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THE EFFECT OF ABSORBED HYDROGEN ON ELASTIC PROPERTIES OF STRUCTURAL STEEL

Summary. *The changes in elastic properties, the Young's modulus in particular, and the speed of extensional wave of the rod made of low-carbon structural steel subjected to reversibly absorbed hydrogen using acoustic pulse-echo method and employing an acoustic emission system SKOP-8 engineered at the Karpenko Physical-Mechanical Institute have been studied. It was found that for the electric charge of 14 kC used for hydrogen reduction on the metal surface, the speed of extensional wave in the rod increased after cathodic charging of the sample by nearly 5 m/s, which corresponds to the increase in the Young's modulus by 0.18%. The results are commented regarding the origins of the detected changes in elastic properties and regarding the future needs for the research in this area. The application of such phenomenon for non-destructive evaluation of hydrogen-induced changes in the materials properties has to be widely investigated since it might create a basis for a novel nondestructive method for control and monitoring of the aged structures, thus increasing reliability and safety of the latter. This is especially important for the incubation period of hydrogen-induced degradation of structural materials, when there is no apparent change in the microstructure, as detected by the established nondestructive methods.*

Key words*: structural steel, hydrogen, Young's modulus, speed of elastic waves.*

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ВПЛИВ АБСОРБОВАНОГО ВОДНЮ НА ПРУЖНІ ВЛАСТИВОСТІ КОНСТРУКЦІЙНОЇ СТАЛІ

Резюме*. Вивчено вплив абсорбованого водню на зміну модуля пружності, а відтак і на швидкість поширення поздовжньої пружної хвилі у стрижні, виготовленому з низьковуглецевої сталі. Для цього використано акустичний метод луно-імпульсу та акустико-емісійну інформаційно-вимірювальну систему SKOP-8, розроблену у Фізико-механічному інституті ім. Г.В. Карпенка НАН України. Встановлено, що внаслідок катодного наводнювання металу після проходження через електролізер електричного заряду 14 кКл для реакції відновлення водню на поверхні металу, швидкість поширення поздовжньої хвилі у стрижні зросла на 5 м/с, що відповідає збільшенню величини модуля Юнґа на 0.18%. Отримані результати проаналізовано щодо причин виявлених змін параметрів пружності та перспективності подальших досліджень у цьому напрямку. Оскільки одним із головних чинників деградування конструкційних матеріалів є абсорбований водень і, як виявилося, він впливає на швидкість поширення пружних хвиль, то дослідження в цьому напрямку слід продовжити із орієнтацією на можливе розроблення нового неруйнівного методу контролю та моніторингу елементів конструкцій чи обладнання тривалого експлуатування, що працюють у водневмісному середовищі. Це особливо важливо для виявлення інкубаційного періоду водень-ініційованого деградування конструкційних матеріалів, у яких ще не відбулися незворотні процеси руйнування мікроструктури.*

Ключові слова: *конструкційна сталь, водень, модуль Юнґа, швидкість пружних хвиль.*

Statement of the problem. Among the urgent engineering problems faced by different industries worldwide is the detection of materials ageing processes in structures and equipment, i.e. in-service damage of structural materials caused by synergetic action of thermal and mechanical fatigue often complicated with possible influence of the surrounding environment resulted in the microstructural changes of the material with corresponding decline of its mechanical strength and fracture toughness. A significant effort is being put into the search of nondestructive methods that would be sensitive enough to detect the changes in physical properties preceding the materials failure, or even the irreversible changes in the microstructure.

