

UDC 537.634:620.179.17:620.193

V. Skalsky; S. Hirnyj; B. Klym; Ye. Pochapsky; Ya. Tolopko; P. Dolishniy

*Karpenko Physical-Mechanical Institute,
National Academy of Sciences of Ukraine, Ukraine*

THE EFFECT OF HYDROGEN ELECTROLYTICALLY ABSORBED BY STEEL ON THE PARAMETERS OF MAGNETOACOUSTIC EMISSION SIGNALS

The summary. This paper presents preliminary results of study on the applicability of magnetoacoustic emission (MAE) method as a tool for sensing the presence of electrolytically absorbed hydrogen in low carbon steel. It is clearly presented that for the employed laboratory settings a MAE signal parameter, which is the sum of amplitudes of MAE signal impulses, is strongly dependent on the presence of hydrogen in the bulk of the material. It is noted that for the low cathodic current there is a delay in time required, probably, for the removal of the corrosion products from the steel surface and providing the conditions for the sufficient amount of hydrogen to be absorbed by the near-the-surface volume of the sample. The results are shortly discussed regarding the issues connected to the applicability of MAE method for nondestructive evaluation (NDE) of hydrogen absorbed by structural materials.

Key words: low-carbon steel, plastic deformation, elastic deformation, nondestructive evaluation, magnetic field, ferromagnetic materials, magnetoacoustic emission, Barkhausen jumps

В. Скальський, докт. техн. наук; С. Гірний, докт. філос.; Б. Клим, канд. техн. наук; Є. Почапський, канд. техн. наук; Я. Толопко; П. Долішній

ВПЛИВ ЕЛЕКТРОЛІТИЧНО АБСОРБОВАНОГО СТАЛЛЮ ВОДНЮ НА ПАРАМЕТРИ СИГНАЛІВ МАГНЕТОАКУСТИЧНОЇ ЕМІСІЇ

Резюме. Наведено попередні результати досліджень щодо можливості використання методу магнетоакустичної емісії (МАЕ) для виявлення водню електролітично абсорбованого низьковуглецевою сталлю. Наведені результати переконливо свідчать, що за зазначених умов проведення експерименту параметр сигналу МАЕ, яким є сума амплітуд імпульсів МАЕ, дуже залежить від наявності водню в об'ємі матеріалу. Зазначено, що для низьких катодних струмів спостерігається затримка в часі, необхідна, вірогідно, для відновлення продуктів корозії на поверхні сталі та забезпечення умов для абсорбування достатньої кількості водню приповерхневими шарами металу. Результати коротко обговорені з огляду на перспективність застосування методу МАЕ як засобу неруйнівного контролю водню абсорбованого конструкційними матеріалами.

Ключові слова: низьковуглецева сталь, пластична деформація, пружна деформація, неруйнівний контроль, магнетне поле, ферромагнетні матеріали, магнетоакустична емісія, стрибки Баркгаузена.

Hydrogen induced degradation of structural steels: a need for a sensitive NDE method of hydrogen detection. Structural materials aging which is reflected in the losses of plasticity and fracture toughness parameters has long been recognized in many industries: petrochemical, oil and gas production and transportation, civil engineering, nuclear and fossil fuel power, etc [1, 2]. Degradation of material's physical properties starts from the submicrostructural changes usually driven by dislocation dynamics through the dislocation pile-ups or by diffusion that results in irreversible segregation (either to the grain boundaries or to microstructural defects within the grains) of certain elements prone to form a precipitate phase of deleterious properties. In some materials this process could lead to microstructural

inhomogeneities of sufficient size that become the locations of decohesion or microvoid formation, which, in turn, could be the starting places for crack growth with eventual fracture of the material.

Degradation aging of low carbon and low alloy steels – the most widely used classes of structural materials – is a well documented phenomenon pertaining, e.g., to fossil-fuel boiler piping or natural gas transmission pipelines. Among the key players in this aging process are varying stress and temperature fields and diffusible hydrogen [3, 4]. However, if the effect of mechanical and thermal fatigue have been well treated to the microstructural changes in metal, the understanding of the role of diffusible hydrogen still remains somewhat unclear despite of more than half-century dedication of scientists and engineers to the issue of hydrogen in metals.

