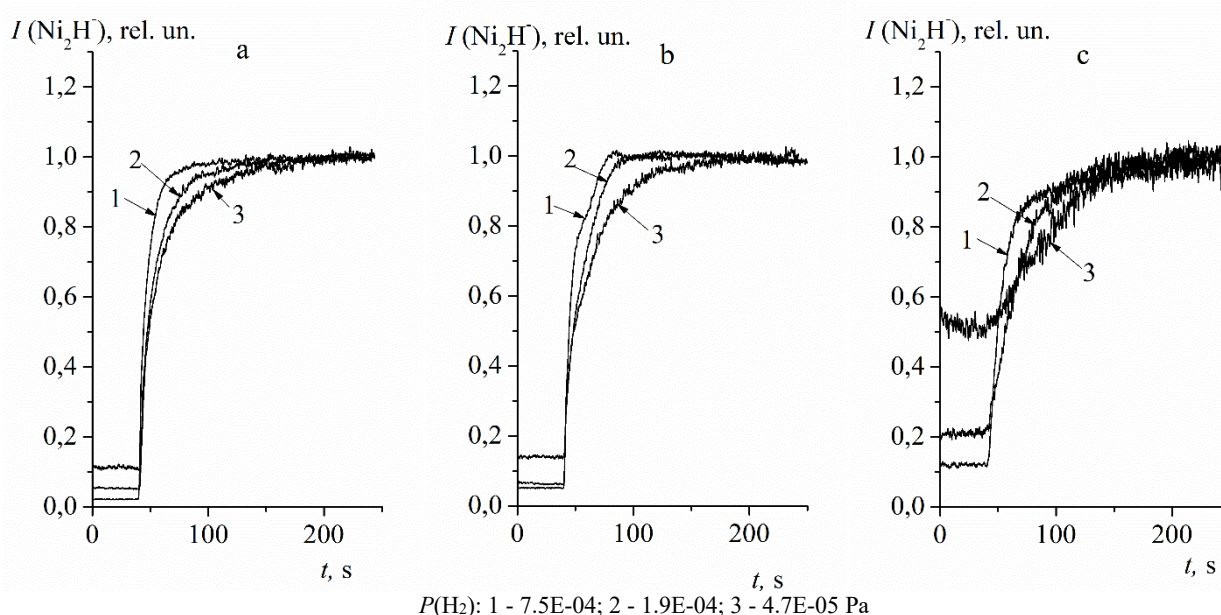


Figure 32. The normalized time dependence of the emission intensity of Ni_2H^+ ions from the LaNi_5 surface for different oxygen-precovered surfaces and different values of hydrogen partial pressure: a) residual oxygen pressure; b) $P(\text{O}_2) = 4 \cdot 10^{-5}$; c) $P(\text{O}_2) = 1 \cdot 10^{-4}$ Pa.

From Fig. 32 it follows that the oxygen coating has a weak effect on the formation rate of the maximum possible coverage with hydrogen-containing compounds for this combination of parameters. To a greater extent, the rate is affected by the pressure of the hydrogen supplied to the chamber; the higher is the pressure, the higher is the rate of the compounds formation.

Similar experiments were performed for the case, when La_2H^+ ions were used as characteristic secondary ions. The analysis of their results allows drawing similar conclusions.

When studying the effect of the composition of chemical compounds, which are present on the surface (in our case, the effect of surface oxidation), on the kinetics of hydrogen desorption processes, the experiments were performed in the following way. The surface of the sample was cleaned with the primary beam, then the primary ion current density $j=0.14 \mu\text{A} \cdot \text{cm}^{-2}$ was set (a lower density than that in other experiments was used to minimize the decrease of the amount of chemical compounds on the surface by sputtering); the sample chamber was supplied with oxygen and various oxygen pre-coatings were created on the clean surface of the sample, next, the oxygen was pumped out and the chamber was supplied with hydrogen, which created its own coverage on the partially oxidized surface. After the formation of the specified coverage, hydrogen was pumped out and the sample was heated up linearly with at the rate of 1.62 K sec^{-1} , simultaneously, the emission intensity of the characteristic ions Ni_2H^+ was recorded. After the experiment was over, the surface was cleaned with the primary beam to the initial state. The measurements were repeated for different values of the exposure both in oxygen and in hydrogen. The results are presented in Fig. 33.