Acoustic and magnetoacoustic methods are gaining more and more attention owing to high sensitivity of acoustic and magnetic properties of structural materials to submicrostructural changes caused by ageing. For the acoustic methods the propagation of acoustic elastic waves in solids (generated either inside the material, or induced by the external transducer) is directly related to their density ρ and elastic moduli [1, 2]. The Newton-Laplace equation establishes such relationship for liquids and gasses [3]:

$$c = \sqrt{\frac{P}{\rho}}\ , \qquad (1)$$

where c – speed of sound and P – bulk modulus, while in the case of isotropic solids, this relation – due to the different types of waves – turns into:

$$c_L = \sqrt{\frac{E(1-\nu)}{(1+\nu)(1-2\nu)\rho}} \quad \text{and} \quad c_T = \sqrt{\frac{G}{\rho}} = \sqrt{\frac{E}{2(1+\nu)\rho}}\ , \qquad (2)$$

where c_L and c_T – speed of longitudinal and transverse waves, respectively, E and G – elastic moduli, and ν – Poisson's ratio. For relatively thin rods (diameter is significantly smaller than the wavelength of propagating elastic waves), the propagation speed equals to:

$$c_E = \sqrt{\frac{E}{\rho}}\ , \qquad (3)$$

where c_E – speed of extensional wave, which is slower than the longitudinal wave in isotropic solids.

Such a simple relationship between the Young’s modulus and the speed of sound seems very attractive for studying the influence of ageing factors on mechanical properties of structural materials. Since hydrogen absorbed by metal from the surrounding media is one of the key factors in materials degradation, the question arose regarding its possible influence on such mechanical properties as elasticity parameters, namely c_E and E. Should the relationship between the parameters of absorbed hydrogen and elasticity parameters be established, it might create a basis for a novel nondestructive method for control and monitoring of the aged structures, thus increasing reliability and safety of the latter.

Literature review. A list of papers concerned with the changes of elasticity parameters of iron-based materials with hydrogen is rather short, though the earliest publication was written as early as 1950 [4]. In most cases however, the studied materials were subjected to such levels of hydrogen activity that caused irreversible destruction of the microstructure with formation of a network of pores and microcracks. Degradation of such material could easily be detected by the known nondestructive methods with a consequent need for replacement of the damaged part.

Of higher importance seems the need for detection of material’s response to the combined action of hydrogen and stress preceding the irreversible degradation, i.e. when microstructure of metal is retained intact, as far as traditional nondestructive inspection is concerned. In this regard only a few published sources could be mentioned. The work by Lunarska *et al* [5] employed internal friction technique and free oscillation frequency measurements for studying ultrapure polycrystalline α-Fe, which contained 5 ppm of non-metallic and 23 ppm of metallic impurities. The absorbed hydrogen, which concentration was estimated about 3 ppm, resulted in reduction of calculated value of shear modulus G of the order of 0.05 % per 1 ppm of H. The author’s suggested that there was no microstructural damage and the effect of hydrogen was narrowed down to the changes in interatomic bonding or/and to hydrogen-defect interaction, provided that 28 ppm of impurities had an insignificant effect on hydrogen-related interactions, – an effect, most probably, originated from the distortion of the matrix.

Another important reference published recently [6] was concerned with the effect of hydrogen on the elastic and anelastic responses of iron (total concentration of impurities exceeded 1000 ppm). Using dynamic mechanical analyzer the authors detected both effects. As to elasticity, desorption of H caused a slight increase in Young’s modulus – about 0.5 % as deduced from stress-strain relations. As to anelastic time-dependent responses, H seems to enhance anelastic relaxation connected with dislocation dynamics or other relaxation mechanisms. This study did not include measurements of hydrogen activity, but authors believe that no structural damage was done to the material by H absorption-desorption. They suggested also, that H-induced changes in Young's modulus could reflect either the changes of Fe-Fe bonding strength according to the decohesion theory of hydrogen embrittlement of metals introduced by Troiano and developed by Oriani [7,8], or some other effects.

These two papers on high-purity iron samples are seemingly the only sources which we could refer to in our introductory studies on the effect of the absorbed H on elastic parameters of steel [9,10]. The published results are not unanimous in their conclusions on the effect of hydrogen on elastic properties of Fe and Fe-based materials and thus there is a need for further investigation.

