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SPUTTERING OF OXIDES FROM $LaNi_5$ SURFACE[†]

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The changes in chemical composition of the intermetallic alloy $LaNi_5$ surface monolayers were studied using secondary ion mass spectrometry (SIMS) in the process of the alloy interaction with oxygen. The investigated samples were pellets made by pressing the fine-grained $LaNi_5$ alloy. Ar^+ ions having energies of 10-18 keV were used as primary ions. The primary beam current density was 9-17 $\mu A \cdot cm^{-2}$, which corresponds to the dynamic SIMS mode. The emission intensities of secondary ions were measured within the dynamic range of at least 6 orders of magnitude. Before the measurements, the samples were annealed in residual vacuum at a temperature of ~ 1000 K. After the annealing, the sample surface was cleaned using the primary ion beam until the mass-spectrum composition and secondary ion emission intensity stabilized completely. The gas phase composition was monitored using a gas mass spectrometer. The conducted studies showed that a complex chemical structure including oxygen, lanthanum and nickel is formed on the surface and in the near-surface region of $LaNi_5$ as a result of its exposure to oxygen. Oxygen forms strong chemical bonds in such a structure with both components of the alloy. This is evidenced by the presence of a large set of oxygen containing emissions of positive and negative secondary ions with lanthanum, with nickel, and oxygen containing lanthanum-nickel cluster secondary ions in mass spectra. The resulting oxide compounds have a bulk structure and occupy dozens of monolayers. In such a bulk oxide structure, the outer monolayers are characterized by the highest ratio of oxygen atom number to the number of matrix atoms. This ratio decreases along the transition from surface to the underlying monolayers. This process occurs uniformly, without any phase transformation. The observed secondary ions are not a product of association between sputtered surface fragments and oxygen in the gas phase at the fly-off stage after sputter-ejection, but they are products of the oxide compounds being sputtered, hence they characterize the composition of surface and near-surface region.

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$LaNi_5$ intermetallic alloy is of great importance among other hydrogen storage materials for a number of technical applications. It is used in systems for stationary accumulation and transport of hydrogen, for thermosorption compression, catalysis, hydrogen purification, separation of its isotopes, as well as in fuel cells. The alloy has a high hydrogen capacity, high cyclic stability and can be activated or reactivated easily. $LaNi_5$ alloy is able to absorb and release a large amount of hydrogen at near room temperatures and relatively low pressures [1-3]. The hydride phase $LaNi_5H_{6,7}$ contains 1.4·wt. % hydrogen. The enthalpy of hydride formation is 15.7 kJ/mol·H, the enthalpy of decomposition is 15.1 kJ/mol·H [4].

It is well known that one of the main problems of most hydride-forming alloys limiting their practical application is their susceptibility to surface contamination by reactive gases like oxygen. Oxygen on the surface of the alloys produces a reactive effect, i.e., it initiates a chemical reaction that results in volumetric corrosion of the alloy and, as a result, irreversible reduction of the hydrogen capacity. The high activation energy between the physisorption and chemisorption states of hydrogen on the oxidized surface prevents dissociative chemisorption and associative desorption. Molecular hydrogen cannot penetrate the oxide surface layer to dissociate on the metal surface below the oxide. On the other hand, dissolved hydrogen cannot leave the surface because associative desorption is prevented [5]. Even low oxygen concentrations in hydrogen gas can cause problems with repeated cycling of an alloy [6].

These problems, in principle, are also relevant for the intermetallic $LaNi_5$ alloy, but unlike most hydride-forming alloys, $LaNi_5$ is relatively resistant to oxygen impurities in hydrogen. Traces of oxygen, which are always present in varying amounts in hydrogen, do not catastrophically poison the active surface of $LaNi_5$ when multiple cycles of hydrogen absorption-desorption are performed. During the first few cycles, oxygen absorption-desorption does have a poisoning effect on $LaNi_5$, but as cycling continues in hydrogen with oxygen admixture, the kinetics and hydrogen capacity are substantially restored. After this initial transition period, oxygen becomes a classical reactant, i.e., it produces a reactive effect and slowly converts lanthanum atoms into La_2O_3 or various lanthanum hydrates or hydroxides [7-11].