The increase of the sample exposure in oxygen at the same unchanged exposure in hydrogen leads to a decrease in the number of hydrogen-containing chemical compounds on the surface. This, in fact, confirms the results of the experiments on sorption. (Figs. 29-31). After small exposures in hydrogen (Fig. 33a), that is, with a small amount of hydrogen-containing compounds on the surface, the hydrogen desorption is noticeable with an increase in temperature, and therefore the decrease in the number of hydrogen-containing chemical compounds for all the investigated oxygen

pre-exposures begins only at the temperatures above ~ 450 K. After relatively larger exposures in hydrogen (Fig. 33b), that is, with a relatively large number of hydrogen-containing compounds on the surface, the hydrogen desorption begins almost immediately after the onset of heating for all the investigated oxygen pre-exposures. In each case, however, at the temperature of ~ 575 K, the emission of characteristic ions becomes negligible, so the surface becomes free of hydrogen-containing chemical compounds; in this case, such a situation occurs for all the oxygen pre-exposures.

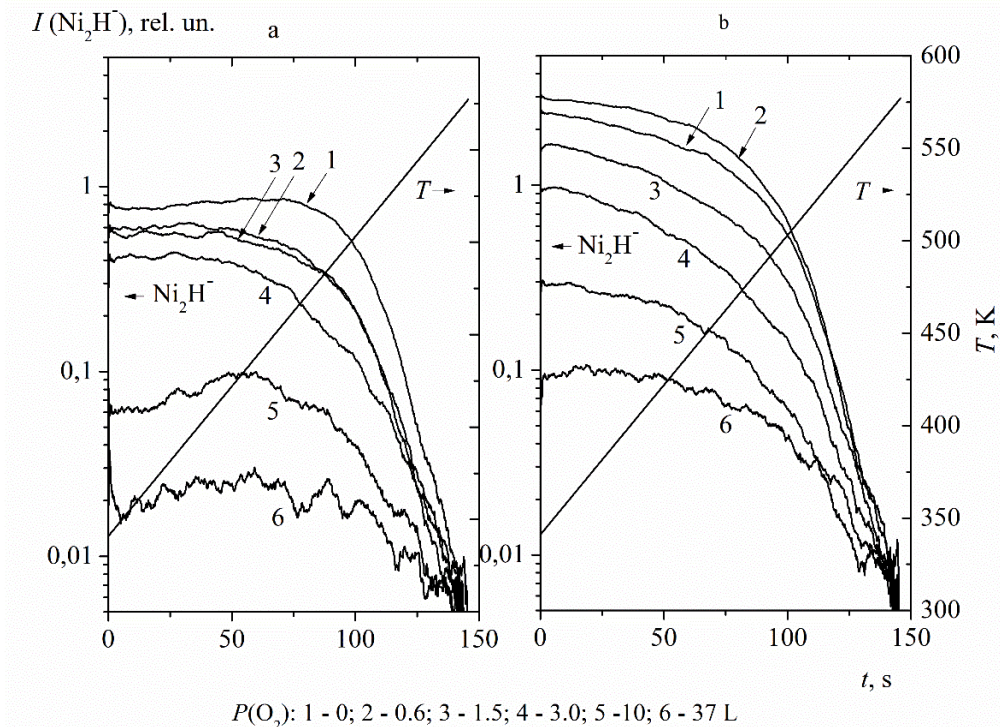


Figure 33. Time dependence of the Ni_2H^+ ions emission intensity from the $LaNi_5$ surface at a linear increase in temperature after different values of pre-exposure in oxygen for the exposure in hydrogen: a) – 4 L; b) – 60 L