The objective of the work is to reinvestigate the effect of electrolytic hydrogen charging on the speed of propagation of extensional waves in thin rod and corresponding change in Young's modulus. In order to achieve this goal we employed the available acoustic emission instrumentation developed at Karpenko Physical-Mechanical Institute and conventional approaches to electrolysis.

Experimental approach. We used a cylindrical sample 2122 mm long and 12 mm in diameter made of cold-rolled low carbon steel grade 15.

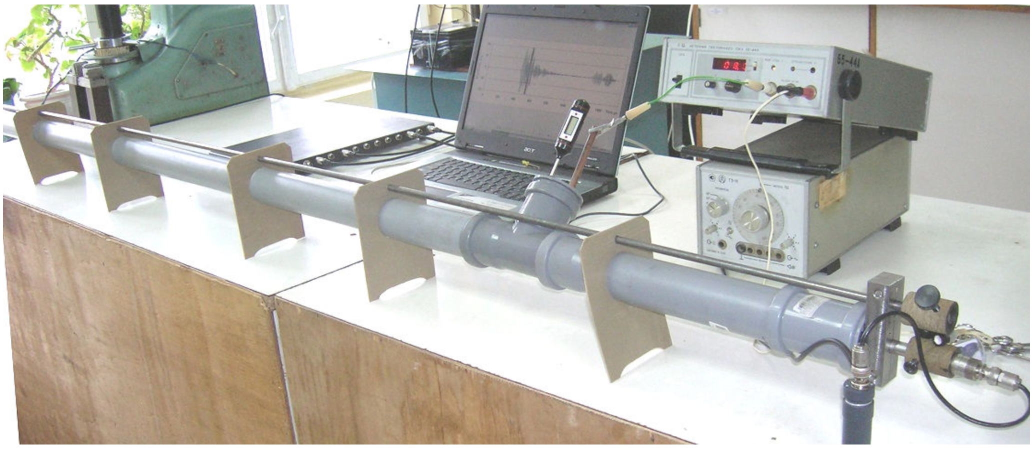

Figure 1. General view on the experimental setup

Рисунок 1. Загальний вигляд експериментальної установки

The sample was placed into a 50 mm diameter plastic pipe that served as an electrolyser chamber (Fig. 1) filled with 0.1 N NaOH solution. To prevent the material from hydrogen-induced cracking, no catalyst was used for promotion of hydrogen absorption. Two steel rods 8 mm in diameter on both sides of the studied sample served as anodes. The anodes and a sample-cathode were connected to the stabilized constant current source with the total amount of charge equals to 14 kC that have passed for hydrogen evolution reaction.

Making two assumptions: i) that all the electric charge was spent only for reduction of hydrogen from the electrolyte according to (simplified):

$$H^+ + e^- \rightarrow H_{ads}(Me), \tag{4}$$

and ii) that about 0.1 – 1 % of reduced hydrogen atoms were absorbed by metal:

$$H_{ads}(Me) \rightarrow H_{abs}(Me), \tag{5}$$

while the other 99 – 99.9 % have been turned into molecular form:

$$2H_{ads}(Me) \rightarrow H_2, \tag{6}$$

which was removed from metal surface in the form of hydrogen gas bubbles, we obtained 0.1–1 ppm of average concentration of hydrogen in the rod complying with literature data [11]. This concentration does not include the metallurgical hydrogen that was absorbed by steel during the manufacturing and storage history and which, we assume, is immobile being located near the traps like dislocations or grain boundaries and is not released during the cathodic hydrogen charging. The charged hydrogen is supposedly mobile, diffusible and reversibly absorbed with chemical potential of H on the metal surface being the driving force.

The temperature of the rod (as measured by the digital thermometer at 0.5 m from the sample's edge) was kept to 300 ± 1 K by gradual refreshing of the electrolyte. Both machined edges of the sample were attached to piezoceramic transducers: one to a transmitter and the other to a receiver. A transmitter was connected to a square impulse generator and a receiver – to an acoustic emission measuring system SKOP-8, both synchronized by a single timer. A sample signal digitized at 4 MHz contained 8200 datapoints that covered 2.05 ms of the signal train sensed by a receiver. The diameter of the rod was much smaller than the wavelengths of the carrier wave frequencies (40–100 mm), enabling direct determination of the isothermal Young's modulus change from time-of-flight of extensional waves.