It has been clarified that hydrogen transport from hydrogen-containing gas (H_2 , H_2O , H_2S , NH_3 etc.) or liquid (H_2O , H_2SO_4 , HCl etc.) into the metal requires several steps. The process of hydrogen sorption from aqueous electrolytes starts from electrosorption of hydrogen-containing species with formation of chemisorbed hydrogen atom according to equations (1) or (2) [5]:



electrons being provided by either external electric current source (cathodic protection, stray current, etc.) or by the electrochemical oxidation of iron either in the vicinity of the hydrogen-sorbed location or at the far distance through the work of an electrochemical macrocell:



Part of the chemisorbed hydrogen atoms undergo absorption and enter the bulk of the material:



followed by the transport process through diffusion, which is driven by the gradient of the chemical potential of hydrogen $\mu(H)$; or by dislocation tunneling, which is driven by the hydrogen-dislocation interaction and dislocation dynamics. As to $\mu(H)$, it depends on the parameters like thermal and stress fields, chemical composition, free volume distribution, etc.

Due to the complexities of the transport mechanisms of hydrogen from the outer media to under the metal surface and through the bulk of the material, it is practically impossible to use any but statistical approach in the studies of hydrogen-induced degradation phenomena in structural materials of commercial quality. This approach has to be based, on the one hand, on the empirical relations between the measured bulk physical parameters, such as temperature, hardness, impact fracture toughness, applied stress, content of non-metallic phases in steel, activities of chemical species, and, on the other hand, on the dynamics of degradation of several physical properties of the material, like impact fracture toughness, relative elongation, or tensile strength. As to the parameters related to hydrogen, which could be directly measured or calculated from the measurements, one can name cathodic current surface density, effective hydrogen diffusion coefficient, concentration of irreversibly trapped hydrogen, bulk hydrogen concentration, and hydrogen flux through the metal.

Each of the listed “hydrogen” parameters has a complicated origin that excludes the linear relationships with the “degradation” parameters and could not be simply applied to either the judgment on the health of the material, or the prediction of its lifetime. However,

some tendencies between these parameters do exist and they have to be explored as deep as possible, especially considering the eager need of the society for the non-destructive evaluation (NDE) of the exploited structures. Actually, there exist only the electrochemical methods that can non-destructively evaluate “hydrogen” parameters like flux through the metal or effective diffusion coefficient [6-8]. These methods are very sensitive and accurate when used in the laboratory settings on the samples with rather large surface areas. Application of such methods becomes complicated in the field conditions on the objects like pipelines, so is the quest for other methods like microhardness, magnetic, or acoustic [9-11].

Objective. In this paper we present an attempt to use the magnetoacoustic emission (MAE) method as a tool for sensing hydrogen activity in low carbon steel. The explanation of principles of MAE is given in the other paper submitted to this conference and will not be elaborated here.

Experimental procedure. We studied cylindrical samples ~260 mm long and 12 mm in diameter made of low carbon steel grade 15. The sample was placed into a solenoid wound on a 50 mm diameter plastic pipe that also served as an electrolyzer. The coil was connected to the PC-controlled digital signal generator through the power amplifier and current measuring unit, so that the magnetic field strength could be calculated. An electrolyzer was filled with 0.1 NaOH solution which prevented the metal surface from excessive corrosion. A platinum anode coiled on a 35 mm diameter mesh was coaxial with the sample rod and the solenoid. A sample (cathode) and platinum anode were connected to the stabilized constant current source in order to generate atomic hydrogen on the metal surface. The machined edge of the rod sample was attached to the piezoceramic transducer that converted the surface displacements into the electric signals recorded by the specially engineered MAE measuring system, which in more details is described in another paper submitted to this conference. Surface displacements measured by the piezoceramic sensor are caused by the elastic waves generated in the bulk of the material during the magnetization process in the alternating external magnetic field. Actually, for steels, we listen only to the sudden jumps of the 90°-domain walls [12]. The domain wall dynamics being dependent on the bulk distribution of defects could have been dependent also on the hydrogen absorbed by metal during electrolytic charging. The dependencies of the acoustic emission signal (specifically such MAE parameter as sum of impulses' amplitudes) on i) the cathodic current with which hydrogen activity on the metal surface is controlled, ii) the magnetic field strength, and iii) the time of electrolytic charging were looked for in this study.

