Kinetics of Hydrogen Desorption From Ni—In Composites, Synthesized by Electrochemical Method

Alla Zvyagintseva

ABSTRACT

The results of the study of the kinetics of the thermal desorption spectrum of deuterium accumulated with Ni$_{64}$In$_{36}$-D$_x$ composites synthesized by the method of electrochemistry are presented. The limits of desorption temperatures for ion-implanted deuterium were determined depending on the implanted dose. The measured content of deuterium alloy is 4 at. D/at. Met (~8.7 wt. % D; ~4.6 wt. % hydrogen). The formation of the deuterium thermal desorption spectrum depends on the implantation dose. An increase in the content of implanted deuterium contributes to the formation of a solid solution of hydrogen isotope in the electrochemical composite Ni$_{64}$In$_{36}$ with a destruction temperature in vacuum of ~520 K and nickel hydride with hydrogen with a decomposition temperature of ~330 K. The calculation of the activation energy of thermal desorption is produced for a hydrogen peak with a temperature of maximum 500 K. Arrhenius polyterms were obtained for two values of the reaction order index: $\gamma = 1$ and $\gamma = 2$. Arrhenius polyterms demonstrate the second order of reaction and the quadratic dependence of the desorption rate on the number of implant particles. The activation energy for a peak with a maximum temperature of 500 K is 2.9 eV, which indicates low energy extraction of the hydrogen isotope.

INTRODUCTION

Possessing enormous prospects, hydrogen energy is one of the important directions in the modern development of energy throughout the world. An
important component of the development progress in this area is the development of highly efficient and safe hydrogen storage systems.

The analysis of the methods studied shows that hydrogen storage in solid-state materials is superior to other methods, such as, for example, balloon or cryostat. The storage of hydrogen in the solid matrix is superior, in particular, in optimal characteristics of bulk and gravimetric density, in safe storage without complex cryostat systems, and also in hydrogen extraction under acceptable thermodynamic conditions, without high temperatures and pressures.

Works by foreign authors demonstrate various ways of storing hydrogen: in the form of combination hydrides [1, 2], metal hydrides [3], organometallic composites [4], carbon nanomaterials [5], however, not all of the proposed materials fully provide harmony production and consumption [6].

The strategy of the research is to form a material in which, for a specific technical application, accumulation processes with high density and hydrogen extraction of the required amount with minimal costs were fairly easily carried out.

To meet these requirements, it is most preferable to use nickel-based metals and alloys.

The purpose of this publication is to study the possibility of using nickel and materials based on it as energy storage devices.

The work clearly shows the fundamental possibility of changing the hydrogen permeability of the object of study due to the creation in the metal structure of various kinds of hydrogen traps (structural, impurity) in order to retain hydrogen in the metal structure. As an object of study, an electrochemical system was chosen - Ni-In alloy.

In the previously published work of the author, the properties of this alloy were already investigated and it was noted that when nickel was doped with indium [7] with indium content up to 10 % Ni-In alloy hydrogenation decreased.

However, new studies conducted by the author have shown that in materials synthesized by the electrochemical method, intermetallic metal compounds can serve as structural traps for hydrogen atoms. Therefore, this particular system, Ni-In, which is not prone to hydrogen accumulation and the formation of chemical compounds of hydrogen with metal in the form of hydrides, was the object of research in this article.

Physically, this can be interpreted as follows.

When the concentration of indium is 9 % wt. in solid solutions with nickel, the alloy does not constitute a trap for hydrogen atoms. The indium atom radius is larger than the nickel radius (rNi = 0.138 nm; rIn = 0.184 nm), and during the synthesis of the Ni-In composite, in the vicinity of indium, compressive stresses arise that displace hydrogen. Therefore, electrochemically synthesized Ni-In composites with an indium content of less than 9 % wt. are unable to occlude hydrogen. With increasing indium concentration of more than 10 % wt. intermetallic phases are formed and can act as structural traps for hydrogen.
atoms, provided that the intermetallic phase is not coherent with the Ni matrix through a network of dislocations. Consequently, the accumulating properties of the composites will improve. Information on the possibility of formation of hydride phases in Ni-In composites was not found in publications, with the exception of the author's works [8–10].

EXPERIMENTAL TECHNIQUE

Ni-In composites were formed by electrochemical deposition on a copper substrate (0.05 mm thick) from the electrolyte composition: 140 g/l NiSO$_4$·7H$_2$O; 20 g/l Na$_2$SO$_4$·10H$_2$O; 1–12 g/l In$_2$(SO$_4$)$_3$. Some components of the electrolyte cannot be disclosed [8]. The electrolysis was performed with a platinum anode and a copper cathode. The content of components in the composite Ni-In was measured by x-ray fluorescence method. X-ray diffraction studies were performed on HZG-4 diffractometer in CuKα radiation (β-filter).