The specific effect of oxygen on $LaNi_5$ is explained by a number of authors as follows. Lanthanum diffuses to the surface in the surface layer of a freshly prepared $LaNi_5$ sample since the surface energy of lanthanum is lower than that of nickel; the surface is enriched with lanthanum, achieving thermodynamic equilibrium state [12, 13]. Given that there is some preferential oxidation of lanthanum over nickel, the interaction with oxygen produces La_2O_3 or $La(OH)_3$. Some surface nickel is also thought to be oxidized. The resulting complex oxides are disproportionated by surface diffusion,

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resulting in the formation of composite films of nickel clusters within the stable lanthanum oxide or hydroxide [11]. Such clusters are catalytically active. Metallic nickel catalyzes hydrogen dissociation being the first stage of the hydrogen absorption process. Segregation and reduction of Ni occurs in each hydrogenation cycle. This process represents the mechanism of $LaNi_5$ active surface self-regeneration. Thus, according to the above, oxygen causes the separation of the alloy components into lanthanum oxidation products (oxides or hydroxides) and nickel clusters.

A somewhat different picture is given in papers [14-16]. According to these authors, exposure of $LaNi_5$ to oxygen leads to complete oxidation of surface lanthanum to La_2O_3. All the nickel present on the surface is also oxidized. Its oxides consist of NiO, $Ni(OH)_2$, and Ni_2O_3, but the latter two components exist only in a few upper monolayers. The La_2O_3 layer extends to a greater depth than the NiO layer. The latter is present only as thin oxide layers. Thus, it is believed that the NiO oxide is distributed over the La_2O_3 surface and essentially behaves as a system on a metal carrier, which has a higher catalytic activity towards hydrogen.

It was also shown in [17, 18] that although lanthanum oxidizes quite rapidly when exposed to oxygen, nickel oxide is present in the first few surface monolayers along with lanthanum oxide. The authors believe that the lanthanum-rich oxide layer is important not because it provides large nickel clusters on the surface, but rather because it protects the underlying material, i.e., the $LaNi_5$ itself. In [19] it was shown that when $LaNi_5$ is exposed to oxygen, only the lanthanum atoms are oxidized, not the nickel atoms. Nickel segregation occurs in each hydrogen sorption-desorption cycle. The lanthanum in this model actually serves as a gas absorber that provides the formation of pure nickel clusters.

Thus, the above hypotheses indicate that at present there is no consensus on the processes and results of interaction between oxygen with the $LaNi_5$ intermetallic alloy surface. There is no consensus on how the alloy components react to the presence of oxygen and which chemical compounds are in fact formed on the surface. This fact gives grounds for further research.

The purpose of this work is to study the chemical composition of surface monolayers of $LaNi_5$ intermetallic alloy during interaction with oxygen as well as to study the change in this composition depending on oxygen pressure and on the depth of oxygen location by using the secondary ion mass spectrometry method.

RESEARCH METHODS

The chemical composition of the alloy surface, as well as the change in this composition depending on the experimental conditions, was studied using the secondary ion mass spectrometry method. This method makes it possible to directly detect hydrogen and its compounds, as well as to study the changes in the composition of such compounds depending on the experimental conditions.

The samples under study were pellets pressed from moderately fine-grained (less than 1 mm) $LaNi_5$ alloy. Ar^+ ions with energies of 10 keV in the analysis of positive ions and 18 keV in the analysis of negative secondary ions were used as primary ions. The primary beam current density and vacuum conditions corresponded to the SIMS dynamic mode. The experimental setup was equipped with an energy filter for secondary ions, which allowed measuring the emission intensities of only low-energy secondary ions that mostly characterized the presence and composition of chemical compounds on the surface under study. The emission intensities of secondary ions were measured within the dynamic range of at least 6 orders of magnitude. The samples were annealed before the measurements in a residual vacuum at a temperature of ~ 1000 K in order to partially clean the surface from chemical compounds that are either desorbed or dissolved into the volume of the material during annealing. After the annealing, the sample surface was cleaned using the primary ion beam until the mass-spectrum composition and secondary ion emission intensity stabilized completely. The composition of the gas phase was monitored using a gas mass spectrometer, which also was used for measuring small partial pressures of gases in the vacuum chamber after the necessary calibrations had been performed. In the cases when the multi-atomic secondary ion emissions are complexly overlapped by their mass numbers, their specific contributions were separated according to the usual procedure, taking into account the natural distribution of isotopes. The temperature of the alloy sample during the measurements, including studies of oxygen interaction with the alloy, was ~ 325 K.

EXPERIMENTAL RESULTS

After the annealing and cleaning of the sample with the primary beam, the mass spectra of both positive and negative secondary ions were measured. The analysis of the spectra showed that they contain numerous emissions of atomic and cluster ions of the alloy components. There are also emissions of ions that indicate the interaction between the alloy atoms on the surface with the gas phase and bulk impurities, i.e., emissions corresponding to compounds of lanthanum and nickel with hydrogen, oxygen, and carbon. This indicates that even after annealing and primary beam cleaning there are some chemical compounds which include hydrides, oxides, hydroxides and carbides on the surface of the samples studied. Similar results regarding the mass spectra composition of secondary ions sputtered from the $LaNi_5$ surface are given in [20-22].