Results and Discussion. Figure 1 depicts the relationships between the parameter ΣA_i which is the sum of amplitudes (expressed in thousands of arbitrary units) of the registered MAE signal impulses and time of electrolytic hydrogen charging under cathodic current $I_c = 50$ mA. As could be deduced from this graph, initially ($t_H = 0$) the sum of impulses ΣA_i is about 100 and this level of MAE signal continues for more than 5 minutes – time needed for reduction of the surface oxyhydroxides and for atomic hydrogen to penetrate sufficiently deep and to a sufficient amount so it has an effect on the MAE parameters. In 600 s the sum of amplitudes ΣA_i exceeds 400 and it keeps increasing till more than 500 during the rest of the experiment. Thus, we received a spectacular manifestation on the influence of electrolytically absorbed hydrogen on the parameters of the MAE signals.

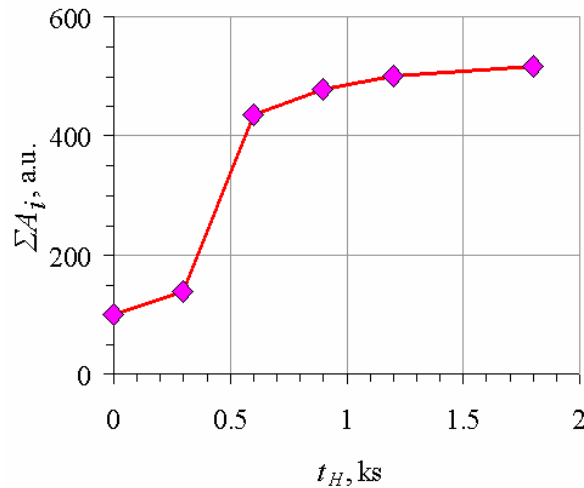


Figure 1. Change of MAE parameter ΣA_i with time of hydrogen charging t_H . Cathodic current $I_c = 50 \text{ mA}$, the amplitude of magnetic field strength $H_a = 8.7 \text{ kA/m}$

Let us now look at how this MAE sensitivity to the absorbed hydrogen depends on the magnetic field strength. Figure 2 presents two dependencies of ΣA_i on the amplitude of magnetic field strength H_a : one for the non-charged sample (graph 1) and one for the sample electrolytically charged with hydrogen at 50 mA for half hour (graph 2). The magnetic field strength varied within 10 kA/m, which is below the saturation knee on the B–H hysteresis curve for this steel. The difference between the non-charged and hydrogen charged condition is outstanding, as in the previous graph (Figure 1). It seems that under the used settings, the dependency of $\Sigma A_i = f(H_a)$ is close to linear. As per Figure 2, the increase in ΣA_i is not as high as in Figure 1, but still more than twofold, which again suggests that the method MAE could be further explored for its use as a non-destructive method for hydrogen detection.