To record the kinetics spectrum of deuterium desorption from Ni–In composites depending on the concentration of components and the dose of implanted deuterium, the method of thermal desorption mass spectrometry (TDS) was used. The introduction of deuterium and the recording of the spectra of thermal desorption were carried out on the SKIF facility, described in more detail in [8, 9]. In order to reduce the effect of background hydrogen contained in the composites and in the target chamber, the accuracy of the measurements was used as implant deuterium.

The implantation of deuterium ions into composites was carried out by bombardment with 12 keV ions and doses in the range of 3×10$^{17}$-3×10$^{18}$ atD/cm$^2$. The amount of desorbed deuterium extracted from the composite when heated was calculated graphically from the area of the figure lying under the gas emission curve, according to the method described in [9, 10].

EXPERIMENTAL SECTION

Diffraction patterns of Ni-In composites with different concentrations of the components are shown in Figure 1. On diffractograms, one can observe intense narrow lines of the substrate (copper FCC structure), the line (220) is more intense than the other lines.

For composite no. 1 composition of 24 wt. % In, only the substrate lines (Cu) are visible on the diffractogram: a very intense line (220) and weak lines (111), (200) and (311) (Figures 1a and 1e). The increase in the concentration of indium in composites for samples no. 2 of 38 wt. % In and no. 3 composition of 45.6 wt. % In is accompanied by the appearance and increase in the intensity of new lines in diffraction patterns (Figures 1b and 1c).
The appearance of new lines can be explained by the formation of intermetallic compounds \( \text{Ni}_3\text{In} \) and \( \text{In}_2\text{Ni} \), the possible formation of which is indicated by the phase diagram of the Ni–In system [11]. A further increase in the concentration of indium in sample no. 4 to 61.3 wt. % In (Figure 1d) indicates the formation of additional structural formations - intermetallic compounds: \( \text{Ni}_3\text{In} \), \( \text{In}_2\text{Ni} \), \( \text{InNi} \), the existence of which was found on the phase diagram of the Ni-In system [11]. The presence of free indium is recorded on a diffraction pattern from pure indium (Figure 1g).

Experimental studies made it possible to select both the electrolyte composition and the electrolysis modes that synthesize the structure of the Ni-In composite with indium and nickel intermetallics. By the diffractometric method, it was found that with increasing indium concentration in the Ni–In composite phases of intermetallic compounds of the composition \( \text{InNi}_2 \), \( \text{InNi}_3 \), \( \text{In}_3\text{Ni}_2 \), \( \eta\)-\( \text{In}_{27}\text{Ni}_{10} \) are formed.

For the first time, the results on thermal desorption of deuterium from Ni–In electrochemical composites were obtained and published in [8–10]. In this paper, the results on the registration of thermally desorbed deuterium from the Ni-In composite were summarized and verified.

First, the amount of hydrogen embedded in the composites in the process of their production by electrolysis was recorded and taken into account, Figure 2. Thermal desorption of hydrogen for sample no. 2 of composition 38 wt. % In is observed at temperatures of 550 and 850 K. The amount of occluded hydrogen in composites of composition 38 % wt. In and 45.6 % wt. In corresponds to 2 at. H/at. Meth, 4 at.H/at.Met respectively. On the curves in Figure 2, two hydrogen peaks are observed at 550 K and 850 K. It is possible that hydrogen desorption at temperatures above 650 K is caused by both the desorption of hydrogen and hydrogen-containing gases from the measurement chamber designs during sample heating and the annealing of hydrogen traps at temperatures above 650 K. For the first time, the possibility of additional doping of hydrogen into an electrochemical system was demonstrated in [8–10]. The possibility of doping hydrogen into composites of the selected atomic composition \( \text{Ni}_{70}\text{In}_{30} \) with an indium content of 38 wt. % and nickel 62 wt. %; composition \( \text{Ni}_{64}\text{In}_{36} \) with an indium content of 45.6 mas. % and nickel 54.4 wt. %.
Figure 3 shows the characteristic thermal desorption spectrum of deuterium implanted in electrochemical Ni\textsubscript{64}In\textsubscript{36} composite samples depending on the implanted deuterium dose and for one sample phase composition. The deuterium DTP spectra are a function of the implantation dose. The deuterium content of the composite with the Ni\textsubscript{64}In\textsubscript{36} phase composition is 4 at. D/at. Met., which corresponds to (~8.7 wt. % D; ~4.6 wt. % hydrogen) at low doses of implanted deuterium, a single peak with a maximum temperature of ~ 550 K is present in the spectrum (Figure 3, curve 1). Increasing the dose leads to the appearance of a low-temperature peak with a maximum temperature of ~ 450 K (Figure 3, curve 2). With a further increase in the dose of implanted deuterium, the maximum temperature of the peak of gas evolution gradually shifts to lower temperatures (Figure 3, curves 3-5).