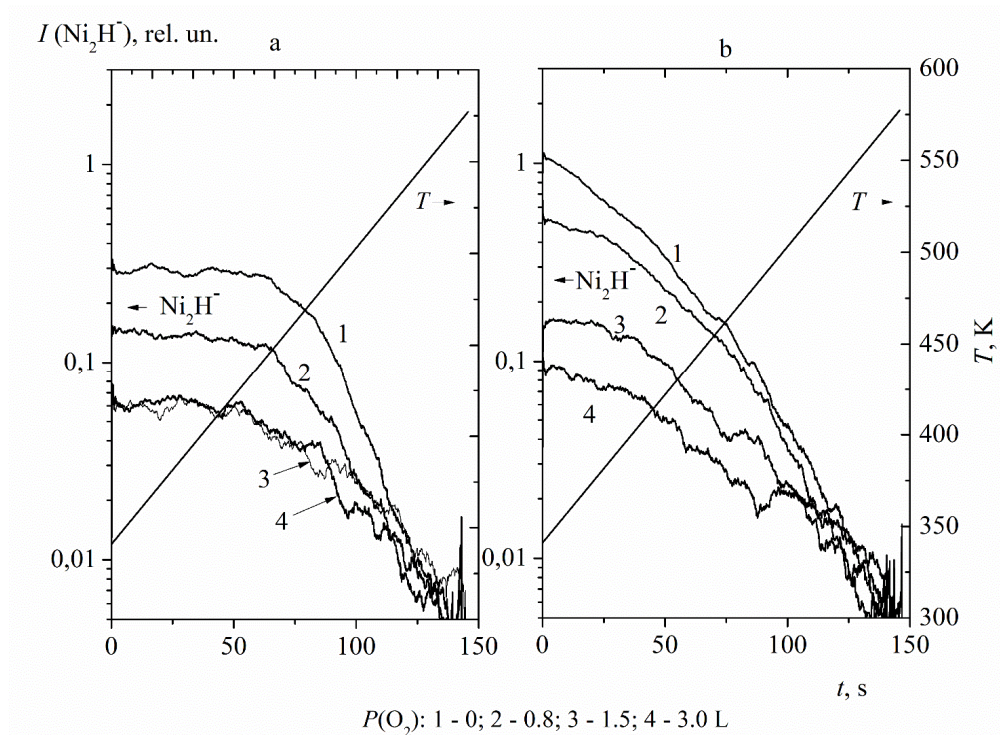


Figure 34. Time dependence of the Ni_2H^+ ions emission intensity from the $LaNi_5$ surface with a linear increase in temperature after the sample exposure in hydrogen: a) residual pre-coverage; b) – 60 L, for several values of exposure in oxygen (1-4)

Next, the conditions for the desorption experiment, in contrast to the above, were slightly changed. First, a hydrogen coverage was formed on a clean surface, and then the effect of oxygen was investigated. The surface of the sample was cleaned with a primary beam, after that the primary current density $j=0.14 \mu\text{A}\cdot\text{cm}^{-2}$ was set; the chamber was supplied with hydrogen (instead of oxygen, as in the first case), and a certain hydrogen pre-coverage was formed on the sample surface (the experiment was carried out for the residual hydrogen pre-coverage and for the pre-coverage corresponding to the exposure of 60 L); then hydrogen was pumped out and the chamber was supplied with oxygen (instead of hydrogen, as in the first case), which interacted with the hydrogen-precovered surface. After the specified oxygen exposure was reached, the oxygen was pumped out and the sample was heated up linearly (in time) at the rate of $1.62 \text{ K}\cdot\text{sec}^{-1}$, while, just as in the first case, the emission intensity of the characteristic Ni_2H^+ ion was recorded. When the experiment was over, the surface was cleaned with the primary beam to the initial state. The measurements were repeated for different exposure values in both hydrogen and oxygen. Fig. 34 presents the measured dependences for the residual surface pre-coverage with hydrogen and for the hydrogen exposure of 60 L at several values of the oxygen exposure.

The analysis shows that the conclusions drawn when considering the results of the first experiment (Fig. 33) are fully valid for the experiment, when the coverage with hydrogen-containing compounds was formed before the exposure to oxygen. This allows concluding that both in the first and second cases, an increase in temperature causes the decomposition of similar chemical compounds on the surface. Therefore, regardless of what comes first to the clean surface, hydrogen or oxygen, the chemical compounds similar in composition will be formed, as Fig. 3 shows, the compounds are, likely, hydroxides. Thus, the oxygen poisoning of the surface of the hydride-forming alloy LaNi_5 can occur regardless of whether the alloy surface was clean from the very beginning or was covered with a layer of hydrides.

