Статья поступила в редакцию 12.11.15. Ред. рег. № 2404 The article has entered in publishing office 12.11.15. Ed. reg. No. 2404

УДК 544.6.018 doi: 10.15518/isjaee.2015.21.012

ОСОБЕННОСТИ ПОВЕДЕНИЯ ВОДОРОДА В МЕТАЛЛАХ И СПЛАВАХ, ПОЛУЧЕННЫХ ЭЛЕКТРОЛИЗОМ, И ВОЗМОЖНОСТИ ИХ ПРИМЕНЕНИЯ В АЛЬТЕРНАТИВНЫХ ИСТОЧНИКАХ ЭНЕРГИИ

А.В. Звягинцева[1], Ю.Н. Шалимов[2], М.В. Лутовац[3]

[1]Воронежский государственный технический университет
394026 Воронеж, Московский пр., д. 14
E-mail: zvygincevaav@mail.ru
[2]НПП «ЛУЧ», г. Воронеж, Россия
E-mail: shalimov_yn@mail.ru
[3]Факультет бизнеса и промышленного менеджмента Белградского союзного университета,
Сербская Королевская Академия Наук, Белград, Сербия
E-mail: gsmmitar@gmail.com

Заключение совета рецензентов: 15.11.15 Заключение совета экспертов: 18.11.15 Принято к публикации: 21.11.15

Вопрос о роли водородной энергетики в развитии благосостояния общества можно рассматривать только в одном аспекте, а именно достойное существование того или иного сообщества может быть обеспечено только при всестороннем использовании водородных технологий. Потенциал водорода далеко не исчерпан в традиционной энергетике. По мере успешного решения проблем хранения водорода и создания высокоэффективных топливных элементов будет реализована абсолютно надежная система резервирования собственных нужд при нештатных режимах работы электростанции. Одним из сдерживающих факторов развития водородной энергетики являются существующие технологии хранения (криогенная и балонная) небезопасны и энергоемки.

Ключевые слова: металлы, сплавы, электролиз, температурная зависимость внутреннего трения, накопители водорода

TO THE FEATURE OF BEHAVIOR OF HYDROGEN IN THE METALS AND ALLOYS, GOT ELECTROLYSIS, AND POSSIBILITY OF THEIR APPLICATION IN ALTERNATIVE ENERGY SOURCES

A.V. Zvyagintseva[1], Yu.N. Shalimov[2], M.V. Lutovats[3]

[1]Voronezh state technical university, Voronezh, Russia
E-mail: zvygincevaav@mail.ru
[2]OJSC research and production Association " LUTCH",
Voronezh, Russia
E-mail: shalimov_yn@mail.ru
[3]Faculty of business and industrial management
Belgrade, Serbia,
E -mail: gsmmitar@gmail.com

Referred: 15.11.15 Expertise: 18.11.15 Accepted: 21.11.15

The question of the role of hydrogen energy in the development of the welfare society can be seen in only one aspect, namely the decent life of a community can only be achieved with full use of hydrogen technologies. The potential of hydrogen is far from being exhausted in the traditional energy sector. As the successful solution of the problems of hydrogen storage and the creation of highly efficient fuel cells will be implemented absolutely reliable backup system own needs when abnormal modes of operation of the power plant. One of the limiting factors in the development of hydrogen energy are existing storage technologies (cryogenic and bottled) and energy consuming unsafe.

Keywords metals, alloys, electrolysis, temperature dependence of internal friction, hydrogen stores.

Алла Витальевна Звягинцева
Alla V. Zvyagintseva

Сведения об авторе: канд. техн. наук, доцент, доцент кафедры химии ВГТУ.
Образование: Воронежский гос. университет им. Ленинского комсомола (1983).
Область научных интересов: электрохимические системы и процессы, материаловедение, водородная энергетика; моделирование и прогнозирование опасных природных явлений.
Публикации: более 200, 3 монографии.

Information about the author: candidate of technical sciences, associate professor, Department of Chemistry of the Faculty of Radio Engineering and Electronics, Voronezh State Technical University.
Education: Voronezh State University (1983).
Research area: electrochemical systems and processes, materials, hydrogen energy; modeling and forecasting of natural hazards.
Publications: more than 200, 3 monographs.

Юрий Николаевич Шалимов
Yuri N. Shalimov

Сведения об авторе: д-р техн. наук, профессор кафедры электромеханических систем и электроснабжения ВГТУ. Руководит лабораторией экспериментальных технологий энергоресурсосбережения.
Основной круг интересов: электрохимические процессы в водородной энергетике.
Публикации: более 500, 2 монографии.