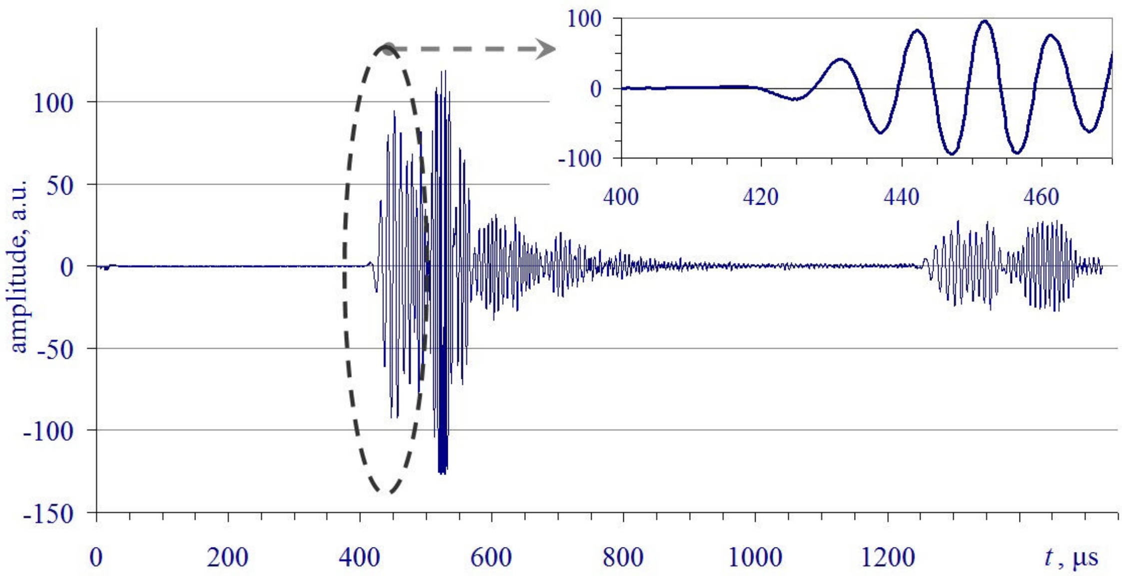

Figure 2. A typical signal train averaged from 20 signals with digital filtering and a scaled fragment of extensional wave (inset)

Рисунок 2. Типовий сигнал, отриманий усередненням 20 сигналів із цифровим фільтруванням, і масштабований фрагмент поздовжньої хвилі

As far as determination of the parameters describing hydrogen activity, we have to notice that there are at least two reasons why such studies are relatively complicated. Firstly, the solubility of hydrogen in iron is of the order of 10^{-6} (ppm) [12,13], which makes it hard to measure accurately by conventional methods. Secondly, the diffusivity of hydrogen at ambient laboratory temperatures is high, which further complicates the task of hydrogen determination. This is why the studies concerned with reversible hydrogen absorption by α-Fe are usually lacking the accurate evaluation of hydrogen activity parameters. In our work, before we employ any sophisticated method for accurate H determination, we use coulometric evaluation of hydrogen activity.

Results and discussion. A signal averaged from 20 acoustograms recorded by the acoustic emission system SKOP-8 and digitally filtered to remove a d.c. shift of the measuring system is depicted on Fig. 2. The sonic speed evaluated from the time delay between the first and the second arrival of the extensional wave to the receiver at 410–420 μs and 1240–1250 μs was $c_E = 5.09 \pm 0.02$ km/s corresponding to $E = 204$ GPa, provided density was $\rho = 7870$ kg/m^3.