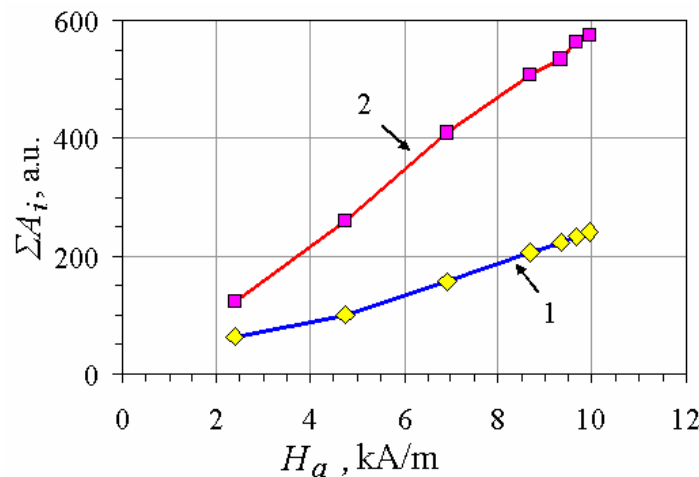


Figure 2. The effect of the amplitude of magnetic field strength H_a on MAE parameter ΣA_i for the non-charged sample (1) and the sample electrolytically charged at $I_c = 50 \text{ mA}$ for $t_H = 1800 \text{ s}$ (2)

Several sets of experiments have been conducted to verify the effect of the higher cathodic currents during the hydrogenation process. Figure 3 illustrates the case of hydrogen charging at cathodic current $I_c = 150 \text{ mA}$ with MAE signals recorded for the magnetic field strength $H_a = 8.7 \text{ kA/m}$. Two principal differences between Figs. 1 and 3 could be noted. Firstly, for the higher cathodic current the time of charging of the order of 300 s was

sufficient to increase the MAE parameter ΣA_i to almost maximum level, while for 50 mA this parameter remained close to the background noise. Secondly, in the case of $I_c = 50$ mA, the tendency for ΣA_i was to increase till the end of the experiment, while for $I_c = 150$ mA the MAE parameter reached its maximum at about 10 minutes and then gradually decreases by some 8 % till the end of the experiment.

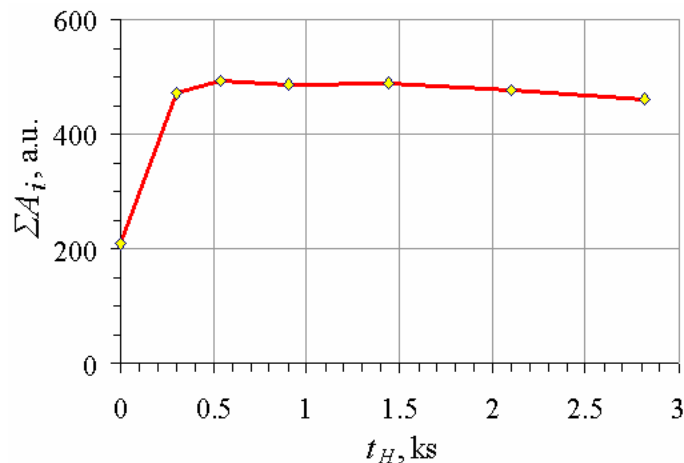


Figure 3. Change of the MAE parameter ΣA_i with time of hydrogen charging. Cathodic current $I_c = 150$ mA. Magnetic field strength $H_a = 8.7$ kA/m

Let us see how the parameter ΣA_i changes with the magnetic field strength during cathodic charging at $I_c = 150$ mA. Figure 4 illustrates this dependency for the sample charged for 1800 s. One can notice that these dependencies are quite similar to the ones presented at Figure 2. The levels of ΣA_i in the latter case are a little smaller than those obtained for 50 mA cathodic charging. This fact needs future investigation for explanations, but still the effect of hydrogen on the MAE parameter remains about two-fold, which is more than enough to seek the implementation of MAE method as a NDE tool for hydrogen detection in structural materials.