In the further experiments, the mass spectra of positive and negative secondary ions at elevated oxygen partial pressures of $6.6 \cdot 10^{-7}$ to $8.8 \cdot 10^{-4}$ Pa and residual hydrogen partial pressure were measured. Such mass spectra contain a large set of oxygen-containing emissions of positive and negative secondary ions. Emissions of oxygen-containing ions, which include lanthanum atoms, were the most intensive in the positive ion spectra. In the spectra of negative ions, there was a large set of oxygen-containing ion emissions, which included nickel atoms. There were also a large number of oxygen-containing emissions of complex secondary ions that include lanthanum, nickel, and oxygen atoms with various atomic ratios. In spite of the fact that the residual partial pressure of hydrogen in the sample chamber during the experiments is $4\text{-}5\cdot10^{-6}$ Pa, there was emission of hydroxide ions in the spectra, along with the emission of corresponding oxide ions.

We also measured the dependences of the emissions intensities for a number of oxygen-containing secondary ions on the oxygen partial pressure in the sample chamber at the residual hydrogen partial pressure. The positive secondary ion spectra were measured at the primary beam current density of 9 $\mu A\cdot cm^{-2}$ and the negative secondary ion spectra were measured at the primary beam current density of 17 $\mu A\cdot cm^{-2}$. Figures 1a, 2a, 3a, 4a show examples of the most characteristic intensity dependences on oxygen partial pressure measured for some positive and negative oxygen-containing secondary ions with lanthanum and nickel, as well as for some intermetallic lanthanum-nickel ions.

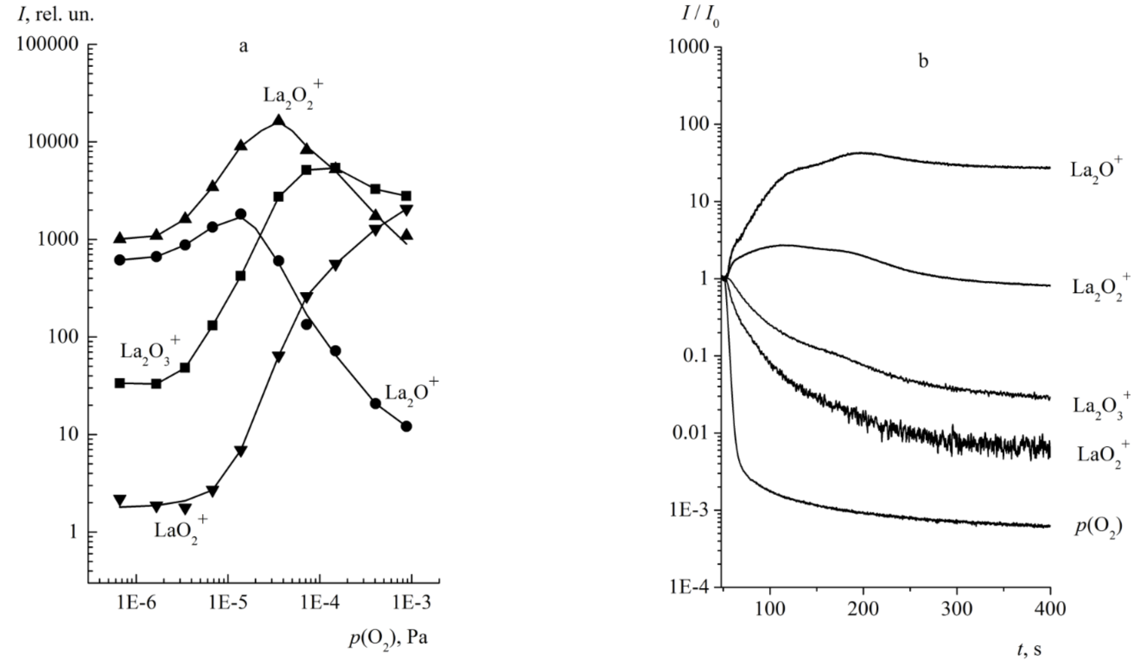

Figure 1. a: Dependences of the emission intensities of positive secondary ions with two lanthanum atoms on the oxygen partial pressure; b: Dependences of the emission intensities of positive secondary ions with lanthanum on sputtering time after the exposure in oxygen.