Using an example of a sample of composition 24 wt.% In and 76 wt.% Ni implanted with deuterium ions with a dose of 3×10\textsuperscript{17} D/cm\textsuperscript{2}, the activation energy of thermal desorption was calculated for a peak with a maximum temperature of 500 K (Figure 4a, curve 1) using the known equation desorption kinetics [12]:

\[
\frac{dn_i}{dt} = -K_i n_i^\gamma(t) e^{-E_i/kT},
\]
where $\frac{dn}{dt}$ - is the desorption rate, which at each moment of time corresponds to the ordinate of the envelope of the i-th peak of thermal desorption; $n_i(t)$ - the number of particles remaining in the sample to a given desorption point; $K_i$ - desorption rate constant for the i-th peak; $\gamma$ - reaction order; $E_i$ - activation energy of desorption; $k$ - is the Boltzmann constant; $T$ - is the current temperature value.

Figure 2. Spectra of thermal desorption of hydrogen released from Ni–In electrochemical composites: 1 - composition of 38 wt. % In; 2 - composition of 45.6 wt. % In.

Figure 3. The thermal desorption spectra of deuterium implanted in electrochemical Ni$_{64}$In$_{36}$ composite samples: 1–$3\times10^{17}$ D/cm$^2$; 2 – $7.5\times10^{17}$ D/cm$^2$; 3–$1.3\times10^{18}$ D/cm$^2$; 4 –$2\times10^{18}$. 
Figure 4. Arrhenius polyterms for the peak of the deuterium thermal desorption spectrum from sample composition of 24 wt.% In and, respectively, 76 wt.% Ni, implanted with deuterium ions with a dose of $3 \times 10^{17}$ D/cm$^2$, calculated for two values of the reaction order $\gamma = 1$ and $\gamma = 2$.

The transformation of equation (1), taking into account $T = T_0 + \alpha t$ (where $\alpha$ is the heating rate of the sample) and the subsequent logarithm, leads to the relation:
\[
\ln \left[ -\frac{dn_i}{dT} / n_i^\gamma \right] = -\frac{E_i}{k T} + \ln K_i / \alpha.
\]

Substituting the values from the experimentally measured spectrum of thermal desorption, Arrhenius polyterms were constructed for two values of the reaction order index: \( \gamma = 1 \) and \( \gamma = 2 \).

Summarizing the above, we can conclude that the accumulating properties of nickel in the presence of indium intermetallics increase. In the vicinity of the indium intermetallic, tensile stresses can occur and hydrogen is segregated at the boundary of these compounds, which is confirmed by the thermal desorption data. Indium intermetallic compounds with nickel are traps for hydrogen atoms in the Ni-In composite. Mathematical modeling of the hydrogen permeability of metals in the presence of traps of different types was carried out by the author in the monograph [12].

CONCLUSION

During the work, the following main results were achieved:

1. The spectroscopies spectra of deuterium from electrochemical composites Ni\(_{64}\)In\(_{36}\)-D\(_x\) were studied by mass spectroscopy, from which the temperature ranges of desorption of ion-implanted deuterium were determined depending on the implantation dose. The maximum achievable deuterium concentration of 4 at. D/at. Met, which corresponds to ~4.6 wt. % hydrogen.

2. The formation of the deuterium thermal desorption spectrum depends on the implantation dose. An increase in the content of implanted deuterium contributes to the formation of a solid solution of hydrogen isotope in the electrochemical composite Ni\(_{64}\)In\(_{36}\) with a destruction temperature in the vacuum of ~ 520 K and nickel hydride with hydrogen with a decomposition temperature of ~ 330 K.

3. The activation energy of thermal desorption was calculated for a hydrogen peak with a maximum temperature of 500 K. The Arrhenius polyterms were obtained for two values of the reaction order index: \( \gamma = 1 \) and \( \gamma = 2 \). The data of the Arrhenius polymer indicate the second order of reaction and the quadratic dependence of the desorption rate on the number of particles deuterium. The value of the activation energy for a peak with a maximum temperature of 500 K is 2.9 eV, which indicates low energy extraction of the hydrogen isotope.

REFERENCES