

The hydrogen material interaction during cyclic mechanical loading

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Abstract

The two-continuum model of solid allows one to describe the influence of small concentration of hydrogen on the mechanical properties of materials in terms of changing the bonding energy of the second continuum, the latter being responsible for the hydrogen concentration. The experimental technique and experimental results are described in the report. We discuss and model the hydrogen redistribution during fatigue loading.

1 Introduction

Hydrogen is contained in all structural materials. It is known that under mechanical loads the hydrogen inside the metal is concentrated in the areas of tensile mechanical stresses (the Gorsky effect [1]).

On the other hand, elevated hydrogen concentrations are often one of the causes of destruction. Saturation with hydrogen from the outside ultimately leads to hydrogen brittleness.

Accumulation of hydrogen in the destruction zone occurs both by ingress from outside and by redistribution of natural hydrogen inside the material.

For practically all the structural materials, natural hydrogen concentrations are as low as decimal ppm fractions to ppm units, and there have been very few studies of their effect on the mechanical properties.

It is known that the hydrogen inside the materials, is located in traps with different binding energies. In steels the total hydrogen content is 0.1-6 n.sm³/100g, while it is only hydrogen with a low binding energy that affects the strength, i.e. diffusively mobile hydrogen. In aluminum alloys the entire hydrogen diluted in the metal has a low binding energy - about 0.2-0.8 eV. The concentrations that are critical for the mechanical strength of weakly bound hydrogen in steels and aluminum alloys are similar - they are decimal ppm fractions. In aluminum alloys it includes the entire diluted hydrogen, while in steels it is up to 5-10% of the total amount of diluted hydrogen.

Measuring such low hydrogen concentrations for the sample mass of 1-3 g presents a scientific and engineering problem. Therefore, as a rule all the information on the connection between hydrogen concentrations and the mechanical state of the metals was obtained after preliminary saturation of the samples with hydrogen. Saturation from the outside results in a disturbance of the natural picture of hydrogen distribution in accordance with binding energies, and thus the laws established experimentally do not always work in case of usual mechanical loading.

We have developed a precision analyzer (AV-1) that allows accurate measuring of the natural concentrations. The sensitivity of the analyzer is such that it is possible to measure the amount of hydrogen in the traps whose volume is several thousand times lower than the total amount of hydrogen extracted from the sample.

The method of high-temperature vacuum extraction using analyzer AV-1 was applied for investigating the defective structure of materials subjected to fatigue failure and to destruction at uniaxial tension. When this method is applied, the sample does not heat up to a melting temperature; consequently “natural” hydrogen must carry the information on the status of the crystal lattice of the metal after its manufacture and operation.

The method developed for analysis of the dynamic curves of vacuum extraction enables us to determine the binding energy and the volumes of traps of various nature, and the constants of hydrogen diffusion in the sample under examination.

2 Experimental equipment

The precision hydrogen analyzer AV-1 was developed for determination of hydrogen content in metals and alloys under plant laboratory conditions and used for output control of castings from different alloys.

The analyzer operates on the mass-spectrometric principle. The sample preparation includes the application of a vacuum extractor and an oven. In the process of analysis the metal sample inside the metal extractor gradually heats up to an extraction temperature of 400-800 °C. The temperature of the analysis is below the melting temperature of the sample. The gases released at heating in vacuum are analyzed by the mass-spectrometer. The time dependence of the hydrogen flow $q(t)$ is registered by the digital registration system in the form of an extraction curve. We have developed a highly measurement complex for absolute measurement of hydrogen content in a solid sample of practically any composition.

3 Assessment of the hydrogen binding energy in metal and of diffusion constants

The high sensitivity of AV-1 and representative statistical data (about 30,000 points per curve) make it possible to see a number of maxima on the extraction curve. By the position of the maximum and by its shape, one can determine the binding energy, the diffusion constants and the cumulative volume of the flux which each peak corresponds to [2].

The highly sensitive hydrogen analyzer AV-1 utilizes the mass-spectrometric principle. The specimen preparation requires a vacuum extractor and an oven. The specimen inside the metal extractor is heated gradually up to an extraction temperature of 400-900°C. The temperature needed for analysis is below the melting temperature of the specimen. The gases released at heating in vacuum are analyzed by means of the mass-spectrometer. The time-dependence of the hydrogen flux $q(t)$ registered by means of the data acquisition system yields the so-called extraction curve.

Fig. 1 shows the experimental curve for titanium alloy PT-7M. Near the peaks one can see the hydrogen binding energies that correspond to them.