CONCLUSION

The studies of the lanthanum-based alloys performed by the SIMS method showed that under normal conditions the surface of LaNi_5 , $\text{LaNi}_{4.75}\text{Al}_{0.25}$ and $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ samples, which are used mainly as the hydrogen storage materials, is, to a certain extent, covered with a layer of chemical compounds including oxides, hydrides, hydroxides, carbides of the alloy components. Moreover, judging by the presence of lanthanum cluster ions in the emission spectra, this coverage is not continuous, that is, the surface of the samples has some regions free of chemical compounds. The annealing and bombardment with the primary beam, although reducing the amount of these compounds, does not lead to complete cleaning of the surface.

The study of the time dependences of the emission intensity for the secondary ions characterizing the presence of hydrogen-containing compounds on the surface, measured in the process of hydrogen adsorption and then in the process of sputtering of the formed surface compounds, which was performed at different temperatures of the sample, showed the following. The processes of the alloys interaction with hydrogen under experimental conditions (at the room temperature and hydrogen pressure in the sample chamber $1\cdot 10^{-6}$ - $7\cdot 10^{-2}$ Pa) are limited only to the near-surface region, i.e. the hydrogen, reaching the surface, interacts only with the surface and near-surface atoms of the alloy components and, in the best case, saturates only the near-surface region without diffusing in a noticeable amount into the alloy volume.

In the process of the hydrogen adsorption, the amount of the hydrogen-containing compounds, formed on the surface and in the near-surface region, monotonically decreases with the increase of temperature; the steady state coverage with the compounds is also realized faster. In the investigated temperature range, the hydrogen diffuses in noticeable quantities to the depth of ~ 10 monolayers. Thus, the processes of hydrogen interaction with the alloys in the given experimental conditions take place only on the surface and in the near-surface region. This, in turn, allows interpreting the obtained results as the initial stages of hydrogenation processes, and not taking into account the diffusion of hydrogen into the volume, as one of the channels for changing the surface composition.

The study of the initial stages of the processes of these alloys interaction with hydrogen under experimental conditions showed, that on the regions of the clean surface, hydrogen forms chemical compounds with the both main components of the alloy, nickel and lanthanum. As the hydrogen accumulates on the surface and in the near-surface region, a hydrogen-containing structure is formed, which is characterized by a certain stoichiometric ratio of components. Nickel in this structure has strong chemical bonds with two hydrogen atoms, and lanthanum with two or more hydrogen atoms. Along with such a compound, the structures with lower hydrogen content are also formed. The formed hydrogen-containing structure includes the both main components of the alloy La and Ni for all the studied samples, even only lanthanum is generally believed to be the hydride-forming element in such alloys.

The hydrogen sorption from the gas phase to the alloys surface causes a significant change in the emission properties of the alloy, in terms of secondary ion emission. The yield of the positive secondary ions increases and the yield of negative secondary ions increases especially greatly, first of all, due to the hydrogen-containing ion emissions. Such an increase is due to the processes of formation on the surface and in the near-surface area of the structures, whose sputtering by the primary beam is characterized by significantly higher coefficients of secondary ion emission as compared to the clean metal surface.

In the case of the $\text{LaNi}_{4.5}\text{Mn}_{0.5}$ alloy, the manganese, as an additional alloy component, is also a part of the forming hydrogen-containing structure and, therefore, takes a direct part in the processes of hydride formation. In the case of the $\text{LaNi}_{4.75}\text{Al}_{0.25}$ sample, unlike the manganese, the aluminum does not form direct chemical bonds in

significant quantities with hydrogen. That is, the aluminum atoms themselves in this alloy do not take participation in the processes of hydride formation, in the sense of the formation of chemical bonds. Their main role of aluminum is in the crystal lattice reconstruction.

The studies of the temperature influence on the emission intensity of hydrogen-containing secondary ions have shown that with the increase of temperature, the number of hydrogen-containing compounds on the surface and in the near-surface region decreases. Such a decrease is, primarily, related to a decrease in the sticking coefficient of the hydrogen molecules.

The SIMS studies of the chemical composition of the surface monolayers of the intermetallic alloy LaNi₅ in the process of interaction with oxygen showed the following. As consequence of the oxygen interaction with the alloy, a complex chemical structure including oxygen, lanthanum and nickel is formed on the surface and in the near-surface region of LaNi₅. Both oxygen and hydrogen in such a structure form strong chemical bonds with the both components of the alloy. This is evidenced by the presence in the mass spectra of a large set of oxygen-containing emissions of positive and negative secondary ions with lanthanum and nickel, as well as cluster oxygen-containing lanthanum-nickel secondary ions. The formed oxide compounds have a three-dimensional structure and occupy dozens of monolayers. In such a three-dimensional oxide structure, the outer monolayers are characterized by the highest ratio of the number of oxygen atoms to the number of matrix atoms. This ratio decreases in the deeper lying monolayers.

