The Effect of Electrolytically Absorbed Hydrogen on Young's Modulus of Structural Steel

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Abstract

The effect of absorbed hydrogen on Young’s modulus of cold-rolled low-carbon steel rod was investigated using a time-of-flight approach. Speed of sound increased after hydrogen charging of the sample, with corresponding increase in elastic modulus of the material. The obtained results are discussed regarding the possible origins of the change in elastic modulus.

Introduction

Historically, Young's modulus E is being determined as the slope of the stress-strain curve according to ASTM Standard E111, developed in 1955, periodically updated, and multiplied into standardization documents of many countries ever since [1]. However, this test method is of little use when a tested material is scaled down to micro- and nano-level. For such cases, a variety of novel testing procedures have been developed that employ such instruments as analytical balances [2], optical interferometers [3], ellipsometry [4], atomic force microscopes, scanning and transmission electron microscopes with the *in-situ* use of piezoceramic nanoindentation [5-8].

Alternative in evaluation of Young's modulus is an acoustic approach, since the propagation of elastic waves is strongly dependent on elastic properties of the material [9-12]. Propagation of elastic waves is usually described by two parameters – sound speed c and attenuation coefficient α [12]. Among a variety of different techniques pertained to the solid-state sonic speed studies, a few could be mentioned: time-of-flight for bulk waves, guided surface waves, continuous wave or resonance methods, which could be classified into two distinct approaches – a) resonant and b) time-of-flight, a.k.a. pulse-echo [12,13]. According to the time-of-flight approach, c is obtained from the Newton-Laplace equation (Eq. 1):

$$c = (P / \rho)^{0,5}, \tag{1}$$

where P – the coefficient of stiffness and ρ – density of the material, which for thin rods turns into Eq. 2:

$$c_E = (E / \rho)^{0,5}, \tag{2}$$

where c_E – speed of pure longitudinal wave (called extensional wave), provided the diameter of rod is significantly smaller than a wavelength (note that this speed is smaller than the speed of a longitudinal wave in bulk isotropic materials).

This simple relationship is very attractive for the studies of elastic properties of materials subjected to different influences, like thermal, magnetic or chemical. It is especially interesting for studying the effect of hydrogen (H), which is known for its embrittling action in iron-based structural materials even in concentrations of the order of ppm [14-16]. Despite extremely low solubility in α-Fe, such concentrations of absorbed H (usually much lower than the concentrations of numerous non-metallic inclusions like S, P, As etc.), when combined with thermo-mechanical fatigue over a period of time, can result in ageing and unexpected failures of equipment or structures [17].

A bibliography related to the studies of the effect of H on elastic modulus of iron-based materials is rather short [18-25]. Mostly, they are concerned with severe H charging that results in permanent damage of the material's microstructure manifested in numerous inner voids and microcracks especially near the surface. Such studies have to consider a large number of effects: H-induced cracking in the form of surface and inner cracks or voids; hydrostatic pressure in the inner cracks/voids induced by molecular H_2; complete redistribution of the strain field due to the partial damage of the material, and the effect of atomic H dissolved in the crystalline structure, or entrapped by the material's defects, like boundaries between grains or phases, and, for that matter, any 0D-, 1D-, 2D-, or 3D-defects of the crystalline matrix. For such a complicated picture, it should be extremely difficult to define the changes in material's mechanical properties pertained specifically to H, especially if these effects are manifested on different scales.

For instance, Carpenter and Fawks [19] have studied Armco iron of two different purities under severe cathodic charging conditions by measuring the changes in the resonant frequencies of the standing longitudinal waves in the rods. A gradual decrease in the frequency (and conclusively in apparent Young's modulus) during cathodic hydrogenation were attributed mainly to the severe formation of voids and internal microcracking. Similarly, Zhang *et al* [20,21], who (under even more severe charging conditions) studied the effect of H on elastic modulus with the changes in flexural resonant frequencies of thin rectangular samples made of high-purity and commercial-purity iron, concluded that the observed changes of Young's modulus were attributed to the structural changes and stress relaxation rather than any effect of H present in solid solution.

