DOI: http://dx.doi.org/10.15407/tpwj2018.11–12.11

MAGNETOACOUSTIC DIAGNOSTICS OF HYDROGEN DAMAGE OF FERROMAGNETICS

Z.T. NAZARCHUK and **V.R. SKALSKY**
H.V. Karpenko Physico-Mechanical Institute of the NAS of Ukraine
5 Naukova Str., Lviv, 79050, Ukraine. E-mail: pminasu@ipm.lviv.ua

The experimental investigations were carried out in order to quantitatively determine a change of parameters of signals of magnetoelastic acoustic emission under effect of structural transformations and level of hydrogenation of ferromagnetic materials. It is shown that application of a phenomenon of magnetoelastic acoustic emission can make a basis for development of the new high-sensitive nondestructive technologies for detection of hydrogen accumulated by material during long-term operation of structures. 7 Ref., 9 Figures.

Keywords: *nondestructive testing technologies, metallic structures, hydrogen-containing media, magnetoelastic emission, parameters of signals, increase of sensitivity*

Diagnostics of state of the products and elements of structures as well as equipment operating in hydrogen-containing media is important in a majority of industry branches, in particular, aerospace, chemical, power, oil-refining, in pipeline transport and machine building. During this it is especially important to determine the places of material hydrogenation in addition to the areas of accumulation of small defects or local plastic deformations. Since their expansion can result in accelerated nucleation of microcracks, and, therefore, to failure and disastrous effects for the equipment as well as environment.

Modern methods of nondestructive testing (NDT), which are used for technical diagnostics of such objects, in particular, ultrasonic and X-ray flaw detection, require corresponding treatment of surface of object being tested, they are laborious enough, and it is difficult to use them under equipment operation conditions. A method of acoustic emission (AE) [1, 2] is perspective for solution of this problem. However, during its realization it is necessary to apply to the object being tested additional external mechanical loading, which locally sometimes can significantly exceed allowable optimum modes of stresses in the material, that limits application of AE-diagnostics. In order to expand these boundaries as well as increase detection efficiency of places of hydrogenation of ferromagnetic elements in the structures and products it is proposed to use the phenomenon of generation of signals of magnetoelastic acoustic emission (MAE) under effect of external magnetic field [3]. The latter, as it is known, provokes displacement of walls of magnetic domains (Barkhausen effect). These processes are the most intensive in the vicinity of separate defects or their accumulations, i.e. in the places of significant gradients of mechanical stresses. Besides, changes of material structure, level of its hydrogen degradation during operation etc. considerably effect the parameters of MAE signals.

Aim of this work is to determine quantitative indices of change of MAE parameters under effect of structure-mechanical and other physical factors during remagnetizing of ferromagnetics in the external quasi-static magnetic field and, in particular, under presence of occluded hydrogen in them.

Evaluation of effect of structural factor on MAE generation. To determine the content of carbon in material the plate samples of 240x30x2 mm size were remagnetized in solenoid. Remagnetizing frequency made 9 Hz. MAE were selected by primary transducer (AET) with working band of frequencies 0.2–0.6 MHz and registered by MAE-1L system. The conditions of experimental investigations hereinafter for all samples were the same. Work [4] presents the structural scheme of measurements.

Figure 1 shows a dependence of sum of MAE signals amplitude on magnetic field intensity for alloys with different content of carbon. It can be seen that the highest MAE activity is observed for steel 08kp (boiling), since its microstructure consists of coarse ferrite grains with insignificant inclusions of pearlite on grain boundaries. Thus, during remagnetizing of this material neither grain boundary, no presence of carbide inclusions or other phases effect steplike domain rotation.

MAE signals with somewhat smaller amplitudes are generated during steel 15 remagnetizing. It is explained by insignificant refinement of steel structure and presence of grain boundaries, along which pearl-

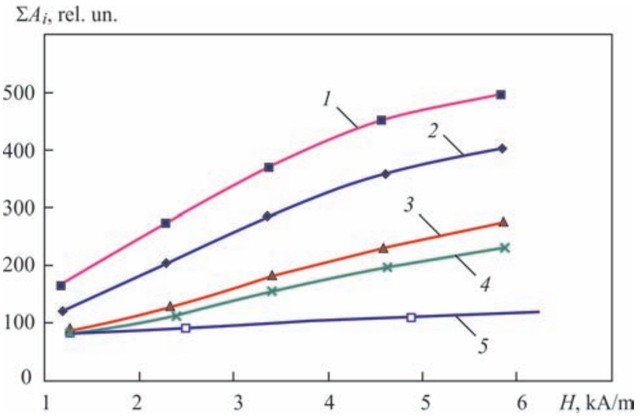

Figure 1. Dependence of sum of MAE signal amplitudes on amplitude of magnetic field intensity during remagnetizing of alloys with different content of carbon: *1* — steel 08kp (boiling); *2* — steel 15; *3* — steel 65G; *4* — U8; *5* — grey cast iron SCh10

ite inclusions are located. As it is known [3], fine grain structures and presence of phases on grain boundaries complicate rotation of domains during material remagnetizing, so activity of generation of the elastic waves, provoked by their jumps, is reduced.