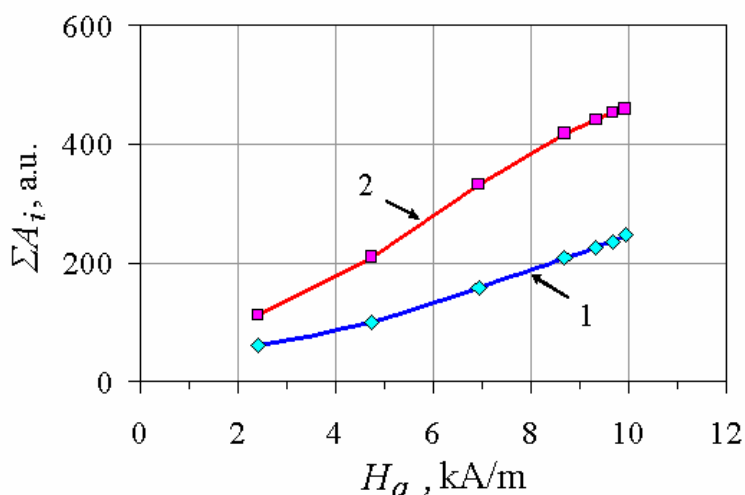


Figure 4. The effect of the amplitude of magnetic field strength H_a on MAE parameter ΣA_i for the non-charged sample (1) and the sample cathodically charged at $I_c = 150$ mA for $t_H = 1800$ s (2)

Last set of experiments has been conducted for the cathodic charging current of $I_c = 200$ mA and it has exhibited pretty similar result for an increase in the ΣA_i parameter as in the case of 150 mA. The dependency of ΣA_i on the maximum value of the magnetic field

strength H_a is presented in Figure 5. It could be noticed that, again, the value of ΣA_i increases about two-fold, though in this case a little less than in the case of 150 mA, the same tendency as was mentioned above.

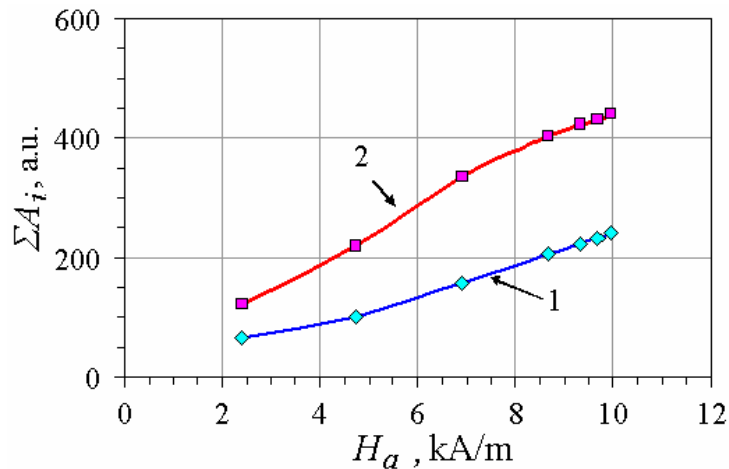


Figure 5. The effect of the amplitude of magnetic field strength H_a on the MAE parameter ΣA_i for the non-charged sample (1) and the sample cathodically charged at $I_c = 200$ mA for $t_H = 1800$ s (2)

The obtained results are very encouraging and motivating for further studies. If these dependencies are verified for different conditions and different materials so the boundaries for the testing procedures could be established that the hydrogen-containing samples could always be revealed when the value of MAE parameter ΣA_i crosses a threshold value of "hydrogen danger", this would open the door for the time- and cost-effective procedure for detection of hydrogen in the exploited structures. Obviously, these experiments raised many questions which are to be addressed in the near future, such as:

- a) why ΣA_i decreases with an increase of cathodic current?
- b) why ΣA_i decays after 10 minutes for the higher currents and keeps increasing for the lower one?
- c) what is the threshold of hydrogen content in the material for MAE method to sense it?
- d) what should be the parameters of the time changed magnetization $B(t)$ to produce the maximum sensitivity of MAE method to hydrogen?

However, regardless of the answers to these questions, it seems that the MAE method is indeed sensitive to hydrogen absorbed by steel. It worth noting that the cathodic current densities used in these studies are far from endangering values and could be compared to the currents widely used for cathodic protection of underground of underwater structures. It is well known that exactly for the reason of cathodic protection the aggressive carbonate-containing electrolytic environments are created under the disbonded coatings of buried natural oil and gas transmission pipelines, which are usually protected from corrosion by organic protective coatings and cathodic protection. Also, similar levels of stray currents could be applied to the networks of piping for gas and water distribution. Besides, the same levels of cathodic currents could easily be achieved in the structures galvanically coupled with dissimilar metals like zinc or corroding aluminum, or at macro- or mega-cells which could be formed on the structures of substantial sizes, provided that different parts of these structures exhibit different physical and chemical conditions, like temperature, concentration of oxidizers on the surface, porosity of the contacting soil, dynamics and nature of the contacting fluids, etc. Such current densities could not result in a quick degradation of metal, but, over the longer periods of time, being accompanied with mechanical and thermal cycling,