It is not exactly correct, however, to evaluate the effect of H on mechanical properties by comparing the initially "healthy" material with the one, which microstructure is irreversibly destroyed. In order to get the insights into the mechanisms of H-induced processes, the effect of H should be studied under reversible hydrogenating conditions, i.e. when H is absorbed/desorbed as an interstitial in the solid solution before any irreversible damage takes place. However, such investigations are facing the major problem of extremely low ambient solubility of H in α-Fe, being of the order of 10^{-7}, i.e. 10^{-1} at. ppm. Moreover, since the materials of commercial quality contain very significant concentrations of impurities (compare to the concentration of H), be it metallic, or nonmetallic, and high concentrations of structural defects, the judgment on the effect of H from the point of view of H–Fe interaction has to have a high degree of uncertainty. This is why any attempt of studying H-Fe system, where the effects of other elements are minimized, is of great value. In this respect, of the key importance have been the theories of H-enhanced local plasticity – HELP, proposed by Birnbaum [26], and of H-decohesion, which was delineated by Oriani [27]. Should H be responsible for lowering the cohesive interatomic forces, it would be reflected on the changes of elastic constants, e.g. Young's modulus, while, if H only acts to facilitate dislocation dynamics, according to HELP, the anelastic response should be manifested [25].

In this regard only few sources could be mentioned. Employing internal friction and free oscillation frequency measurements, Lunarska *et al* [18] have studied the changes of shear modulus of ultrapure polycrystalline α-Fe (containing only 5 ppm of non-metallic and 23 ppm metallic impurities) under the effect of ca. 3 wt. ppm of absorbed H. It could be deduced that the reduction of shear modulus G for the studied material was of the order of 0.05% per 1 wt. ppm of absorbed H, though the H concentration in Fe samples was not evaluated accurately.

A recent work by Ricker and Pitchure [25] has brought continuation to this discussion. They investigated the effect of H on the elastic and anelastic responses of iron (total concentration of impurities exceeded 1000 wt. ppm) using dynamic mechanical analyzer and found that both effects are present. Absorbed H (with no knowledge on its low concentration) slightly decreased the modulus of elasticity (0.5-1% as deduced from stress-strain relations) and also caused higher anelastic relaxation that might have reflected, in part, movement of dislocations (other relaxation mechanisms are possible). No structural damage of the material took place.

Other than these vibrational studies on pure iron samples, we were unable to find any other sources that relate the absorbed H with the changes of elastic properties of iron. Though it seems that the listed sources are unanimous in the tendency of absorbed H to slightly reduce elastic moduli of iron, they all employed a resonance method, which is sensitive not only to the physical properties of the material, but also depends on the surrounding of the sample and the state of its surface. It seemed attractive to verify the effect of H on Young's modulus employing time-of-flight approach using in situ cathodic hydrogenation conditions. The obtained results have been unexpectedly interesting and, we hope, that even at this preliminary stage, they are worth sharing with colleagues who work in areas of applied physics and materials science, including fracture mechanics.