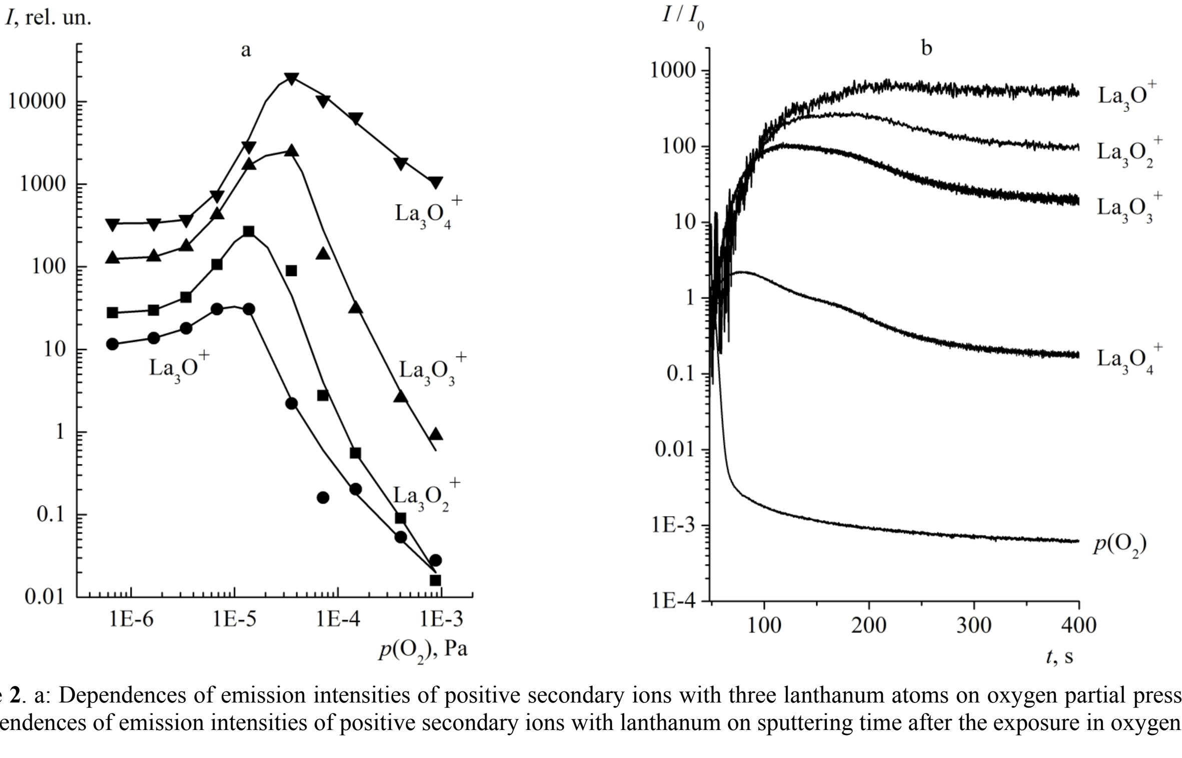

Figure 2. a: Dependences of emission intensities of positive secondary ions with three lanthanum atoms on oxygen partial pressure; b: Dependences of emission intensities of positive secondary ions with lanthanum on sputtering time after the exposure in oxygen.

As a continuation of studying the interaction between $LaNi_5$ and oxygen, the experiments were conducted to obtain the dependences of the emission intensities for previously studied secondary ions on the sputtering time after the sample exposure to oxygen. An oxide structure, which, as noted above, is characterized by a set of oxygen-containing secondary ions and by the ratio of their emission intensities, was formed on the sample surface at the increased oxygen partial pressure. This structure was then sputtered by the primary beam. As the sputtering proceeded, changes in the emission intensities of the selected secondary ions were recorded.

These experiments were carried out as follows. After the surface of the sample was cleaned by the primary beam in a residual vacuum with continuous recording of the selected ion emission intensity, oxygen was injected into the chamber up to a pressure of $\sim 3.3\cdot10^{-4}$ Pa. After 46-48 seconds, the oxygen inlet was shut off and then the time dependences of the secondary ion emission intensity and oxygen pressure in the sample chamber were measured. The oxygen pressure was recorded using a gas mass spectrometer. Fig. 1b, 2b, 3b show the measurement results at the sputtering stage after shutting off the oxygen inlet for oxygen-containing positive ions with lanthanum and for negative ions with nickel. For comparison convenience, the real emission intensities in these figures are divided by the intensity at the time point corresponding to the oxygen shutting off. Thus, the curves in Figs. 1b, 2b, 3b show how many times the emission intensity changes during the sputtering time with respect to the starting point. The same figures show the dependences of the oxygen partial pressure in the chamber also normalized to their initial value.