Rapid reduction of activity of MAE generation was observed during remagnetizing of the samples from high-carbon steel 65G. In this case, displacement of domain walls is blocked by presence in the microstructure of large amount of pearlite and fine carbide inclusions that are located not only along the boundaries, but in grain body solid solution.

In the case of remagnetizing of eutectoid steel of U8 grade, structure of which after full annealing consisted of fine pearlite, MAE signals with amplitudes lower than in mentioned hypoeutectoid steels were observed. Apparently, such an effect is provoked by structure refinement and presence of large number of pearlite grain boundaries, which are an obstacle for domain wall rotation. The lowest activity to MAE generation has grey cast iron, microstructure of which consists mainly of pearlite, graphite inclusions and insignificant amount of ferrite.

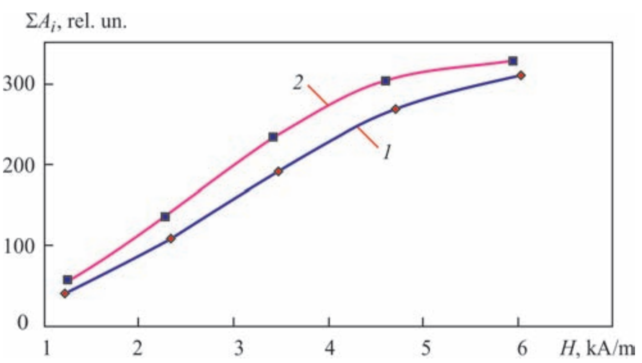

Figure 2. Dependence of sum of MAE signal amplitudes on amplitude of magnetic field intensity during remagnetizing of samples from steel 15: *1* — initial material; *2* — annealed at 900–910 °C

Effect of annealing on MAE generation. The samples of low-carbon steel 15 were remagnetized in the solenoid. They were heated to 900–910 °C temperatures with further cooling together with furnace. Such a heat treatment results in growth of ferrite grains, thinning of their walls, and coagulation of a part of pearlite phase by joining in single inclusions. This heat treatment also promotes reduction of residual stresses, provoked by plastic deformation during rolling of steel sheets. Such conditions improve displacement of domain walls during remagnetizing of steel as well as increase MAE generation activity. Figure 2 shows dependence of sum of amplitudes of MAE signals on magnetic field intensity for steel 15 subjected to heat treatment. It can be seen that a curve after full annealing of steel is characterized with higher MAE activity.

Peculiarities of MAE generation in quenching structures were investigated by remagnetization of high-carbon steel 65G samples in the solenoid. The samples were quenched in oil and then were subjected to low-, medium- and high-temperature tempering. Figure 3 shows the dependence of sum of MAE signal amplitudes on magnetic field intensity for the samples subjected to different heat treatment. It can be seen that rise of tempering temperature of steel increases activity of MAE generation. This is, first of all, related with relaxation of residual stresses appearing in quenching structure due to increase of volume during transfer of a lattice from face-centered into body-centered cubic one.

Low mobility of domain walls in the quenched metal (Figure 3, curve *1*) is also related with presence in the structure of packages of acicular inclusions of martensite and residual austenite [5].

Heating of quenched steel to T = 80–200 °C results in martensite decay. Transfer from tetragonal to cubic lattice takes place during this. Besides, there is decay of residual austenite, carbide transformation and

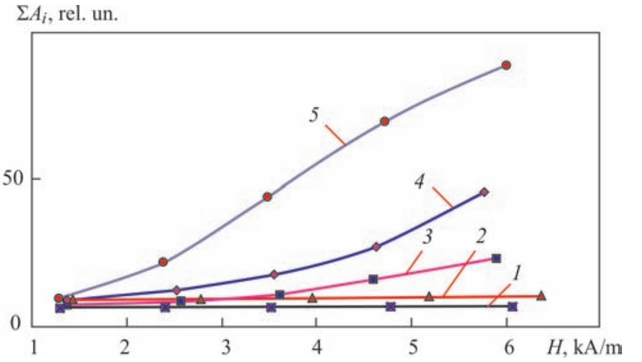

Figure 3. Dependence of sum of MAE signal amplitudes on amplitude of magnetic field intensity during remagnetizing of samples from steel 65G: *1* — quenched material; *2* — tempering at 180 °C; *3* — tempering at 350 °C; *4* — tempering at 580 °C; *5* — output metal

coagulation of carbides; smoothing of irregularity of crystallite structure of α-solid solution; reduction of residual stresses. These processes partially improve mobility of domain wall structure that in turn rises activity of MAE generation (Figure 3, curve *2*).