Fig. 2 shows the experimental extraction curve for monocrystal silicon indicating the hydrogen binding energies that correspond to each peak.

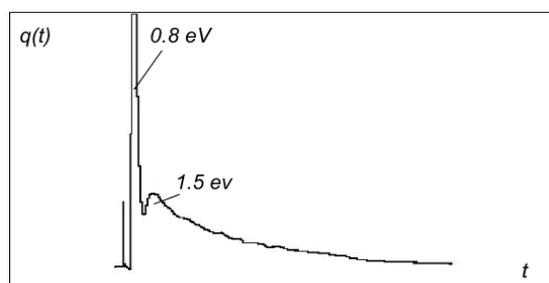


Figure 1: Extraction curve for titanium alloy PT-7M indicating the binding energies that correspond to separate peaks of the curve

As a result of numerous tests it was possible to establish that the hydrogen in metals and semiconductor materials occupies discrete energy levels. E.g., for aluminum alloys, 2-4 levels can be observed within the 0.2 to 0.8 eV range.

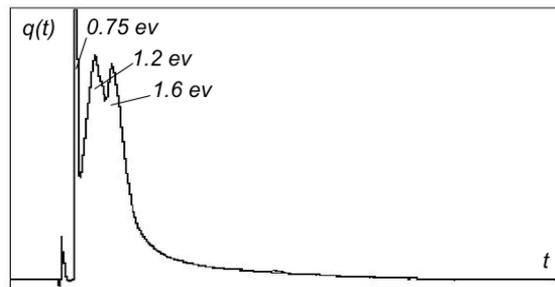


Figure 2: Extraction curve for for monocrystal silicon indicating the binding energies that correspond to separate peaks of the curve

4 Accumulation and redistribution of hydrogen in the process of operation of structural materials

Our equipment enables separating various binding energies, even those of weakly bound diffusely hydrogen, and register redistribution of hydrogen in the traps under destruction. Thus in the case of fatigue destruction the distribution of hydrogen over the binding energies in the destruction zone changes radically. The total amount of the diluted hydrogen also increases, but not so significantly.

Investigations of the hydrogen distribution were carried out on the specimens made of aluminum alloys. These specimens were subjected to cyclic uniaxial tension with the number of cycles up to 10 million. After the mechanical (fatigue) testing has been performed, small specimens from the broken and non-broken large specimens are shown in Figs.3 and 4.



Figure 3: Scheme of cutting small specimens for hydrogen testing from a large specimen broken under fatigue test

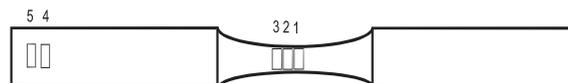


Figure 4: Scheme of cutting specimens for hydrogen testing from a large specimen non-broken under fatigue test

The growth in the hydrogen concentration with increase in the number of cycles is revealed. The hydrogen distribution over binding energy for broken end non-broken specimens is principally different. Figures 5 and 6 display the typical extraction curves for the neck of the broken and non-broken specimens.

The analysis of the experimental data shows that full concentration of hydrogen is approximately equal everywhere. In the destruction zone, practically all the hydrogen is in the diffusively mobile state and, on the contrary, it is in the strongly bound state in the zone without plastic flow

5 A two continuum model

Basic principles of the above mentioned hypothesis can be illustrated on example of analysis of the one-dimensional chain consisting of identical particles which are the point mass m_0 (the atom mass in the crystal lattice of a material). They are connected to each other by the identical nonlinear springs of the length a , cf. Figure 7.