Information about the author: doctor of Technical Sciences, Professor of electromechanical systems and electricity VSTU. Directs the laboratory of experimental energy saving technologies.
Research area: electrochemical processes in hydrogen energy.
Publications: more than 500, 2 books.

Митар В. Лутовац
Mitar V. Lutovac

Сведения об авторе: академик, профессор, доцент Факультета бизнеса и промышленного менеджмента Белградского союзного университета.
Образование: магистратура Технического факультета Чакчак (2008).
Область научных интересов: информационные технологии.
Публикации: более 35.

Information about the author: acad., professor, docent, Faculty of Business and Industrial Management, University Union Belgrade.
Education: magistrature Faculty Cakcak (2008).
Research area: information technology.
Publications: more than 35.

Hydride storage method currently not widespread due to insufficiency knowledge on this issue. Hydride hydrogen accumulators based on intermetallic compounds of rare earths and platinum group metals provide the effective storage, but require large financial costs [1-6]. In recent years particular interest abroad and in Russian works on the use of hydrogen storage cause the alloys based on aluminum and some transition metals. Further development of the works in this direction will allow to hope that the accumulators of high hydrogen capacity will be created. Solving of this problem will speed up the process of introducing of hydrogen energetics in production.

The materials of this work is aimed at considering the possibility of the use electrochemical systems for hydrogen storage, this paper discusses some aspects of the behavior of hydrogen in metals and alloys based on nickel and chromium. Unlike from metals produced by metallurgical method, electrolytic metals and alloys have a different mechanism of interaction.

Firstly: the hydrogen formed on the electrode (cathode) is released together with the atoms of the metal according to the equations:

$$Me^{n+} + ne \rightarrow Me^0; \quad (1)$$

$$H^+ + e \rightarrow H^0; \quad (2)$$

$$H^0 + H^0 \rightarrow H_2. \quad (3)$$

Second, the presence of atomic hydrogen (reaction 2) increases the probability of interaction of metal with hydrogen. If the metal cathode has a great affinity for hydrogen, it becomes probable process:

$$n\mathrm{Me}^0 + m\mathrm{H}^0 \rightarrow \mathrm{Me}_n\mathrm{H}_m\,, \qquad (4)$$

wherein n and m are stoichiometric coefficients.

Thirdly: the formation of structural defects, with greater potential in comparison with the atoms becomes possible during process electrocrystallization of metals. In the presence of such defects the interaction of the hydrogen atom is most likely. Therefore, the process of hydrogenation of electrochemical systems is different from hydrogen interaction with metals of metallurgy.

Consider some features of the behavior of hydrogen in metals and alloys, obtained by electrolysis. Interactions metals, which are obtained by electro-crystallization, with hydrogen has a specific character. On the amount of absorbed hydrogen and the formation of compounds of the type Me-H affects not only the nature of the metal, but also the presence of structural defects. As stated previously [1 - 7], the main reaction of hydrogen with the metal occurs at structural defects. Determination of the binding energy of the hydrogen with metal showed that it forms hydride type compound, the proof of this fact is the decomposition temperature of the compound Cr-H (200 °C). After complete removal of hydrogen from the samples on the basis of Cr they were subjected to a secondary hydrogenation using vacuum extraction method.

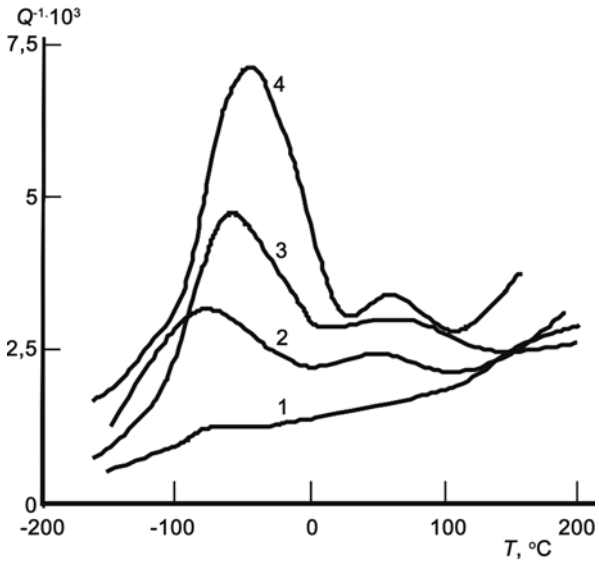

Рис. 1. Температурная зависимость внутреннего трения электролитического хрома, подвергнутого наводороживанию в 1 н H_2SO_4 при $i_к$ = 1 А/дм^2 в течение различного времени (τ): 1 – ненаводороженный образец; 2 – τ = 8 минут; 3 – τ = 14 минут; 4 – τ = 20 минут