Medium and high tempering of steel 65G (T = = 300–400 °C) generates troostite structures and sorbite under 500–600 °C. These temperatures provoke the changes of structure, which are not related with phase transformations, i.e. shape and size of carbides and structure of ferrite are varied. At that, cementite crystals increase and their shape gradually approaches to spheroidal. The boundaries between lamellar ferrite crystals are removed, their size rises and shape approaches to equiaxed. This has positive effect on increase of jumps of domain walls during remagnetizing of such materials and, therefore, activity of MAE rises (Figure 3, curves *3, 4*).

Thus, based on the results of experimental investigations, it is determined that steplike displacement of domain walls during metal remagnetizing significantly depends on its microstructure, and, therefore, influences on MAE generated at that. The factors complicating domain mobility are fine microstructure, presence of grain boundaries, carbides, quenching structures, nonmetallic inclusions, residual stresses, etc. Thus, increase of carbon concentration in steel results in significant changes of structure, which reduce MAE activity. Annealing of low-carbon steel promotes increase of MAE amplitude due to coarsening of ferrite grains and coagulation of pearlite inclusions.

It is shown that activity of MAE is minimum during remagnetizing of quenched steel 65G. This is related with presence in steel structure of martensite packages and inclusions of residual austenite. It is determined that increase of steel tempering temperature rises MAE activity. The latter is provoked by relaxation of residual stresses, increase of cementite crystals, coalescence of boundaries between lamellar crystals of ferrite, size of which rises and approaches to equiaxed by shape.

Work [3] shows negative effect of plastic deformations on MAE generation, namely the higher plastic deformation, the less index of ΣA_i parameter is.

Effect of electrolytic hydrogen. The investigations were carried out in solenoid-electrolytic cell, appearance and structure of which are shown on Figure 4. Solenoid winding was coiled on PVC pipe of 50 mm diameter, which served as an electrolytic cell body. Solenoid base from the both sides was closed by covers with corresponding openings for pour in — pour out of electrolyte, sealing for sample alignment pin, output of sample, input of electron thermometer and anode.

Cylinder samples of 12 mm diameter, 260 mm length made of cold rolled steel 15 were examined. The latter has high content of α-iron, which provides it with high (in comparison with pure iron) ferromagnetic properties. The lower part of the sample was completely located in the electrolytic cell volume, when the other insignificant part comes out over the upper cover of the sample for electric connection and installation of transducers of acoustic emission.

The electrolytic-cell was filled with 0.1 n. NaON solution. It is suitable electrolyte, which provides high electric conductivity, does not promote emission of by-products of electrolysis, apart of hydrogen and oxygen as well as secure the surface of steel sample from excessive corrosion during cathode current cut