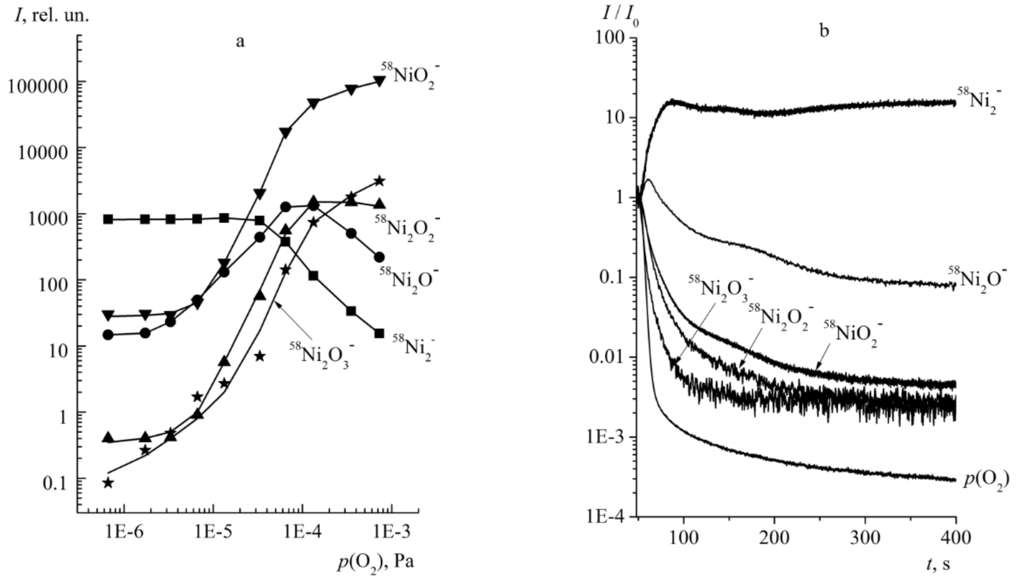

Figure 3. a: Dependences of emission intensities of negative secondary ions with nickel on oxygen partial pressure; b: Dependences of emission intensities of negative secondary ions with nickel on sputtering time after the exposure in oxygen.

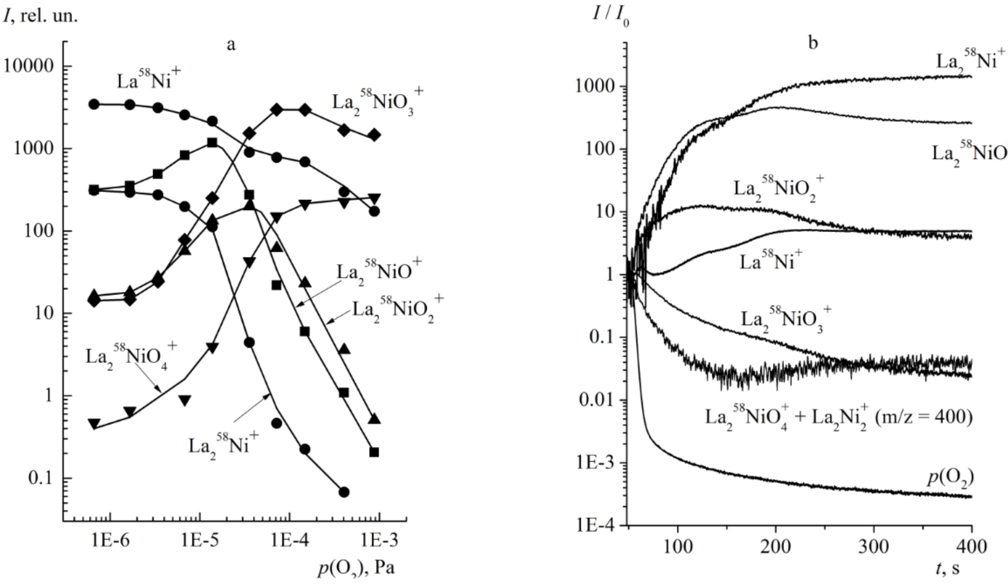

Figure 4. a: Dependences of emission intensities of complex secondary ions with lanthanum and nickel on oxygen partial pressure; b: Dependences of emission intensities of complex secondary ions with lanthanum and nickel on sputtering time after the exposure in oxygen.

Fig. 4b shows the results of measurements at the sputtering stage for complex secondary ions with lanthanum and nickel. In this case, the oxide sputtering experiment was slightly modified. After the sample surface was cleaned with the primary beam in the residual vacuum, the primary beam was shut off. Oxygen was injected into the chamber up to the partial pressure of $3.3\cdot10^{-4}$ Pa. After holding for ~ 50 seconds, the oxygen inlet was shut off, the primary beam was switched on and the sputtering began at this moment. As in the previous case, the actual emission intensities in this figure are normalized to the intensity at the point corresponding to the primary beam turning on. This sequence of actions, compared to the previous, makes it possible to estimate the influence of the primary beam on the oxidation processes.