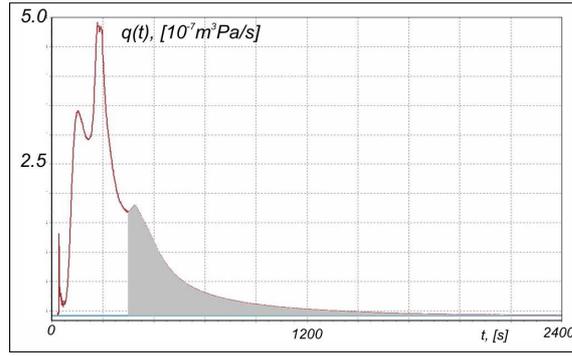


Figure 5: Extraction curve for specimen number 1 cut from broken neck

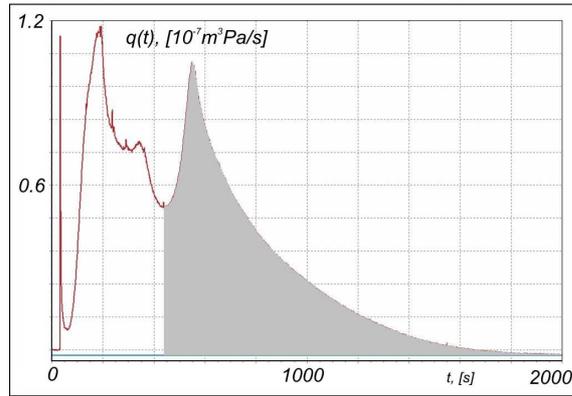


Figure 6: Extraction curve for specimen number 1 cut from non-broken neck



Figure 7: The schematics of the material model

The basic equation of the motion in the long-wave approximation is given by, cf. [3]

$$m_0 \ddot{u} = -a[f(a(1+u'))]' \quad (1)$$

where a dot denotes the time derivative. As for small deformations $\varepsilon = \partial u / \partial x$ we arrive at the following equation

$$\ddot{u} - \vartheta_0^2 u'' = 0, \quad \vartheta_0 = a\sqrt{C/m_0}$$

since $f[a(1+\varepsilon)] \approx -Ca\varepsilon = -Ca\partial u / \partial x$.

The weakening of the internuclear bonds caused by “landing” of the hydrogen particles (or other mobile internal elements of structure) can produce the chain formations of new internuclear bonds, see Figure 8, as the consecutive connections of elastic bonds of the basic lattice and the introduced elastic bonds of new elements (e.g. hydrogen particles). Obviously, such chain is possible under the assumption that the mass of particles of a mobile structure is small, i.e. $m_0 \gg m_H$.

Equivalent rigidity of the new bond can be obtained from the equation

$$\frac{N_\Sigma}{C_\Sigma} = \frac{N_0}{C_0} + \frac{N_H^+}{C_H} \quad N_\Sigma = N_0 + N_H^+$$

The constitutive equation for this medium is as follows

$$\sigma^{(1)} = E_{\Sigma}\varepsilon, \quad E_{\Sigma} = \frac{E_0 E_H}{n_0 E_H + n^+ E_0}, \quad n_0 = \frac{N_0}{N_{\Sigma}}, \quad n^+ = \frac{N_H^+}{N_{\Sigma}}, \quad n_0 + n^+ = 1.$$

Here N_{Σ} denotes the total number of the particles in the elementary volume, is the number of the particles connected by the weaken bonds, N_H^+ is the number of hydrogen particles attached to the lattice with the bonds of rigidity C_H . Finally, n_0 , n^+ are the concentrations of the corresponding particles.

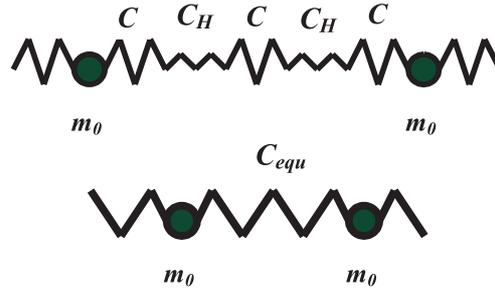


Figure 8: The model of the material with hydrogen particles

For small deformations the nonlinear force $f = f(a(1 + u'))$ in Eq. (1) can be introduced as

$$f = -C_{\Sigma}a\varepsilon = -E_{\Sigma}\varepsilon$$

The equivalent modulus of the lattice E_{Σ} , can be decreased essentially, since $E_H \ll E_0$ ($C_H \ll C_0$), and has a strong dependence on the concentration of the attached particles n^+ .

The number of the lattice settled by the hydrogen particles depends on the stress state of the lattice at every point and, in general, on time. The unknown functional dependence of E_{Σ} on $n^+(\varepsilon, x, t)$ should be determined with the help of the model of two-component continuum.

The details of the theory of two-component continuum can be found in [3]; therefore we are presenting here only the final results with some necessary explanation of the processes.

From the state equation we have $\sigma = \sigma(\varepsilon, n^+(\varepsilon, x, t))$, thus,

$$\sigma = E_0\varepsilon \left[1 - \frac{n_H^+}{n^+ + n_0 E_H E_0} \right], \quad (2)$$

and the essential dependence of the stress state on concentration of the bonded hydrogen becomes evident.