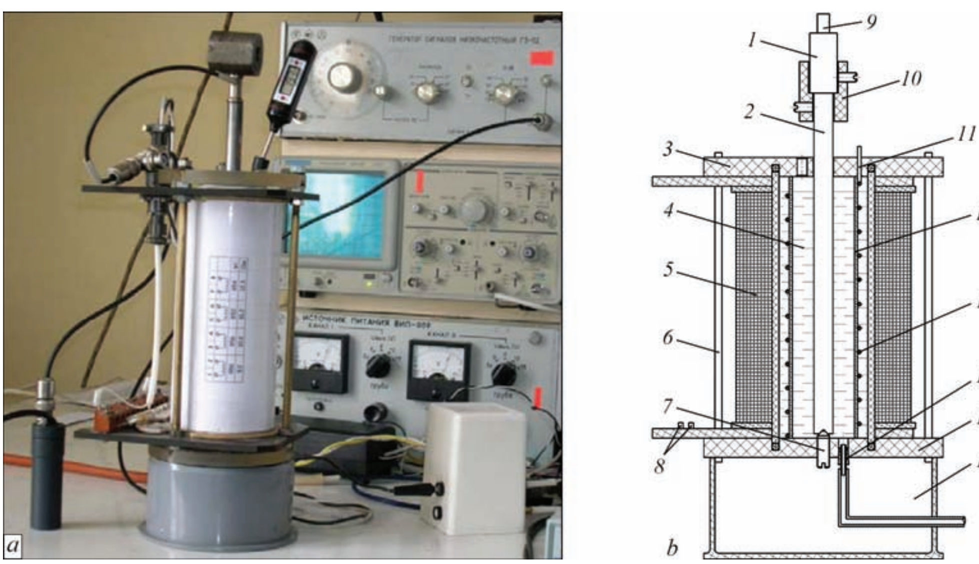

Figure 4. Appearance (*a*) and structure (*b*) of solenoid-electrolytic cell for investigation of effect of hydrogen absorbed by metal on parameters of MAE signals: *1* — AET; *2* — sample; *3* — upper cover; *4* — electrolyte; *5* — solenoid winding; *6* — buckle; *7* — support; *8* — terminals; *9* — high-frequency cable; *10* — nozzle; *11* — anode output; *12* — frame; *13* — platinum electrode; *14* — isolation base; *15* — lower cover; *16* — pan

off. A platinum anode was installed coaxially with the solenoid and sample. It together with sample (cathode) through digital measurement device UT101 that operated in a mode of measurement of electrolytic cell current was connected to a stabilized current source Etalon EP.10010.1.3. An average density of current on the surface of working electrode in 0–20 mA/cm^2 range was provided using these devices.

An electrochemical hydrogenation of metal in comparison with a gas phase hydrogenation has an advantage that metal is not subjected to heat effect, which can promote not only relaxation of internal residual stresses (magnetic properties of ferromagnetics are sensitive to them), but change of microstructure of material: phase transformations, segregation of secondary phase, grain growth, resolidification, etc. In addition activity of the reduced hydrogen on the metal surface is easily controlled by current intensity under conditions of the electrolytic hydrogenation. Under such conditions it is not difficult to reach significant concentration of the atomic hydrogen on the metal surface and it is also easy to control insignificant activity of the reduced atomic hydrogen. It is important since solubility of hydrogen in α-iron is very insignificant, as small and critical concentrations of hydrogen, that causes irreversible failures of microstructure (tens, or even hundredth part of ppm for pure iron [6] and not more than 1 ppm for pipe steel [7]).

In order to establish magnetic field inside the sample, solenoid winding through low-frequency amplifier and system of current measurement was connected to digital functional generator of alternating voltage PCG10/8016, which is controlled by computer. The generator frequency can be varied in 0.01 Hz–1.0 MHz limits. A signal was controlled using the computer oscilloscope module PCS500. Effect of different shapes of alternating supply voltage of the solenoid, namely sinusoidal, meander, saw-tooth, triangular, pulse was checked during investigations.

A broadband high sensitive AET (coefficient of conversion of elastic waves into electric signal is not less than $1.6 \cdot 10^9$ V/m) was connected to upper end of the sample using special holder. It converted elastic oscillations of metal surface due to propagation of MAE waves into electric signal. Nonuniformity of conversion coefficient of primary transducer made ±7dB in a band of operating frequencies 0.2–1.0 MHz.

MAE signal from AET through preamplifier SAA-6 with amplification coefficient 40 dB came into an input of the information-measurement system MAE-1L. It provided amplification, processing and registration of MAE signal. MAE-1L system software designed in DELPHI medium allows setting coefficients of signal amplification, values of their discrimination threshold, digitizing speed and sampling volume. Through a parallel port this block is connected to computer, which saves digitized data and analyses MAE signals using MAESTAT, MS EXCEL, MATLAB, etc. programs. The information-calculation block MAE-1L is synchronized with signal of a functional generator. It means that beginning of MAE signal registration takes place under the same phase delay of the first quarter of the period, i.e. on sine curve rise.

MAE elastic waves that provoked displacement of metal surface appeared due to steplike displacement of the domain walls during steel remagnetizing in variable magnetic field, moreover, dynamics of the domain walls displacement can reflect, on the one hand, unsoundness of metal structure, and, on the other hand, energy distribution of microstructure defects. These both characteristics of metal depend on amount of absorbed hydrogen, which, in turn, depends on current and time of electrolysis and other physical-chemical parameters. Taking into account this, the dependencies of parameters of MAE signals on value of cathode current through the sample surface, magnetic field intensity and time of hydrogenation were investigated.

Two series of experiments were carried out. In the first one, the MAE signals registered by measurement system were subjected to typical post-processing using the algorithm of threshold values. It extracted from the calculations the pulses with lower levels of amplitudes in comparison with threshold ones. In the second series of experiments the registered MAE signals were subjected to other processing procedure. During it displacements of MAE-pulse values caused by a principle of measurement system operation was only removed and (for preservation of fullness of useful MAE signal) low amplitude pulses were not filtered.