The curve labeled in Fig. 4b as $La_2{}^{58}NiO_4{}^+$+$La_2Ni_2{}^+$ represents the sum of $La_2{}^{58}NiO_4{}^+$ and $La_2Ni_2{}^+$ secondary ion emissions (400 amu); separation of their specific contributions was not performed, since the signal recording was performed in continuous mode (in contrast to the curve for $La_2{}^{58}NiO_4{}^+$ in Fig. 4a). It is thus taken into account, that at the indicated experimental conditions the contribution of $La_2Ni_2{}^+$ ions to the total signal is insignificant.

RESULTS DISCUSSION

The basis for the secondary ion mass spectrometry method, which makes it possible to infer a conclusion about the surface composition based on the analysis of measurement results, is the following model. An impact of a primary ion on a solid body initiates a cascade of binary collisions of target atoms. Sputtering of secondary ions from the surface occurs when a sufficiently energetic cascade approaches the surface. [23]. In the sputtering process, multi-atomic complexes as part of the surface and near-surface regions are sputtered along with single-atomic or two-atomic particles. Since the sputtered secondary ions are part of the surface and near-surface region, the composition diversity of positive and negative secondary ions observed in secondary ion spectra is determined exclusively by the surface and near-surface monolayer composition of the solid from which the sputtering takes place. A change in the surface composition also determines the trends of the secondary ion emission intensity dependences on the experimental parameters.

Obviously, the comparison of the secondary ion mass spectra composition with specific chemical compounds on the surface should be done with caution. It should be kept in mind that chemical compounds on the surface correspond to a much greater extent to the composition of the neutral rather than ionic component of the sputtering products. The composition of sputtered multi-atomic ions can be influenced by the processes of charge acquisition and retention.

The analysis of the results obtained in the present work allows us to conclude that oxygen forms strong chemical bonds with both alloy components when it enters the surface of the $LaNi_5$ alloy. This is also evidenced by the presence of a large set of secondary ions of $La_nO_m{}^\pm$ and $Ni_nO_m{}^\pm$ type, as well as by the presence of multi-atomic secondary ions comprising both alloy components like the $La_nNi_mO_k{}^\pm$ type (where n, m and k may take different values in the case of positive and negative ions). The presence of such emissions in the mass spectrum suggests that when oxygen adsorbs on the $LaNi_5$ surface, it not only forms strong chemical bonds with both alloy components, but also forms a common structure consisting of lanthanum, nickel and oxygen.

As can be seen from Figs. 1a-4a, the emission intensities of most oxygen-containing secondary ions pass through a maximum as oxygen pressure increases. Moreover, the more oxygen atoms in the composition of a secondary ion are per metal atom, the higher the oxygen pressure at the point where the maximum is observed for such ions. There are also secondary ions which emission intensities only tend to plateau with increasing oxygen partial pressure. The observed dependences of the emission intensity on the oxygen partial pressure reflect the process of oxygen concentration increasing in the formed oxide structure. In other words, the observed dependences indicate that as the partial pressure of oxygen increases, an oxide structure in which the ratio of oxygen atoms to the number of matrix atoms increases is realized on the surface and in the near-surface region of the $LaNi_5$ sample. From the point of view of the analysis method used, for each specific value of oxygen partial pressure the formed oxide structure is characterized by a certain ratio of emission intensities of oxygen-containing secondary ions.

It should be emphasized that the oxygen concentration on the surface, and so the equilibrium surface coverage with oxygen-containing chemical compounds in our experimental conditions is determined by the dynamic equilibrium between the processes of oxygen adsorption from the gas phase and sputtering by the primary beam. There are also the effects of ion beam mixing. Analysis of the results obtained at oxide sputtering shows the following. The oxygen partial pressure $p(O_2)$ in the sample chamber, after the shut off drops by two orders of magnitude during ~10 seconds. At the same time, the emission intensity of secondary ions changes much more slowly. For some secondary ions, the emission intensity grows with the sputtering time; for others it decreases, and for some ions, it passes through a maximum. This applies to lanthanum ions, nickel ions, and complex lanthanum-nickel ions in Fig. 1b-4b. This behavior of the emission intensity dependences on sputtering time for the selected ions correlates well with the oxygen dependences for these ions in Figs. 1a-4a. Qualitatively, the course of the dependences of the ion emission intensity on sputtering time repeats in reverse order the course of the corresponding dependences obtained when the partial pressure of oxygen is increased.

This correlation allows us to state that in sputtering experiments, after pumping oxygen out of the chamber, and as the formed oxides are being sputtered, the situation on the surface is the opposite of the one that occurs when the partial pressure of oxygen increases, and when the number of oxygen atoms per matrix atom in the surface structure increases. Namely, as the oxygen-containing structure formed at the maximum partial pressures of oxygen in our experiments is sputtered, the number of oxygen atoms per matrix atom decreases.