The hydrogen concentration is described by the equation for n^+

$$\frac{\partial^2 n^+}{\partial t^2} + (\alpha + \beta) \frac{\partial n^+}{\partial t} + A \cdot D(\varepsilon_{st}) \left[\beta \frac{\partial^2 n^+}{\partial x^2} + \frac{\partial^3 n^+}{\partial t \partial x^2} \right] = 0. \quad (3)$$

Here $A = C_H^2 k j$, α and β are some constants, and $D(\varepsilon_{st})$ denotes the hydrogen diffusion constant.

Equations (2) and (3) form a system for modeling the hydrogen influence on the dependence $\sigma(\varepsilon)$ for the material.

Equation (3) is of the hyperbolic type with moving front of the bound hydrogen concentration. The Fourier method assumes the substitution $n^+(t, x) = T_{n^+}(t) \cdot X_{n^+}(x)$ that yields:

$$\frac{\ddot{T}_{n^+}(t) + (\alpha + \beta)\dot{T}_{n^+}(t)}{C_H^2 D(\varepsilon_{st})(\beta T_{n^+}(t) + \dot{T}_{n^+}(t))} = \frac{X''_{n^+}(x)}{X_{n^+}(x)}.$$

Equation for function $X_{n^+}(x)$ is :

$$X''_{n^+}(x) + \gamma_x^2 X_{n^+}(x) = 0.$$

Equation for function $T_{n+}(t)$ is:

$$\ddot{T}_{n+}(t) + (\alpha + \beta + \gamma_x^2 \frac{C_H^2}{k} D(\varepsilon_{st})) \dot{T}_{n+}(t) + \gamma_x^2 \frac{C_H^2}{k} D(\varepsilon_{st}) \beta T_{n+}(t) = 0.$$

Substituting $G(\varepsilon_{st}) = \frac{C_H^2}{k} D(\varepsilon_{st}) \gamma_x^2$ we obtain:

$$\ddot{T}_{n+}(t) + (\alpha + \beta + G(\varepsilon_{st})) \dot{T}_{n+}(t) + G(\varepsilon_{st}) \beta T_{n+}(t) = 0.$$

This is the linear equation with floating factor $G(\varepsilon_{st}(t))$. The term $D(\varepsilon_{st})$ has the physical interpretation as powerful hydrogen diffusion channel. During the cyclic loading by harmonic force we have a harmonic deformation: $\varepsilon_{st} = \varepsilon_1 \cos(\omega t)$. As a first approximation we can take $D(\varepsilon_{st}) = D_0 + D_1 \cos(\omega t)$ and obtain the equation with cyclic coefficients

$$\ddot{T}_{n+}(t) + (\alpha + \beta + (G_0 + G_1 \cos(\omega t))) \dot{T}_{n+}(t) + (G_0 + G_1 \cos(\omega t)) \beta T_{n+}(t) = 0,$$

Here $\omega_0 = \sqrt{G_0 \beta} = C_H \gamma_x \sqrt{\frac{D_0 \beta}{k}}$ is the intrinsic frequency of the hydrogen redistribution. The frequency depends of total hydrogen concentration, the parameter of the volume distribution (γ_x) end energy redistribution coefficient (β). The time-dependent increasing of hydrogen concentration lead to increasing the intrinsic frequency. Hence during the fatigue loading we have $\omega_0 = 2\omega$, or

$$C_H = \frac{2\omega}{\gamma_x} \sqrt{\frac{k}{D_0 \beta}}.$$

This hydrogen concentration is critical for the parametric resonance. And we will have parametric instability that may be interpreted as dynamic hydrogen embrittlement during cyclic loading.

6 Discussion of the results

The capability of gases for dilution in metals is known [4]. In many cases the gases that do not form stable chemical compounds with alloy components are accumulated along the grain boundaries in traps of various nature.

There is a known method of examining the dislocation structure of solids by low-temperature saturation of metals with inert gases (helium, argon etc.). Upon subsequent heating of the samples up to various temperatures, the dynamics of the gas release was studied. The dislocations and the rate of dislocation density change are determined by using the dynamic curves of gas release and the extraction curves. It was experimentally discovered that adsorption of gas molecules with a very high binding energy is possible in micro-defects on the free surface of the crystal. E.g., the binding energy for chemically inert helium is about 1 eV, which is close to the chemical bond energy [5].

In many cases it is impossible to explain elevated concentrations by hydrogen diffusion from the environment as the normal hydrogen concentration in the air is 0.5 ppmv. The literature provides descriptions of two mechanisms of hydrogen accumulation – transfer by micro-defects inside the material and release of hydrogen from water at corrosion.