Experimental approach

We used cylindrical samples ~2100 mm long and 12 mm in diameter made of cold-rolled low carbon steel grade 15. A sample was placed into a 50 mm diameter plastic pipe that served as an electrolyzer chamber. This chamber was filled with 0.1 N NaOH solution, which prevented the metal surface from excessive corrosion. No catalysts were used for promotion of H ingress into steel. Two steel rods 8 mm in diameter served as anodes. These anodes and the sample (cathode) were connected to the stabilized constant current source in order to generate atomic H on the metal surface. The charging was conducted in two stages with time-of-flight measured before and after each of these stages. Over the course of experiment, the amount of charge transferred to the sample was 14 kC during the first stage of H charging immediately followed by 3 kC of the second stage. Making two assumptions: i) that all electric charge has been spent only for reduction of H from the electrolyte according to $H^+ + e^- \rightarrow H$, and ii) that about 0.1-1% of reduced H atoms were absorbed by metal, while the other 99-99.9% have been turned into molecular form $2H \rightarrow H_2$, which was removed from the metal surface in the form of H_2 gas bubbles, we obtained 0.1-1 wt. ppm of average concentration of H in metal sample. Such values are of the same order as suggested by Hirth and Carnahan – 10 at. ppm (0.2 wt. ppm) – for the enhanced concentration of H produced by electrolytic charging [28]. Obviously, this concentration does not include the metallurgical H which has been absorbed by steel during the manufacturing and storage history and contained by the specimen before testing. We assume that this "own" H is immobile, located near the traps like dislocations, grain boundaries, etc. and is not released during H sorption-desorption. The charged H is supposedly mobile, diffusible and reversibly absorbed with chemical potential of H on the metal surface being the driving force.

The temperature of electrolyte in the point of measurements (i.e. ~500 mm from the sample's edge) varied in the range of 27.1-28.1 °C with the following values: before charging – 27.6 °C, after the first stage of charging – 27.2 °C and after the second stage of charging – 27.1 °C, as measured by the electronic digital thermometer. The testing cell was prevented from the possible effects of heating by the current passing through the electrolyte by means of gradual refreshing of the electrolyte. Note, that the temperature increase under adiabatic conditions was estimated to be of the order of 2 °C, if electrolyte was not replaced.

Both machined edges of the rod sample were attached to piezoceramic transducers, as in the through transmission measurements: one served as a transmitter and the other as a receiver. A transmitter was connected to a square impulse generator and a receiver – to an acoustic emission measuring system, both contained in one unit and synchronized by a single timer. Each sample signal was digitized at 4 MHz and contained 8200 datapoints that covered 2.05 ms of the signal train sensed by a receiver. In our case it was sufficient to clearly register not only first arrival of the wave pack that traveled through the rod, but also its second arrival after the wave has traveled the rod's length three times. The Rayleigh waves, which are constricted to the outermost layers of the rod and usually have much higher amplitudes relative to extensional or longitudinal waves, were of little concern due to their significant delay and attenuation owing to such processes as enhanced refraction, the formation of gas phase between the liquid and the solid, and dynamic absorption of mobile H. A signal train contained clearly shaped bells of extensional waves from which sound velocity could have been evaluated. The diameter of the rod (12 mm) was much smaller than the wavelengths of the carrier wave frequencies (40-100 mm), providing the condition for direct determination of the isothermal Young's modulus change from the time-of-flight values for extensional waves.

Results

Fig. 1 depicts an averaged typical signal train. During measurements, twenty acoustic signals have been recorded by the acoustic emission measuring system every other second and were found to be merely identical except for the noise. The averaging of these twenty acoustograms with digital filtering of a d.c. shift (an artifact of the measuring system) resulted in removing most of the noise and unnecessary echoes from the signal trains. 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 (e.g. Fig. 2) is c_E = 5087 m/s, corresponding to E = 203.7 GPa if density is taken ρ = 7870 kg/m^3. Such value of Young's modulus is in perfect agreement with the handbook data on iron and low-carbon steel.