The data shown in Fig. 1b-4b evidence that the sputtering of the formed oxides continues for hundreds of seconds. This indicates that the formed oxide compounds have a bulk structure and occupy dozens of monolayers. In such a bulk oxide structure, the outer monolayers are characterized by the highest oxygen concentration. The oxygen concentration decreases along the transition to the underlying monolayers.

The sputtering results obtained after the exposure in oxygen under the primary beam (Figs. 1b-3b) and after the exposure with the primary beam turned off (Fig. 4b) allow a qualitatively similar interpretation. This suggests that the primary beam does not significantly affect the $LaNi_5$ oxidation processes, while introducing the sputtering and ion beam mixing factors.

Among other things, the results of the conducted sputtering experiments show that there is no direct correlation between the change in the oxygen partial pressure with time and the change in the intensity of oxygen-containing secondary ion emission with time. This is direct evidence that the observed secondary ions are not a product of association of sputtered surface fragment with oxygen in the gas phase at the fly-off stage, but are the products of oxide compounds being sputtered and do characterize the surface and near-surface region composition.

CONCLUSION

SIMS studies of the chemical composition of $LaNi_5$ alloy surface monolayers during interaction of the alloy with oxygen showed the following. As a result of the interaction between oxygen and the alloy sample, a complex chemical structure including oxygen, lanthanum and nickel is formed on the $LaNi_5$ surface and in the near-surface region. Oxygen in such a structure forms strong chemical bonds with both alloy components. This is evidenced by the presence of a large set of oxygen-containing emissions of positive and negative secondary ions with lanthanum, with nickel, and oxygen-containing lanthanum-nickel cluster secondary ions in the mass spectra. The resulting oxide compounds have a bulk structure and occupy dozens of monolayers. In such a bulk oxide structure, the outer monolayers are characterized by the highest ratio of the oxygen atoms number to the matrix atoms number. This ratio decreases along with the transition from the superficial to the underlying monolayers of the alloy. The quantitative and qualitative ratio of elements in the formed oxide structure depends mainly on the oxygen partial pressure and to a much lesser extent on the sputtering action of the primary beam.

The observed secondary ions are not a product of association between sputtered surface fragments and oxygen in the gas phase at the fly-off stage after sputter-ejection, but they are products of the oxide compounds being sputtered, hence they characterize the composition of surface and near-surface region.

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REFERENCES

[1] J.H.N. van Vucht, F.A. Kuijpers, and H.C.A.M. Bruning, Philips Research Report, **25**(2), 133 (1970). OSTI Identifier: 4129528.
[2] P. Dantzer, Materials Science and Engineering, **A329–331**, 313 (2002). https://doi.org/10.1016/S0921-5093(01)01590-8
[3] B.P. Tarasov, M.V. Lototsky, and V.A. Yartys, Russian Chem. J. **L**(6), 34 (2006). http://www.chem.msu.ru/rus/jvho/2006-6/34.pdf (In Russian)
[4] S Luo, J.D Clewley, Ted B Flanagan, R.C Bowman Jr., and L.A Wade, J. Alloys Comp. **267**(1-2), 171 (1998), https://doi.org/10.1016/S0925-8388(97)00536-7
[5] L. Schlapbach, A. Seiler, F. Stucki, and H.C Siegmann, J. Less Common Metals, **73**, 145 (1980). https://doi.org/10.1016/0022-5088(80)90354-9
[6] F. Schweppe, M. Martin, and E. Fromm, Journal of Alloys and Compounds, **253-254**, 511 (1997). https://doi.org/10.1016/S0925-8388(96)03002-2
[7] G.D. Sandrock, and P.D. Goodell, J. Less Common Metals, **73**(1), 161 (1980). https://doi.org/10.1016/0022-5088(80)90355-0
[8] P.D.Goodel, and P.S.Rudman, J. Less Common Metals, **89**(1), 117-125 (1983). https://doi.org/10.1016/0022-5088(83)90255-2
[9] P.D. Goodell, J. Less Common Metals, **89**(1), 45 (1983). https://doi.org/10.1016/0022-5088(83)90247-3
[10] H.C. Siegmann, L. Schlapbach, and C.R. Brundle, Phys. Rev. Let. **40**(14), 972 (1978). https://doi.org/10.1103/PhysRevLett.40.972
[11] W.E. Wallace, R.F. Karlicek, and H. Imamura, J. Phys. Chem. **83**(13), 1708 (1979). https://doi.org/10.1021/j100476a006
[12] J.J. Burton, and E.S. Machlin, Phys. Rev. Lett. **37**(21), 1433-1436 (1976). https://doi.org/10.1103/PhysRevLett.37.1433
[13] S.H. Overbury, P.A. Bertrand, and Q.A. Somorjai, Chemical Reviews, **75**(5), 547-560 (1975). https://doi.org/10.1021/cr60297a001
[14] P. Selvam, B. Viswanathan, C.S. Swamy, and V. Srinivasan, J. Less Common Metals, **163**, 89 (1990), https://doi.org/10.1016/0022-5088(90)90088-2
[15] P. Selvam, B. Viswanathan, and V. Srinivasan, Jnt. J. Hydrogen Energy, **14**(9), 687 (1989). https://doi.org/10.1016/0360-3199(89)90048-7
[16] P. Selvam, B. Viswanathan, C.S. Swamy, and V. Srinivasan, Int. J. Hydrogen Energy, **16**(1), 23 (1991). https://doi.org/10.1016/0360-3199(91)90057-P
[17] J.H. Weaver, A. Franciosi, W.E. Wallace, and H. Kevin Smith, J. App. Phys. **51**, 5847-5851 (1980). https://doi.org/10.1063/1.327544
[18] J.H. Weaver, A. Franciosi, D.J. Peterman, T. Takeshita, and K.A. Gschneidner Jr. J. Less Common Metals, **86**, 195 (1982). https://doi.org/10.1016/0022-5088(82)90205-3