In our experiments we managed to study the fine structure of hydrogen bonds in metal. We studied natural concentrations and discovered that the fatigue phenomenon at uniaxial tension are accompanied by accumulation of weakly bound hydrogen. The accumulation itself can be explained by the processes of hydrogen transfer at formation of new structural micro-defects in the destruction zone. It is most probable that, at application of strains, hydrogen is bound with free surfaces thus causing weakening of the material due to a reduction of the free energy and fixation of the defects. After rupture, the tensile stresses disappear and the hydrogen is squeezed out into a weakly bound state.

We are of the opinion that the hydrogen has the discreet character of the energy levels in the solid body. Therefore each peak of the extraction curves corresponds to a different character of the hydrogen bond with the crystal lattice of the material.

If our hypotheses are true, the prevention of hydrogen diffusion inside the material serves to substantial increase its fatigue strength and the maximum deformations. The same effect can be

obtained by decreasing the gas permeability of the material surface, e.g. by designing parts with an increased surface tension or by using special coatings. The absence of hydrogen inflow from the outside will increase the service life of the part.

This fact makes it possible to use the measurement results for hydrogen concentration distribution according to binding energies not only for analysis of the causes of destruction and material quality control, but also for the development of new materials with enhanced mechanical characteristics.

Application of the methods developed to non-metallic material opens yet another application area of hydrogen diagnostics.

The two continuum model provides us with the ability to determine the critical hydrogen concentration from one of the hydrogen embrittlement sets in [3]. We apply this model to fatigue test and also obtain the critical concentration for dynamic hydrogen embrittlement. The linear approximation makes impossible to model of the hydrogen content with increasing trend, because the eigenfunctions are orthogonal. But we can determine the beginning of the destruction process - the point of instability.

We need for nonlinear approximation for the modeling of the hydrogen accumulation during fatigue test.

It is very important that the intrinsic frequency $\omega_0 = C_H \gamma_x \sqrt{\frac{D_0 \beta}{k}}$ is small, because $C_H \ll 1$. But fatigue loading frequency is also small (often $\omega \ll 1$). Thus the frequencies coincidence during real fatigue loading is very probable.

7 Conclusions

We have developed the equipment that makes it possible to obtain information on the structure of hydrogen bonds within the material according to the hydrogen extraction curve at heating a sample in vacuum. The accuracy of determination of the extraction curve makes it possible to obtain information on both the hydrogen binding energy in the metal and on the concentration of mechanical flaws.

The experiments we conducted have confirmed that the fatigue phenomena and destruction of structural materials are accompanied by increased concentration of lightly bound hydrogen in the destruction zone.

It was first detected that mechanical loads result in a substantial redistribution of hydrogen according to the binding energies inside metals.

The suggested calculation methods enable us to make approximation of the experimental extraction curves and determine the diffusion constant and the activation energy for every peak of the curve.

This approach to investigation of the properties of materials does not require preliminary saturation of the samples under study with hydrogen. Natural hydrogen within the metal carries the information on the past history of the material, which, once the methods are further developed, will make it possible to obtain more detailed information from the measured extraction curves.

The application of the two continuum model to fatigue task give the hydrogen concentration that are critical for material destruction. Such fatigue destruction has a nature of parametric instability during the cyclic redistribution of the hydrogen under the cyclic loading.

Acknowledgements

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References

- [1] W.S. Gorsky “Theorie des elastischen Nachwirkung in ungeordneten Mischkristallen (elastische Nachwirkung zweiter Art)”, *Physikalische Zeitschrift der Sowjetunion*, 8, (1935) 457-471

- [2] A.M. Polyanskiy, V.A. Polyanskiy, D.B. Popov-Diumin, “Diagnostics of mechanical condition of materials by method of high-temperature hydrogen vacuum-extraction”, Proceedings of the Sixth International Congress on Thermal Stresses, vol. 2, Vienna, Austria, (2005) 589-592
- [3] D.A. Indeitsev, B.N. Semenov “About a model of structural-phase transformations under hydrogen influence” Acta Mechanica Vol.195, (2008) 295-304
- [4] B.A. Kolachev, Hydrogen brittleness of metals, Metallurgy, Moscow, 1985.
- [5] O.V. Klyavin “Dislocation dynamic diffusion in crystal bodies”, FTT, v. 35, No 3, (1993) 513-541.

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