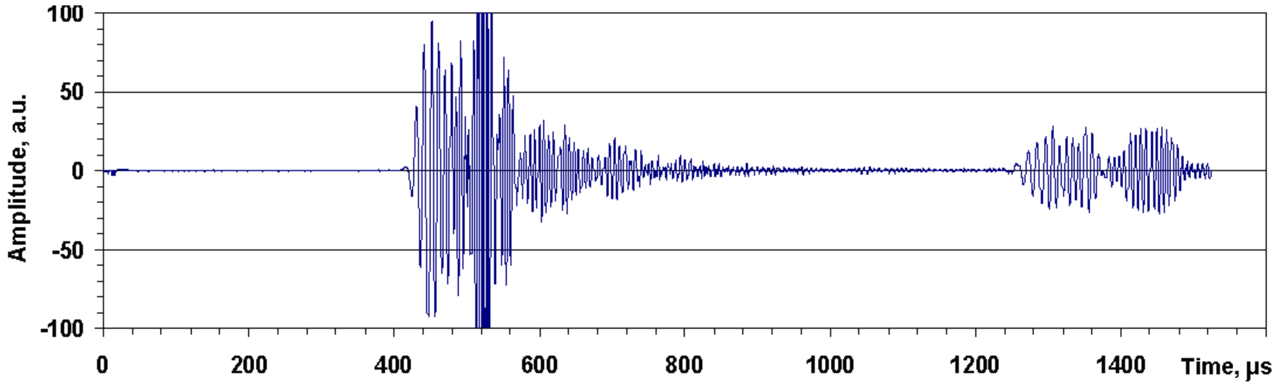

Fig. 1. An averaged acoustic signal train obtained from 20 recorded signals with digital filtering.

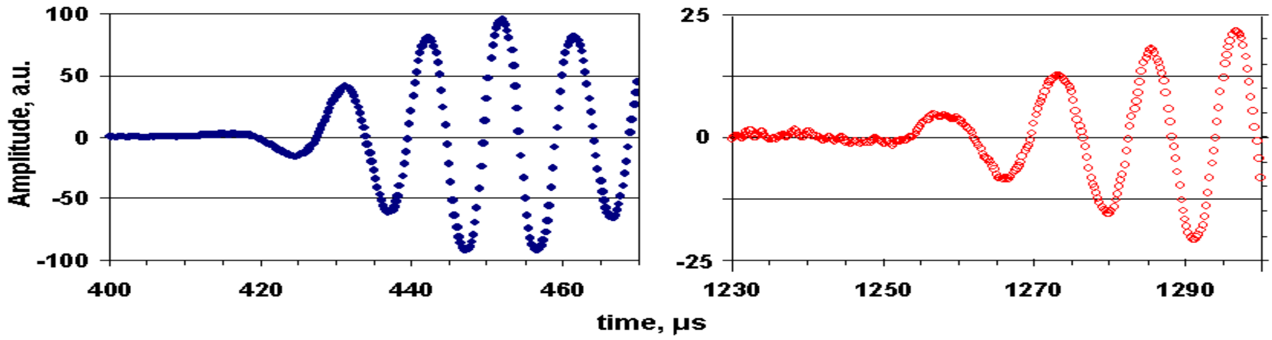

Fig. 2. Typical time windows containing the first (left) and the second (right) arrivals of extensional waves to the receiver.

The effect of the absorbed H on the time of first arrival of the extensional wave to the receiver is shown on Fig. 3 with 10x amplification of the ordinate scale and a narrow time window. It is clear that the speed of sound increased contrary to the expectations derived from the literature. To evaluate this change we linearly interpolate the data in order to obtain the moments of time when the recorded signal changes its polarity (so that we can compare phase velocity) starting from the first half-wave at ~419 μs till the fifth half-wave at ~445 μs. Similar calculations were conducted for the second arrival of the extensional wave. By averaging the differential times for both stages of H charging, we obtained 3.3-4.0 m/s velocity increase after the first stage and 3.9-4.6 m/s after the second stage of H charging relative to the sonic speed in the uncharged sample. These numbers correspond to 0.13-0.16% increase in Young's modulus value for 14 kC of charging and 0.15-0.18% increase for 17 kC of H charging since the changes in isothermal extensional wave phase velocity c_E has to be directly proportional to the $E^{0.5}$.