could well be the reason for hydrogen embrittling action and gradual degradation of structural materials. If the MAE method confirms its applicability at these low cathodic currents, it might find its use for detecting dangerous conditions that could cause accelerated aging of the materials.

For hydrogen-induced phenomena, the condition of a surface is extremely important issue since the influence of surface on the overall outcome of the process could be critical. Consider the following effects of surface on the hydrogen-induced processes in case of application of the MAE method for hydrogen detection. Firstly, the magnetization dynamics is very depth dependent being the highest at the very surface and decaying exponentially with depth (a so-called “skin effect”). This makes the volume, which is actively involved in domain wall dynamics (and thus magnetoacoustic emission from the domain wall jumps), confined to the surface layer with its depth being inversely dependent on the magnetic field frequency. On the other hand, the number of the elastic waves generated in this volume per unit time increases with frequency, so there is an optimal frequency for every particular setting, which produces the largest number of MAE impulses per unit time and thus makes the method most sensitive.

Secondly, the surface is acoustically more active than the bulk of the material. The surface Rayleigh waves and Love waves usually carry higher energy levels than longitudinal waves. The relationships between the contributions of different types of waves strongly depend on the geometrical shape of the studied objects, density, mechanical properties and stress fields. In every case, the contribution of surface vibrational modes is of major importance.

Thirdly, there is a reversible effect – the influence of surface vibrations on the chemical or electrochemical processes that take place on the surface. Since the reduction of hydrogen containing species takes place on the metal surface and the kinetics of such processes as electron transfer, dissociation, recombination are dependent on the movement of surface atoms, the elastic waves that travel through the metal and cause such movements should and do influence the velocity of these chemical processes. Same reasoning has to be applied to diffusion of hydrogen, the process strongly dependent on the atomic movement (as for instance reflected in the temperature dependence of diffusion coefficient) and thus on the vibrational modes that originate from the elastic waves traveling. Thus, the displacements of the surface and near-the-surface atoms have an effect on the kinetics of all stages of the electroadsorption and absorption processes.

Fourthly, both the surface and near-the-surface layers of metal are the places for maximum residual stresses, generated either by hydrogen or by machining operations during the sample preparatory stage. If hydrogen modifies the stress field in this near-the-surface volume of the sample, this can have an effect on the emissivity of elastic waves during the magnetization process as has been established before [13].

Fifthly, since the liquid, which surrounds the sample, is also a condensed media the losses due to refraction of waves are anticipated. This suggests that with different media types, these losses would be different and thus have to be considered if this MAE method will be implemented into the NDE detection of hydrogen. This would be important for the NDE of partially filled tanks, vessels and pipes.

Obviously, not only the surface’s role is important, but there is also a contribution of the bulk properties of the material. They include chemical and phase composition on a macro-, micro- and nano-scales (for instance, the content, morphology and distribution of a Si-containing phase that exhibit different magnetostrictive behavior); anisotropic parameters of the material (preferred orientation due to casting, rolling or heat-treating operations); defect distribution and their concentration; etc. All these parameters are important magnetically, acoustically, chemically and thus should be reflected on the parameters of MAE signals. Obviously, much work has to be done to clarify all these issues.

Thus, the presented results confirm that the method of magnetoacoustic emission is very sensitive to the presence of the absorbed hydrogen under conditions of mild cathodic charging – the conditions extremely important for non-destructive evaluation of materials. Further investigations are required for the possible implementation of this method into the area of materials inspection and evaluation.