Fig. 1. The temperature dependence of internal friction electrolytic chromium in the process of hydriding in 1n H_2SO_4 at i_k = 1 A/dm^2 for a different time (τ): 1) unhydrogenated sample; 2) τ = 8 minutes; 3) τ = 14 minutes; 4) τ = 20 minutes

It has been established that as a result of the secondary hydrogenation the internal friction peak is reproduced on curve $Q^{-1} = f(T)$ the same temperature range, moreover, the size of the peak indicates the amount of absorbed hydrogen [8].

Fig. 1 shows the temperature dependence of internal friction hydrogenated chromium in 1n H_2SO_4 at i_k = 1 A/dm^2. The peak increases in size and shifted towards higher temperatures (curves 2, 3, 4) with increasing time of hydrogenation. The activation energy of this peak is determined from the frequency shift, it differs little from the activation energy of freshly precipitated chromium.

It was experimentally determined half-width of the peak Q^{-1} It was experimentally determined half-width of the peak of the ratio:

$$\Delta\left(\frac{1}{T}\right)_{эк} = \frac{1}{T_л} - \frac{1}{T_п}\,,$$

where $T_л$ and $T_п$ – absolute temperature corresponding to points on the half-width of the maximum of the left and right sides.

The values obtained were compared with the calculated values determined by the formula a simple relaxation process:

$$\Delta\left(\frac{1}{T}\right)_{расч} = \frac{K}{\Delta H} = \frac{K}{\Delta H}\ln\left(\frac{2+\sqrt{3}}{2-\sqrt{3}}\right),$$

where K – the Boltzmann constant; ΔH – activation energy.

Analysis of the data showed that the peak dependence $Q^{-1}(T)$ of electrolytic chromium is too wide (3÷4 times) for the relaxation process. Apparently, in an electrolytic chromium is observed overlay of processes of ascending diffusion of hydrogen atoms randomly distributed at lattice defects. Degree saturation of chromium atoms valency bonds located on local distortions of the lattice, is different, and consequently is unequal. As a result, the activation energy (ΔH) of hydrogen diffusion has no a single value, but a series of relatively similar values. It is known that the relaxation time (τ_r) of diffusion depends on the temperature as follows: $\tau_r = \tau_0 \exp(\Delta H/RT)$.

Thus, diffusion of hydrogen is characterized by a certain spectrum τ_r, that is obviously the cause of the expansion of the internal friction peak in curve $Q^{-1}(T)$ of electrolytic chromium.

From the theory of internal friction is known that deformation of metals containing impurities (H, C, O, N), is the cause of the appearance of peaks on the temperature axis $Q^{-1}(T)$, the magnitude of which depends on the impurity concentration and the degree of deformation [8 9, 10]. Position of deformed peaks on the temperature axis Q^{-1} is dependent on the degree of deformation and its increasing causes displacement of the peak to lower temperatures. Changing the activation energy of the relaxation process in this case is the result

of the interaction of impurity atoms of hydrogen with dislocations [10, 11]. The free energy of interaction of impurity atoms with dislocations in the crystal is defined as the work that commit stresses created by dislocations, when administered impurity atoms into the crystal.

As we stated earlier, hydrogenation metals under cathodic polarization occurs in places of structural defects. In this case, the atomic hydrogen reacts forming compounds with the metal of the type Me-H. The experimental data agree well with the foregoing assumptions. Some discrepancies with research of other authors can be explained by distinction opportunities of the methods and types of sensors used in the experiment. In particular, when estimating the amount of absorbed hydrogen by the classical method of vacuum extraction the results of measurements may be distorted due to the inclusion in the cathode deposit finely dispersed precipitate of chromium hydroxide $Cr(OH)_3$, which under thermal decomposition forms a water vapor distorting indicators of measurements. This disadvantage can be eliminated by the use of additional devices (nitrogen trap). Furthermore the use first time internal friction method for studying the structure of electrolytic metals and alloys has allowed to determine experimentally the binding energy of the metal-hydrogen [8-11]. Therefore, the credibility of the experimental results obtained using the above method is not in doubt. The reproducibility of the measurement results is good enough (deviation in parallel dimensions are within ± 10%).