The quantitative and qualitative ratio of the elements in the resulting oxide structure mainly depends on the partial pressure of oxygen and, to a much lesser extent, on the sputtering action of the primary beam.

The observed secondary ions are not the product of the association of the surface sputtered fragments with oxygen of the gas phase at the fly-off stage, but are the products of the oxide compounds sputtering, therefore the secondary ions characterize the composition of the surface and near-surface region.

The study of the effect of oxygen on the kinetics of hydrogen-sorption processes by the hydride-forming alloy LaNi₅ showed the following. With a fixed number of oxygen-containing compounds on the surface, the higher is the pressure of hydrogen above the surface, the greater is the number of the formed hydrogen-containing compounds. The oxygen coating has a weak effect on the formation rate of the maximum possible (at the specific combination of the parameters) coverage with hydrogen-containing compounds. The greater is the hydrogen pressure above the surface, the higher is the rate of the compounds formation.

The study of the oxygen influence on the kinetics of desorption processes showed that for all the investigated oxygen exposures, at a small amount of hydrogen-containing compounds on the surface, a noticeable decrease in their amount begins only at the temperatures above ~ 450 K. At a relatively large amount of the hydrogen-containing compounds on the surface, the decrease starts almost immediately after the beginning of heating from 300 K. At the temperature of ~ 575 K, the emission of characteristic ions becomes negligible, so the surface becomes free of hydrogen-containing chemical compounds.

Poisoning of the surface of the hydride-forming alloy LaNi₅ with oxygen can occur regardless of whether the surface of the alloy was clean from the very beginning or was covered with a layer of hydrogen-containing chemical compounds.

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РОЛЬ ПОВЕРХНІ У ПРОЦЕСАХ ГІДРИДОУТВОРЕННЯ

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Методом вторинної іонної мас-спектрометрії (ВІМС) проведено дослідження змін хімічного складу поверхневих моношарів інтерметалевих сплавів на основі лантану у процесі взаємодії з воднем і киснем. У якості первинних іонів використовувалися іони Ar^+ з енергією 10-18 кеВ. Дослідження початкових стадій процесів взаємодії цих сплавів з воднем в умовах експерименту показало, що на ділянках чистої поверхні водень утворює хімічні сполуки з обома основними компонентами сплаву нікелем і лантаном. У міру накопичення водню на поверхні і в приповерхневій області утворюється водневмісна структура, що характеризується певним стехіометричним співвідношенням компонентів. Нікель у такій структурі має міцні хімічні зв'язки з двома атомами водню, а лантан з двома або більше атомами водню. Поряд із такою сполукою утворюються також структури з меншим вмістом водню. Водневмісна структура, що формується включає обидва основні компоненти сплаву і La і Ni для всіх досліджених зразків, хоча прийнято вважати, що гідридоутворюючим елементом у таких сплавах є лантан. Проведені ВІМС дослідження хімічного складу поверхневих моношарів інтерметалевого сплаву $LaNi_5$ у процесі взаємодії з киснем показали наступне. В результаті взаємодії кисню з об'єктом, що досліджується, на поверхні і у приповерхневій області $LaNi_5$ утворюється комплексна хімічна структура, що включає кисень, лантан і нікель. Кисень у такій структурі як і водень утворює міцні хімічні зв'язки з обома компонентами сплаву. Про це свідчить наявність у мас-спектрах великого набору кисневмісних емісій позитивних, і негативних вторинних іонів з нікелем, а також кластерних кисневмісних лантан-нікелевих вторинних іонів. Оксидні сполуки, що утворюються, мають об'ємну структуру і займають десятки моношарів. Отруєння поверхні гідридоутворюючого сплаву $LaNi_5$ киснем може відбуватися незалежно від того чи була поверхня сплаву від самого початку чистою, або була покрита шаром водневмісних хімічних сполук.

Ключові слова: ВІМС; поверхня; інтерметалеві сплави на основі лантану; водень; гідриди; кисень; оксиди