The effect of the absorbed hydrogen on the time of first arrival of the extensional wave to the receiver is shown on Fig. 3 in a narrow time window. It could be noted that the speed of propagation of elastic waves increased. To compare a phase velocity change, we linearly interpolated the data in order to obtain the moments of time when the recorded signals changed its polarity starting from the first half-wave at ~419 μs till the third half-wave at ~434 μs. The average change in time arrival for the first three half waves equals to $\Delta t = -0.38$ μs, which would correspond to the velocity increase $\Delta c_E = 4.9 \pm 0.4$ m/s and corresponding Young's modulus increase $\Delta E = 0.18$ % since the changes in isothermal extensional wave phase velocity c_E should be directly proportional to $E^{0.5}$.

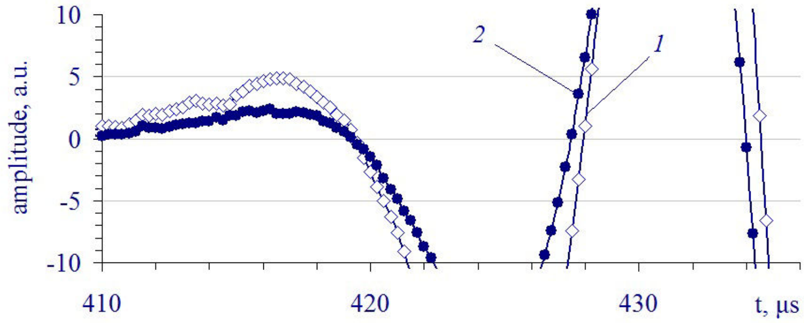

Figure 3. The effect of hydrogen charging on the arrival of the extensional wave: *1* – before and *2* – after hydrogen charging

Рисунок 3. Вплив наводнювання на прихід поздовжньої хвилі: *1* – до і *2* – після наводнювання

The changes in elastic parameters from sonic velocity change incorporate the length change of the sample, the changes in density, and the changes in its physical properties. As we discussed in our recent publications [9,10], neither linear expansion of the rod due to the absorbed hydrogen considering partial molar volume of hydrogen V_m(H) = 2 cm^3/mole [14], no linear expansion of metal due to the temperature change within the temperature window of our experiments, or deviation of density induced by such negligible concentration of the absorbed hydrogen could have affected such changes in elastic properties of the hydrogenated steel rod. Thus, the cause(s) for the observed phenomenon has(have) to be searched within the changes of the physical parameters of the material.

The only reasonable explanation for this observation, in our opinion, could be rooted in redistribution of internal strain field in the rod's cross-section. For the non-steady-state conditions of hydrogenation pertained to our study it has to be associated with "swelling" of the outer layers where chemical potential of hydrogen is high relative to the bulk. Such "swelling" is restrained with the unaffected core which undergoes tensile straining while the outer shell is under compression – a state originated during the cold-drawing procedure on a production stage.

The dependency of the speed of sound on stress could be written as follows [15]:

$$c = c_0 (1 - \beta\sigma), \qquad (7)$$

where c_0 – the initial velocity when the stress σ is not applied and $\beta = g_{222} / f_{22}$ (g_{222} and f_{22} – non-linear and linear elastic constants). Experimental observations [15] suggest that for industrial carbon steel, the change in sonic velocity is ca. –0.1 % per 100 MPa of tensile stress and this relation is linear at least to 450 MPa. Extrapolation of this relationship to 0.09 % change in sound velocity obtained in our experiments would correspond to compressive stress of 90 MPa. These numbers are close to those derived on the basis of more earlier studies on 1018 low-carbon steel [16,17].