Determining the degree of diffusion of cations H+ deep into electrode anode may be accomplished by analyzing the curves of $Q^{-1} = f(T)$, obtained with samples with different thickness metal who are prone to passivation. Receipt of such information on the restructuring of the metal along the normal to the plane of the electrode will allow to make not only theoretical conclusions about the mechanism of diffusion of cations H^+, but also to solve technological problems in the field of secure accumulation of hydrogen as fuel.

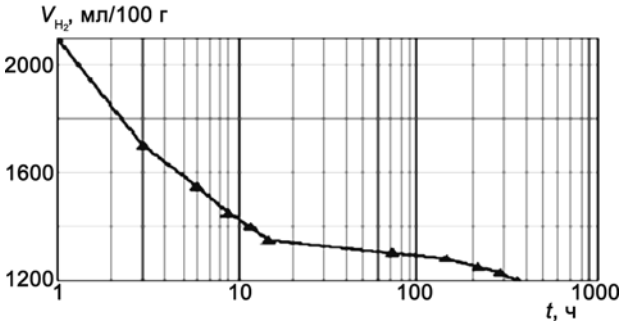

Рис. 2. Зависимость содержания водорода в образцах сплава Ni-B от времени «старения»
Fig. 2. Dependence of the hydrogen content in the samples of the alloy Ni-B from time "aging"

One proof of the theory of the nature of communication in system hydrogen-metal, which determines the basic form of the chemical bond as a hydride is the analysis of the dependence of the amount of hydrogen in the samples of the nickel-boron alloy subjected to "aging". Samples were prepared from sulfaminoacidic electrolyte with a boron-containing additive [12-16]. At identical regimes of electrolysis (current density, the duration of the electrolysis, the chemical composition of the electrolyte and its temperature), the samples were subjected to "aging". The subsequent extraction of hydrogen from a sample demonstrated that the hydrogen content depends on the time "aging". Character histogram is shown in Fig. 2.

Analysis of character of change volumes of extracted from the samples shown at the histogram shows that the most sharply changes in the hydrogen content of freshly precipitated coatings. In accordance with this it can be assumed that the relaxation of structural defects Ni-B alloy is damped in time process. Consequently, with increasing time "aging" normalization alloy structure is more complete. This fact is also serves as confirmation of our findings that the interaction of hydrogen with metals most likely on defects of the metal structure. Finally, the character of changes magnitude and the peak position on the curve $Q^{-1} = f(T)$ confirms our assumption which been said above that samples which have undergone more prolonged "aging" have a strongly pronounced internal friction peak which shifted to region of positive temperatures. The amplitude of the peak in the curve corresponds to the amount of hydrogen absorbed by the sample. The samples with a small period of "aging" characterized by "blurred" (implicit) peak and increased background on curve $Q^{-1} = f(T)$.

Thanks to the "temporary" relaxation of alloy structure and a very low binding energy Me-H appears the above described phenomenon of "flow" of hydrogen. The abnormally large amount of hydrogen-absorbing alloy Ni-B, can be explained as the possibility of the formation of additional hydrogen bonds with boron.

By analyzing been said above, it can be assumed that the effect of spontaneous "flow" of hydrogen from a metal due to the large number of connections H-Me, having a very low energy of rupture. The number of such defects in the Ni-B alloy is several times greater than in the samples of pure nickel. Likely to, the electrolytic nickel and boron form the interstitial solution, which introduces microdistortions into the crystal lattice of the formed alloy. In place of such distortion are stationed hydrogen atoms forming a compound with nickel and boron. Possibility of additional the introduction of hydrogen in an electrochemical system was first considered in [16].

In this paper, composite materials of Ni-In by electrodeposition have been manufactured and temperature ranges of desorption ion-implanted deuterium depending on the ratio of components and the dose of implanted deuterium been studied. It is shown that the structure of the spectrum of thermal desorption (TDS) of deuterium is a function of implant dose. Studying interrelation between the structure, composition, electrochemical composites and with the

ability to absorb the implanted deuterium, and the ability to use these systems for hydrogen accumulation with a view to its storage in metal hydride state is the aim of our further research. The main advantages of metal hydride systems of bound hydrogen storage are: high volume density of hydrogen, an acceptable range of operating pressures and temperatures, the constancy of the pressure in the hydrogenation and dehydrogenation, the ability to control the pressure and rate of release of hydrogen, high purity of the generated hydrogen, compactness, and safety at work, low energy costs. Investigation of technological parameters allows to conclude that the most comfortable in operation, safe, economical and environmentally friendly way of store hydrogen is a metal hydride method. Thus, on the basis of the research, as a result of discussion and analysis of experimental data using the method of internal friction for the examination of samples on the basis of chromium and nickel, we were able to set:

1. The interaction of hydrogen with a metal chiefly occurs on the structural defects of the sample. When you delete these defects as a result of annealing hydrogen peak in the internal friction disappear.