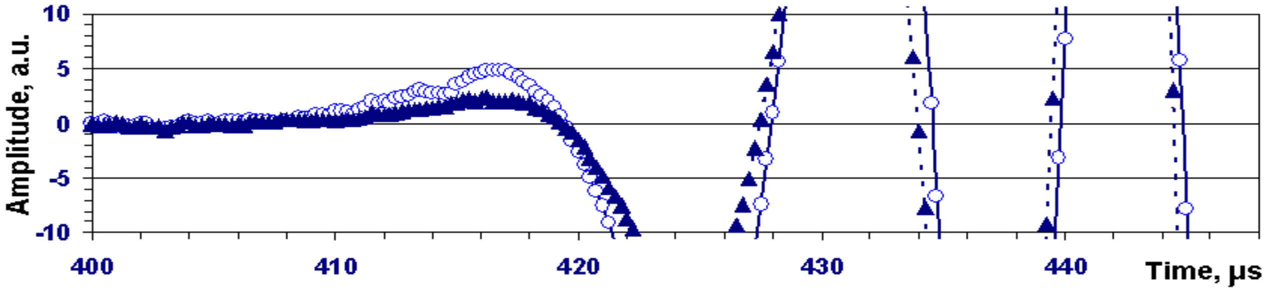

Fig. 3. Superimposed signal trains: before (open circles – solid lines) and after H charging (filled triangles – dashed lines) in the time window containing the first arrival of extensional waves.

We have to note here that the differential times are not identical for different half-waves but exhibit a specific tendency of change. For instance, the time shifts for the zero-amplitude phases after 14 kC of charging vary in a sequence 0.17–0.46–0.52–0.29–0.21 μs (all negative). Similar tendency is observed for the 17 kC case, suggesting a systematic distortion of the shape of the acoustic signal, though the signal from the second arrival is not that smooth and clear due to the interfering echoes.

Discussion

There are several issues that have to be taken into consideration when the change of elastic properties, as calculated from the sonic velocity change, takes place as a result of H absorption by metal. They are at least threefold and include i) the geometry change of the sample, specifically its length since lateral changes are of little concern, ii) the changes in density of the material and iii) the changes in its elastic properties.

Linear expansion due to the absorbed H. If we assume random distribution of 0.1-1 wt. ppm H in the rod, the expansion of the rod could be calculated according to Eq. 3

$$\Delta L/L_0 = 1/3\, C(\mathrm{H})\, (V_m(\mathrm{H})/V_m(\mathrm{Fe})), \tag{3}$$

where ΔL – absolute expansion of the rod, L_0 – initial length of the rod; C(H) – assumed concentration of electrolytically absorbed H; V_m(H) and V_m(Fe) – partial molar volume of H in iron and molar volume of iron, respectively. Taking $V_m(\mathrm{H}) = 2\ \mathrm{cm}^3$/mole (2.66 cm^3/mole was proposed by Bockris [29]), we obtain ΔL = 1–11 μm, which corresponds to 0.5–5 ppm increase in length of the rod. Increase in length works not for the shorter arrival, but for the longer. So, this factor is among competitive factors and is very insignificant in value.

Effect of the temperature change. Among the factors that affect the sonic speed in the material is temperature. Actually, temperature changes both the material's density and its elasticity constants. For BCC α-Fe and most of structural steels the temperature coefficient of sound speed is of the order of -0.6 m $s^{-1}K^{-1}$. E.g., for 1008 and 1020 types steel it is ca. -0.68 m $s^{-1}K^{-1}$ while for 1035 steel is -0.63 m $s^{-1}K^{-1}$ [30]. Since during the experiment the solution in the electrolyzer was continuously refreshed, we recorded a small decrease in temperature of the order of 0.5 °C. This would correspond to the increase in the speed of sound by ~0.3 m s^{-1}, which is 7-8% of the total speed increase. There is no way that during the experiment the temperature could decrease by 6-7 °C to suffice for the quickening of the wave arrival. Thus, the observed positive change in speed velocity could not be attributed to temperature. We have to admit, however, that the stability of this parameter was hard to control and that we have to adopt a different approach for keeping the temperature-induced error smaller.