Since we study a ferromagnetic material, we have to consider its magnetoelastic behavior since the stress field affects the magnetization vectors of magnetic domains contained by individual grains of the polycrystalline material. There is a measurable deviation from the ideal cubic crystal structure with a defined orientational dependencies of all elastic constants. The apparent Young's modulus of a ferromagnetic material E_m could be deduced from [18]:

$$E^{-1} = E_0^{-1} + 0.4\, \lambda_s / \sigma_i\,, \qquad (8)$$

where E_0 – Young's modulus of the demagnetized material, λ_s – saturation magnetostriction, and σ_i – internal stress. Considering the obtained results on the Young's modulus change, and taking λ_s of the order of 10^{-6}, we obtain σ_i of the order of 10^2 MPa comparable with the estimations given above.

Thus, having reaffirmed that the absorbed hydrogen indeed affects the elastic properties of structural materials, and believing that the activity of hydrogen in solid solution was well insufficient to cause any irreversible damage to the microstructure, it does not seem unreasonable to suggest that such studies should be seriously expanded in several directions. Firstly, the steady-state hydrogen charging has to be attained and the results have to be compared with transient sorption experiments conducted so far. Secondly, a different approach, which provides quantitative evaluation of hydrogen concentration, has to be used and the dependency of ΔE([H]) has to be established ([H] – concentration/activity of hydrogen in metal). Thirdly, the reason for the discrepancy on the tendency of the effect of hydrogen on elasticity parameters in the literature has to be found. Thereafter, the application of such phenomenon to non-destructive evaluation of hydrogen-induced changes in the materials properties has to be widely investigated since it might create a ground for a novel nondestructive method for control and monitoring of the aged structures, thus increasing reliability and safety of the latter. This is especially important for the incubation period of hydrogen-induced degradation of structural materials when there is no apparent change in the microstructure, as detected by the established nondestructive methods.

Conclusions. The changes in elastic properties (namely Young's modulus and the speed of extensional wave) of the rod made of low-carbon structural steel subjected to reversibly absorbed hydrogen using pulse-echo method and employing an acoustic emission system SKOP-8 engineered at the Karpenko Physical-Mechanical Institute have been studied. It was found that for the electric charge of 14 kC used for hydrogen reduction, the speed of extensional wave in the rod increased after cathodic charging of the sample by nearly 5 m/s, which corresponds to the increase in the Young's modulus by 0.18%. The results are commented regarding the origins of the detected changes in elastic properties and regarding the future needs for the research in this area.

The application of such phenomenon for non-destructive evaluation of hydrogen-induced changes in the materials properties has to be widely investigated since it might create a basis for a novel nondestructive method for control and monitoring of the aged structures, thus increasing reliability and safety of the latter. This is especially important for the incubation period of hydrogen-induced degradation of structural material when there is no apparent change in the microstructure, as detected by the established nondestructive methods.

Висновки. Вивчено вплив абсорбованого водню на параметри пластичності (модуля пружності і швидкість поширення поздовжньої пружної хвилі) стрижня, виготовленого з низьковуглецевої сталі. Для цього використано акустичний метод луно-імпульсу та акустико-емісійну інформаційно-вимірювальну систему SKOP-8, розроблену у Фізико-механічному інституті ім. Г.В. Карпенка НАН України. Встановлено, що внаслідок катодного наводнювання металу після проходження через електролізер електричного заряду 14 кКл для реакції відновлення водню на поверхні металу, швидкість поширення поздовжньої хвилі у стрижні зросла на 5 м/с, що відповідає збільшенню величини модуля Юнґа на 0.18%. Отримані результати проаналізовано щодо причин виявлених змін параметрів пружності та перспективності подальших досліджень у цьому напрямку.

Оскільки одним із головних чинників деградування конструкційних матеріалів є абсорбований водень, який, як виявилося, впливає на швидкість поширення пружних хвиль, то дослідження в цьому напрямку слід продовжити із орієнтацією на можливе розроблення нового неруйнівного методу контролю та моніторингу елементів конструкцій чи обладнання тривалого експлуатування, що працюють у водневмісному середовищі. Це особливо важливо для виявлення інкубаційного періоду водень-ініційованого деградування конструкційних матеріалів, у яких ще не відбулися незворотні процеси руйнування мікроструктури.

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