2. Dopant to be included in base of the metal structure, to create additional potential wells, fixing hydrogen, contribute to increasing the amount of absorbed gas; with the energy of Me-H should vary quite widely creating multicomponent alloys apparently, you can get hydrogen containers with controlled yield of hydrogen when the temperature changes.

References

1. Gamburg D.Ju., Semenov V.P., Dubovkin N.F., Smirnov L.N.; Pod red. D.Ju. Gamburga, N.F. Dubovkina. *Vodorod. Svojstva, poluchenie, hranenie, transportirovanie, primenenie*. [Hydrogen. Properties, production, storage, transport, use.] Ref. Book. Moscow, Himija Publ., 1989.

2. Oudriss A., Creus J., Bouhattate J., Conforto E., Berziou C., Savall C., Feaugas X. Grain size and grain-boundary effects on diffusion and trapping of hydrogen in pure nickel // Acta Materialia. 2012. № 60. P. 6814-6828.

3. Sudzuki K., Fudzimori H., Hasimoto K. *Amorfnye metally*. [Amorphous metals.] Moscow: Metallurgija Publ., 1987.

4. Fromm E., Uhcida H. Surface phenomena in hydrogen absorption kinetics of metals and intermetallic compounds // J. of Less-Common Metals. 1987. V. 131. P. 1-12.

5. Chene I. Contribution of cathodic Charging to hydrogen storage in metal Hydrides // J. of Less-Common Metals. 1987. V. 131. P. 337-347.

6. Libowitz G.G., Maeland A.J. Hydide formation by BCC solid solution alloys // Materials Science Forum. 1988. V. 31. P. 176-196.

7. Povetkin V.V., Kovenskij I.M. *Struktura jelektroliticheskih pokrytij* [The structure of the electrolytic coatings]. Moscow: Metallurgija Publ., 1989.

8. Grankin Je.A., Shalimov Ju.N., Ostrovskaja E.N. The dependence of internal friction electrolytic chromium by modes electrocrystallisation // *Al'ternativnaja jenergetika i jekologija* [Alternative Energy and Ecology]. 2004. № 7. P. 12-18. (in Russian)

9. Novik A., Berri B. *Relaksacionnye javlenija v kristallah* [Relaxation phenomena in crystals]. Pod red. Je.M. Nadgornogo, Ja.M. Sojfera. Moscow: Atomizdat Publ., 1975.

10. Krishtal M. A., Piguzov Ju. V., Golovin S. A. *Vnutrennee trenie v metallah i splavah* [Internal friction in metals and alloys]. Moscow: Metallurgija Publ., 1964.

11. Aleksandrov L.N., Mordjuk V.S. *Vnutrennee trenie i fizicheskie svojstva tugoplavkih metallov.* [Internal friction and physical properties of refractory metals.] Saransk: Mordovian book publisher Publ., 1965.

12. Zvyagintseva A.V. Interaction peculiarities of hydrogen and Ni-B galvanic alloys. Carbon Nanomaterials in Clean Energy Hydrogen Systems. Springer, 2008. P. 437-442.

13. Zvyagintseva A.V., Shalimov Yu.N. On the Stability of Defects in the Structure of Electrochemical Coatings // Surface Engineering and Applied Electrochemistry. 2014. Vol. 50, No. 6. P. 466-477.

14. Zvjaginceva A.V. The dependence of the interaction of metals with hydrogen from the structure of electrochemical systems. *Uchenye zapiski Tavricheskogo nacional'nogo universiteta im. V.I. Vernadskogo. Serija «Biologija, himija»* [Scientific notes of Taurida National University. Vernadsky. Series «Biology, chemistry»]. 2013. Vol. 26 (65). № 4. P. 259-269. (in Russian)

15. Vlasov N.M., Zvjaginceva A.V. *Matemati-cheskoe modelirovanie vodorodnoj pronicaemosti metallov* [Mathematical modeling of the hydrogen permeability of metals]. Voronezh: Voronezhskiy Gos.Univ. Publ., 2012.

16. Zvyginceva A.V., Morozov O.M., Zhurba V.I., Progolaieva V.O. Effects of Deuterium Concentration on Deuterium Desorption Temperature Range from Ni-In Composites // Scientific Journal. Proceedings of the international conference. nanomaterials: applications and properties. 2013. Vol. 2, No. 1. 01NTF37(3pp).