Density change. Taking 0.1–1 wt. ppm of the dissolved H and 2cm^3 of its partial molar volume in iron, we obtain 2–16 ppm of the density decrease due to the absorption of H. Since $E = \rho c^2$ (Eq. 2), a decrease in density works for the decrease in elastic modulus but this change is insignificant again.

Redistribution of strain in the rod's cross-section. Due to a significant partial molar volume of H in iron one might expect a type of *swelling* of the outer layers where chemical potential of H is high relative to the bulk. Before the steady-state is reached, such swelling would be restrained with the unaffected (or less affected) core, which should exhibit tensile straining to balance the compression stress of the outer shell. In real cold-formed rods the residual stress field should be accounted for. The distribution of residual stresses heavily depends on the technology of forming and could vary significantly, which is unknown to us. It seems, however, that the effect of redistribution of a strain field in the rod could be among the most important factors impacting the measurements of the deviation of elastic modulus under the effect of absorbed H. Should this effect exists, it would be rooted in the dependency of the velocity of the elastic wave propagating through the solid on stress, which in the simplified form as applied to the rod could be expressed as Eq. 4 [31]:

$$c = c_0 (1 - \beta\sigma), \tag{4}$$

where c_0 – the initial velocity when the stress is not applied and $\beta = g_{222} / f_{22}$ (g_{222} and f_{22} – non-linear and linear elastic constants [31]). Experimental observations [31] suggest that for industrial bolts M16 made of carbon steel, the change in the 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 0.08-0.09% change in sound velocity obtained in our experiments would correspond to compressive stresses of 80-90 MPa.

These numbers are close to those derived on the basis of more earlier studies suggesting a speed increase of 0.1% per 20 ksi of compressive stress in 1018 low-carbon steel (Lynnworth is quoting the work of Hsu [12,32]). Converting to metric system we obtain for the extensional wave in steel (~5100 m/s) a corresponding compressive stress of about 105-125 MPa, which do not sound like unreasonable numbers, but easily fall into the range of residual stresses characteristic to the cold-forming operation.

Acoustoelastic effect. It seems that the observed changes in the speed of sound under the influence of absorbed H could not be attributed to acoustoelasticity [33,34].

Magnetoelastic effects. In continuation of the above discussion on the possible influence of the stress field in the material affected by H charging, we have to notice that α-Fe that constitute the major part of studied steel, is a ferromagnetic material, known also for its magnetoelastic properties. This means that the applied stress, be it externally applied, or internally induced by the absorbed H, affects the magnetization vectors of magnetic domains contained by individual grains of the polycrystalline material. Though the effect is supposedly small, there is a measurable deviation from the ideal cubic crystal structure with defined orientational dependencies of all elastic constants, including Young's modulus. The apparent Young's modulus of a ferromagnetic material E_m could be deduced from Eq. 5 [35]:

$$E^{-1} = E_0^{-1} + 0.4\,\lambda_s / \sigma_\mathrm{i}\,, \tag{5}$$

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 10^8 Pa, or 10^2 MPa, i.e. quite a reasonable order of magnitude, though more precise evaluation of this parameter requires further study.

Since the absorbed H during our experiment was unevenly distributed in the bulk of the studied steel rod, being located mostly near the surface, this region should have experienced an addition of compressive stress while the core should have experienced an increase in tension, provided the core is already under tension. However, the distribution of residual stress could be complicated, in which case the effect of hydrogen would depend on such distribution. We could not exclude that the distortion of the shape of the first wave bell is caused by the redistribution of stresses, induced by the absorbed H.

Conclusion

The effect of absorbed hydrogen on Young's modulus of cold-rolled low-carbon steel rod was investigated using a time-of-flight approach. Speed of sound increased after hydrogen charging of the sample, with corresponding increase in elastic modulus of the material. The obtained results are discussed regarding the possible origins of the change in elastic modulus.

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