For the first series of experiments Figure 5 shows a dependence of sum of amplitudes of magnetoacoustic emission ΣA_i signals (in thousands of relative units) on time of electrolytic hydrogenation of the sample by cathode current $I_c = 50$ mA. As can be seen from the Figure, initial ($t_i = 0$) values of ΣA_i makes approximately 100, and such level of MAE signal intensity lasts more than 5 min.

Reasonable that such a time is necessary for reduction of surface oxide-hydroxide films and for penetration of sufficient amount of atomic hydrogen on such a depth that to effect ΣA_i integral parameter of MAE signals. In 600 s after start of cathode hydrogenation the sum of ΣA_i amplitudes exceeds 400 and continue to rise reaching the value $\Sigma A_i = 500$ after 72 min of action of cathode current.

Change of sensitivity of ΣA_i parameter of MAE signals on amplitude of magnetic field intensity H_a

due to electrolytic hydrogenation (Figure 6) was also evaluated.

Considerable difference in the MAE signal intensity before and after samples hydrogenation can be observed. Although, relative increase of value of ΣA_i parameter due to metal hydrogenation is smaller than in Figure 5, it still makes more than 100 %. It indicates exceptionally high sensitivity of the MAE method before electrolytic hydrogenation and perspective of the investigations in this direction.

It is important to evaluate the change of intensity of MAE signals at increase of the cathode current applied to the sample, and, thus, with pressure of atomic hydrogen on the metal surface. ΣA_i parameter from time t_i of electrolytic hydrogenation for cathode current I_c = 150 mA at the same amplitude of magnetic field intensity H_a = 8.7 kA/m that is on Figure 4 was registered. It can be seen that 300 s was enough for high cathode current to provide ΣA_i parameter with almost its maximum value. At the same time, this parameter remained still on noise level for I_c = 50 mA after 300 s. Secondly, in the case of lower cathode current ΣA_i parameter has stable tendency to insignificant rise during hydrogenation, whereas for I_c = 150 mA this parameter reached its maximum in 10 min of hydrogenation, after what it gradually decreases approximately by 8 % till the end of experiment.

After the dependencies mentioned above were obtained, a second series of experiments was carried out with similar remagnetizing conditions, but somewhat lower levels of cathode currents and another processing of measurement results. Figure 6 presents the dependences of ΣA_i parameter on amplitude of remagnetizing field intensity H_a and cathode current of hydrogenation. If obtained dependencies of ΣA_i on H_a are parabolically approximated (approximation curves are not shown) than for the method of least squares the coefficients of determination within R^2 = 0.9982–0.9999 limits are obtained, that indicate functional dependence of the variables. A parabolic nature of these dependencies means that the induction level during the experiments does not reach ferromagnetic saturation. Thus, the main source of MAE elastic waves was steplike displacements of 90° domain walls due to change of directions of magnetizing vectors from one axis of body-centered iron crystal to another. It is necessary to note that the peaks of parabolic approximations are located at the levels of registered noises ΣA_i = 58±1 (rel. unit) in the limits of experimental data scatter.

As can be seen from Figure 7, the intensity of MAE signal significantly rises, in particular for the cathode currents of hydrogenation higher than 50 mA, under conditions of electrolytic hydrogenation of the

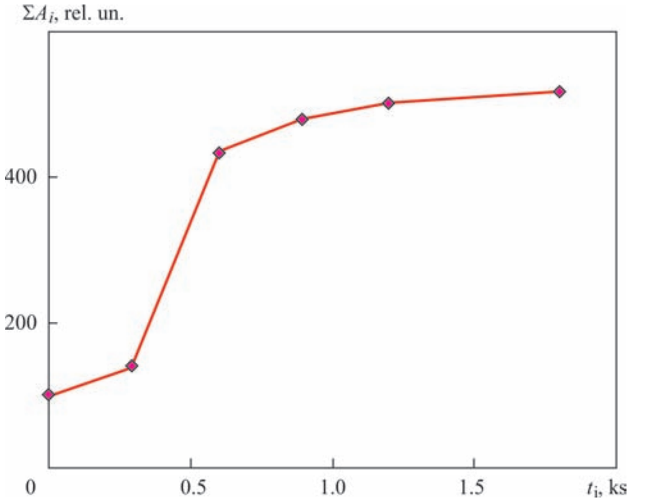

Figure 5. Dependence of ΣA_i parameter on time t_i of electrolytic hydrogenation of sample (cathode current I_c = 50 mA, amplitude of magnetic field intensity H_a = 8.7 kA/m)

sample-ferromagnetics. However, as in the previous series experiments, in these experiments increase of MAE signals intensity with the cathode current took place in 25→100→150→50 mA sequence, i.e. was non-systematic, reflecting, maybe, simultaneous effect of several mutually competitive factors. Application of hydrogenation cathode current of 25 mA value provides only insignificant rise of MAE signal intensity above the level that is generated before cathode current switch-on, i.e. before hydrogenation process. Therefore, taking into account high reproducibility of MAE signals for initial samples (before the start of hydrogenation) this current can be considered as a boundary of method sensitivity for the cathode hydrogenation of metal.