Conclusions. This paper presents preliminary results from a study of the effect of electrolytically charged hydrogen on the magnetoacoustic emission response of carbon steel. It is clearly shown that introduction of hydrogen into a ferromagnetic material such as steel, results in manifold increase of a MAE parameter ΣA_i , which is a sum of amplitudes of impulses from the MAE signal. It is noted that there is a delay in time required, most probably, for the removal of the corrosion products from the steel surface and providing the conditions for the sufficient amount of hydrogen to be absorbed by the near-the-surface volume of the sample. The results are shortly discussed together with the issues connected to the applicability of MAE method as a NDE tool for hydrogen detection.

References

1. Batchelor A., Chandrasekaran M., Lam L.N. Materials degradation and its control by surface engineering. – World Scientific Publishing Co. Inc., 2010. – 450 p.
2. Handbook of environmental degradation of materials, Edited by M. Kutz. – William Andrew Publishing, Technology & Engineering, 2005. – 598 p.
3. Kurzydowski K.-J., Lunarska E. Hydrogen degradation of steels under long-term in-service conditions // Environment-Induced Cracking of Materials, Edited by S. Shipilov, R. Jones, J.-M. Olive and R. Rebak. – Amsterdam: Elsevier Ltd., 2008. – P. 349–361.
4. Okura I., Tahara J., Nishioka T., Yasuda O. Chapter 36 - Effects of cyclic plastic strains on fracture toughness of structural steels // Stability and Ductility of Steel Structures SDSS'97, Edited by: T. Usami and Y. Itoh. – Amsterdam: Elsevier Ltd., 1998. – P. 415–424.
5. Protopopoff E., Marcus Ph. Control by surface of the hydrogen evolution and absorption reactions on/in transition metals // Proceedings of the Symposium on Electrochemistry and Materials Science of Cathodic Hydrogen Absorption and Adsorption, Edited by B.E. Conway and G. Jerkiewicz. – The Electrochemical Society. Physical Electrochemistry Division, ECS PV 97-16, 1997. – P. 159–179.
6. Devanathan M.A.V., Stachurski Z. The adsorption and diffusion of electrolytic hydrogen in palladium // Proceedings of Royal Society, London. – 1962. – A270. – P. 90–102.
7. Manolatos P., Duret-Thual C., Le Coze J., Jerome M. The electrochemical permeation of hydrogen in palladium: Boundary conditions during a galvanostatic charging under low charging current densities // Corrosion Science. – 1995. – 37. – P. 1797–1807.
8. Chaudhari B.S., Radhakrishnan T.P. Evaluation of hydrogen diffusivity in mild steel from electropermeation transients under conditions of galvanostatic charging // Surface and Coatings Technology. – 1986. – 28. – P. 261–280.
9. Katz Y., Tymiak N., Gerberich W.W. Nanomechanical probes as new approaches to hydrogen/deformation interaction studies // Engineering Fracture Mechanics. – 2001. – 68. – P. 619–646.
10. Coluzzi B., Biscarini A., Mazzolai G., Mazzolai F.M., Tuissi A., Agresti F., Lo Russo S., Maddalena A., Palade P., Principi G. Physical properties of hydrogen in TiVMnCr bcc alloys as deduced from hydrogen absorption/desorption and mechanical spectroscopy experiments // Journal of Alloys and Compounds. – 2008. – 456. – P. 118–124.
11. Termsuksawad P., Niyomsoan S., Goldfarb R. B., Kaydanov V. I., Olson D. L., Mishra B., Gavra Z. Measurement of hydrogen in alloys by magnetic and electronic techniques // Journal of Alloys and Compounds. – 2004. – 373. – P. 86–95.
12. Buttle D.J., Briggs G.A.D., Jakubovics J.P., Little E.A. Magnetoacoustic and Barkhausen emission in ferromagnetic materials // Philosophical Transactions of the Royal Society, London. – 1986. – A320. – P. 363–378.
13. Kusanagi H., Kimura H., Sasaki H. Stress effect on the magnitude of acoustic emission during magnetization of ferromagnetic materials // Journal of Applied Physics. – 1979. – 50. – P. 2985–2987.