[19] L. Schlapbach, Solid State Communications, **38**(2), 117 (1981), https://doi.org/10.1016/0038-1098(81)90802-4
[20] H. Züchner, R. Dobrileit, and T. Rauf, Fresenius J. Anal. Chem. **341**, 219 (1991). https://doi.org/10.1007/BF00321552
[21] H. Züchner, P. Kock, T. Bruning, and T. Rauf, J. Less Common Metals, **172-174**(Part A), 95 (1991). https://doi.org/10.1016/0022-5088(91)90437-9
[22] V.A. Litvinov, I.I. Okseniuk, D.I. Shevchenko, and V.V. Bobkov, J. Surf. Invest. X-ray, Synchrotron and Neutron Techniques, **12**(3), 576 (2018). https://doi.org/10.1134/S1027451018030321
[23] *Sputtering by Particle Bombardment I: Physical Sputtering of Single-Element Solids* edited by R. Behrisch (Springer-Verlag, Berlin-Heidelberg, 1981), pp. 284. https://doi.org/10.1007/3-540-10521-2

РОЗПИЛЕННЯ ОКСИДІВ З ПОВЕРХНІ $LaNi_5$

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Методом вторинної іонної мас-спектрометрії (ВІМС) проведено дослідження змін хімічного складу поверхневих моношарів інтерметалевого сплаву $LaNi_5$ в процесі взаємодії з киснем. Досліджувані зразки представляли собою таблетки, спресовані з дрібнозернистого сплаву $LaNi_5$. В якості первинних іонів використовувалися іони Ar^+ з енергією 10 – 18 кеВ. Щільність струму первинного пучка становила 9-17 мкА·см$^{-2}$, що відповідає динамічному режиму ВІМС. Інтенсивності емісій вторинних іонів вимірювалися у динамічному діапазоні не менше 6 порядків. Перед вимірами зразки відпалювали у залишковому вакуумі при температурі ~ 1000 К. Після відпалу проводилась очистка поверхні пучком первинних іонів до повної стабілізації складу мас-спектра та інтенсивності емісій вторинних іонів. Склад газової фази контролювався за допомогою газового мас-спектрометра. Проведені дослідження показали, що в результаті впливу кисню, на поверхні і в приповерхневої області $LaNi_5$ утворюється комплексна хімічна структура, що включає кисень, лантан і нікель. Кисень, в такій структурі утворює міцні хімічні зв'язки з обома компонентами сплаву. Про це свідчить наявність в мас-спектрах великого набору кисневмісних емісій позитивних і негативних вторинних іонів з лантаном, з нікелем, а також кисневмісних кластерних лантан-нікелевих вторинних іонів. Оксидні сполуки, що утворюються, мають об'ємну структуру і займають десятки моношарів. У такої об'ємної оксидної структурі зовнішні моношарі характеризуються найбільшим відношенням кількості атомів кисню до кількості атомів матриці. При переході до нижчого моношару це відношення зменшується. Цей процес відбувається рівномірно, без будь-яких фазових трансформацій. Спостережувані вторинні іони є продуктами розпилення оксидних сполук і не є продуктом асоціації розпилених фрагментів поверхні з киснем газової фази на етапі відльоту. Вони характеризують хімічний склад поверхневої і приповерхневої області сплаву при його взаємодії з киснем.

Ключові слова: ВІМС, інтерметалевий сплав $LaNi_5$, кисень, поверхня, оксиди