Another series of experiments, the results of which are presented on Figure 8, was dedicated to study of time change of ΣA_i parameter after switch-on of the sample hydrogenation current for different values of the cathode currents values (amplitude of remagnetizing field for all cases was similar and made

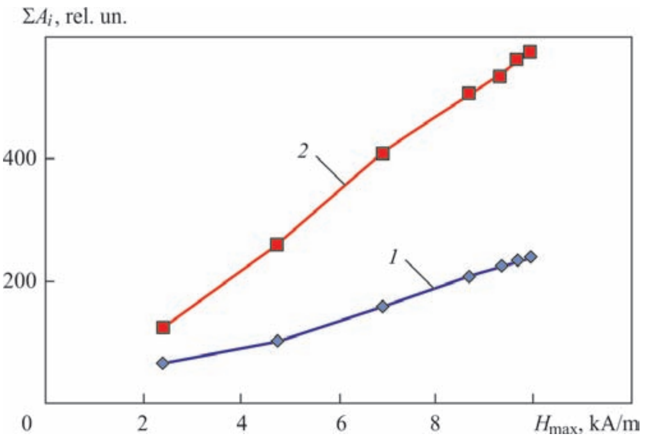

Figure 6. Dependence of ΣA_i parameter on magnetic field intensity H_a for sample before (*1*) and after (*2*) of electrolytic hydrogenation by cathode current I_c = 50 mA during 1800 s

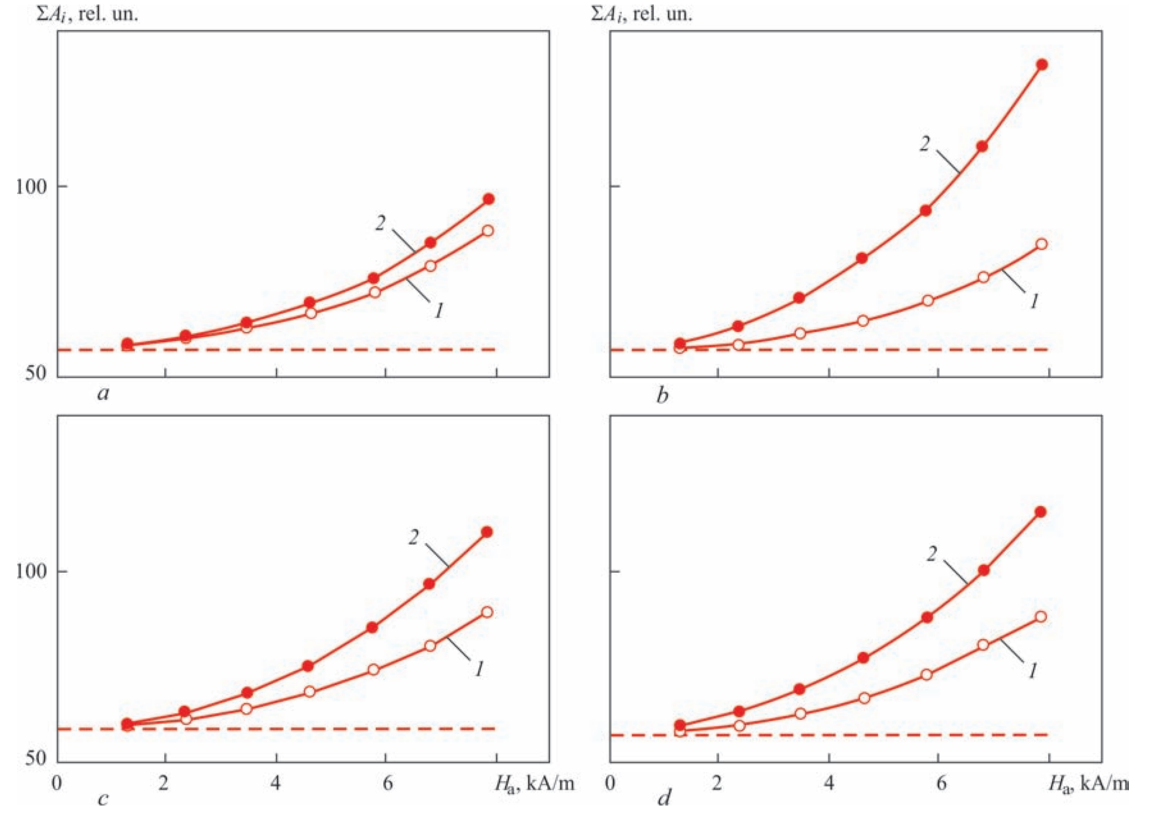

Figure 7. Effect of remagnetizing field intensity H_a on ΣA_i parameter for samples to (curve *1*) and after (curve *2*) electrolytic reduction of 1.8 ks duration by current, mA: *a* — 25; *b* — 50; *c* — 100; *d* — 150 (level of noise is shown by dashed line)

$H_a = 6.8$ kA/m). At the moment of switch-on $t = 0$, ΣA_i parameter was in the limits of 76.6–80.6 (rel. units) and already in 0.4–0.8 ks reached its maximum value.

Based on obtained dependencies (Figure 8) the duration of transition process rises with the current value. It should be noted that for 25 mA cathode cur-

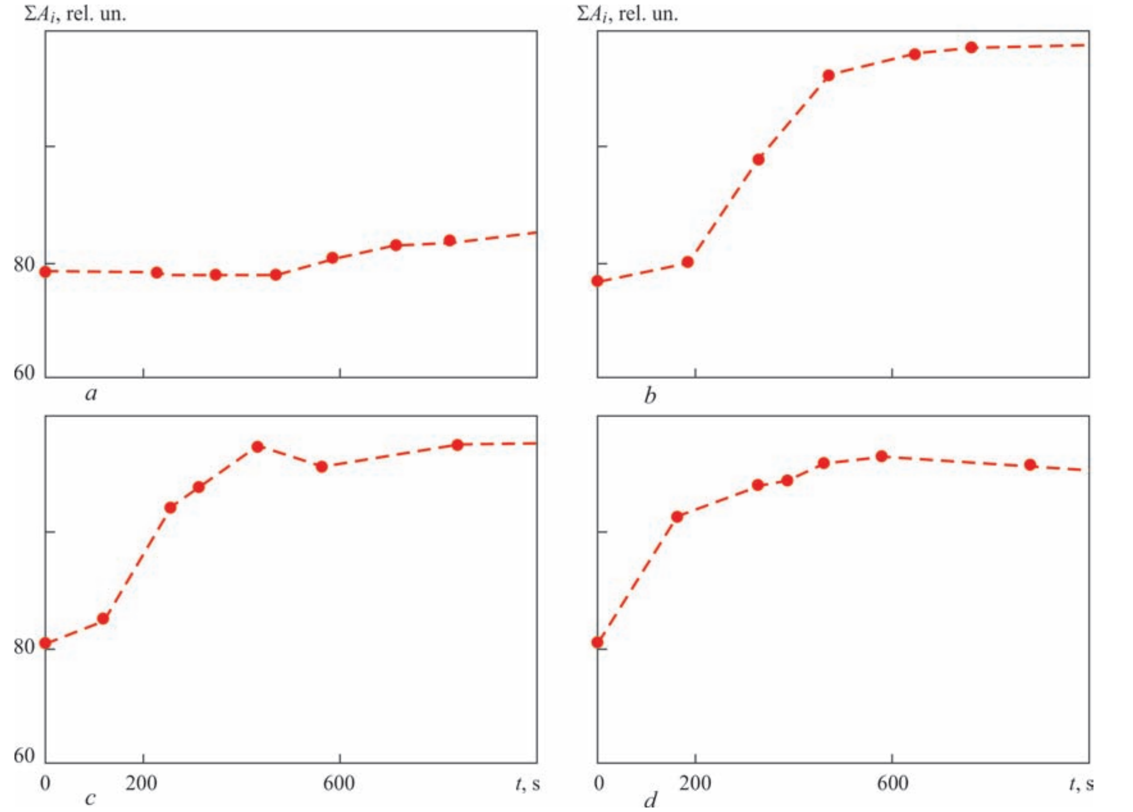

Figure 8. Time dependence of ΣA_i parameter at electrolytic hydrogenation by current, mA: *a* — 25; *b* — 50; *c* — 100; *d* — 150

rent the level of MAE signal during the first 0.47 ks is stable, similar to the signal, obtained at absence of cathode hydrogenation. Therefore, ΣA_i gradually increases, reaching the stationary value in approximately 2.0 ks after current switch-on. Movement of ΣA_i parameter to a stationary level increases with current growth. At that it should be noted that a hydrogenation of MAE signal level for stationary reproducibility deteriorates that matches with the results given above. Moreover, for I_c = 150 mA the level of MAE signal is somewhat reduced after reaching its maximum value (in moment t = 0.58 ks), again confirming the results obtained above.

Delay in process of ΣA_i increase, after cathode current switch-on is apparently caused by reduction of surface oxyhydroxide films and creation of the conditions of high activity of atomic hydrogen on metal surface. The time necessary for reaching the stationary level of MAE signal is considerably shorter than the time necessary for hydrogenation of volume of 12 mm diameter sample. It can mean, for example, that only sub-surface layers of metal are responsible for increment of MAE signal, or another phenomenon comes into action, which suppresses the signal level at metal volume hydrogenation. As previously, MAE signal significantly reduces under conditions of elastic deformation of iron through magnetocrystalline anisotropy and during plastic deformation due to increment of unsoundness of its structure.

For comparison Figure 9 shows the results of remagnetization of samples, which were hydrogenised from gas phase [3].

Comparing obtained results for electrolytic hydrogenation with data after gas phase hydrogenation it can be noted that MAE parameters during cathode hydrogenation have considerably higher sensitivity. It can be explained by a role of diffusion active hydrogen under conditions of electrolysis and its absence in the experiments with gas-like hydrogenation. Combining these two methods it is possible to separate effect of active and nonactive hydrogen on the parameters of MAE signals, but such issues require further investigation.

Conclusions

Application of phenomenon of magnetoacoustic emission can become the basis for new high-sensitive nondestructive method of hydrogen detection in structural materials. At that, it refers to nonactive hydrogen that is kept in microstructure traps, as well as diffusion active one. This phenomenon allows detection of such level of hydrogenation, which do not provoke a danger at short-term effect, but can be significant factor of degradation of structural materials under long-term operation. In comparison with initial state of metal increase the MAE intensity depends on concentration of electrolytic hydrogen as well as from gas phase, absorbed by metal.

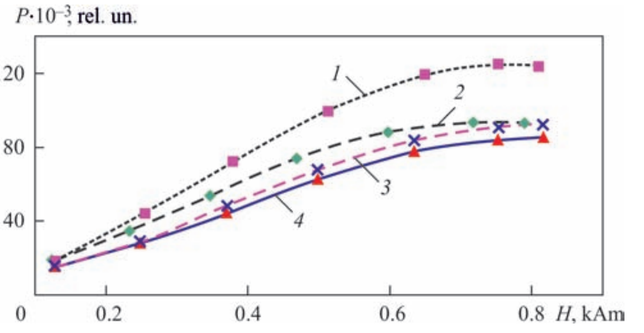

Figure 9. Dependence of power P of MAE signals on change of magnetic field intensity H of solenoid for samples of steel 15 (d = = 2 mm; f = 9 Hz) with different concentration of hydrogen (hydrogenation from gas phase) *1* — C_h = 5.6 ppm; *2* — 1.85; *3* — 1.1; *4* — 0.74 (initial material)

1. Nazarchuk, Z., Skalskyi, V., Serhiyenko, O. (2017) *Acoustic emission. Methodology and application*. Springer Int. Publish. AG.
2. Nazarchuk, Z.T., Neklyudov, I.M., Skalskyi, V.R. (2016) *Method of acoustic emission in diagnostics of NPP reactor vessels*. Kyiv, Naukova Dumka [in Ukrainian].
3. Nazarchuk, Z.T., Andrejkiv, O.E., Skalskyi, V.R. (2013) *Estimation of hydrogen degradation of ferromagnets in magnetic field*. Kyiv, Naukova Dumka [in Ukrainian].
4. Skalskyi, V., Stankevych, O., Dubytskyi, O. (2018) Estimation of effect of hydrogen on the parameters of magnetoacoustic emission signals. *J. of Magnetism and Magnetic Materials*, 375–385.
5. Gorkunov, E.S., Novikov, V.F., Bakharev, M.S., Yatsenko, T.A. (1997) Piezomagnetic effect of residually-magnetized state of steels 45 and 60G. In: *Proc. of Regional Sci.-Tekhn. Conf. on New Materials and Technologies in Mechanical Engineering*. Tyumen, TyumGNGU, 58–59 [in Russian].
6. Beck,W., Bockris, J. O'M., McBeen, J., Nanis, L. (1966) Hydrogen permeation in metals as a function of stress, temperature and dissolved hydrogen concentration. *Proc. of the Roy. Soc. London A*, **290**, 220–235.
7. Maccagno, T.M., Ikeda-Cameron, K., Jack, T. et al. (1998) Hydrogen effects in gas transmission pipeline steels. In: *Proc. of the Int. Pipeline Conf. New York, ASME Int*., **1**, 479–484.

Received 18.06.2018