Hydrogen Diffusion in Metals under fatigue failure

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Abstract. In our experimental studies it was found that cyclic and long-term static loads lead to a redistribution of the natural concentration of hydrogen in metals both in volume and in the binding energies. The distribution of the hydrogen concentration along the metal sample has a distinct character under uniaxial cyclic loading. It has many extremes with the one major peak.
A model describing of phenomenon is proposed. The closed system of the equation is presented. This equation describes the hydrogen transport under the body deformation. These were obtained from the general laws of continuum mechanics and a generalized diffusion equation.
Consideration of mutual relations of the diffusion and the deformation processes is in the study actually. The deformation processes is accompanied by vibration and alternating cycles of loading and unloading of the material with hydrogen. Under the transient deformation of the body the movement of hydrogen could be directed against the entropy flux of the hydrogen diffusion. This diffusion leads to the hydrogen localization and, as a result, to the irreversible mechanical degradation embrittlement and failure of the metal in areas in which the diffusion-mobile hydrogen is concentrated.
The theoretical results are compared with the experimental data for rods from the aluminum-copper-magnesium alloy. The hydrogen accumulation in the central part of the rods, which is determined in experiments has a good agreement with the theoretical results.

Introduction

The hydrogen is contained in all metals and alloys. The initial hydrogen concentration accumulated during the melting process in the casts. Then, during the processes of the crystallization, forging, stamping, rolling, cutting, the concentration of hydrogen can either decreases or increases due to internal hydrogen diffusion and exchange with the environment. As a rule, the source of hydrogen is water. For many alloys, the concentration of the "metallurgical hydrogen" in the castings is controlled. Its levels must be below the limits of the hydrogen embrittlement.
During further exploitation of the finishing products the hydrogen concentration inside the material, usually increases. It was established that hydrogen is accumulated in the zone of tensile stresses and structural defects of the material, such as the cracks, pores and micro-cracks. These defects are the sources of the different types of metal fracture. Consequently, hydrogen can be used in industrial control as the defects indicator.
Modern hydrogen analyzers can measure the hydrogen concentration from the level at 0.001 [ppm]. Moreover, it is possible to measure not only the concentration of hydrogen, but also its binding energy distribution if we use the vacuum extraction methods for the measurements.
Consequently, there are all necessary conditions for the development and application of the hydrogen diagnostic of the metals and alloys mechanical state.

As was established during investigations the accumulation of hydrogen occurs in areas of fatigue damage evenly over time. There is not only the result of the hydrogen diffusion but also of its redistribution among the bond energy levels. This makes it possible to evaluate resource material according to the hydrogen diagnosis.

Experimental study

Ten specimens made of the alloy of Al-Cu-Pb (Fig.1) were suggested for tests on fatigue strength.

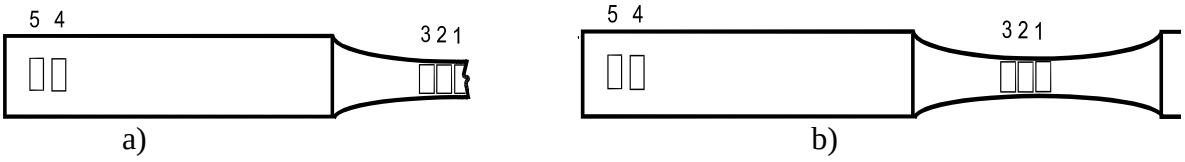
Fig.1. The form of the specimen

The specimens were subjected to a cyclic tensile load. The load parameters and test results are shown in Table 1.

Table 1. Amplitude and the number of cycles of the load

Specimen number	amplitude	cycle numbers	Test results
	MPa	millions.	
01	140	10	not broken
02	160	5,44	not broken
03	180	3,21	broken
04	180	3,60	broken
05	180	2,84	broken
06	180	1,02	not broken
07	180	0,84	not broken
08	180	0,35	not broken
09	180	0,25	not broken
10	0	0	not tested

In order to analyze the hydrogen content the cylinder specimens of diameters of 7 mm and height of 3 mm would be prepared. Figure 2 shows the cutting scheme of the broken and no-broken specimens.



a) b)

Fig.2. Scheme of cutting: a) of the broken specimens , b) for the non-broken specimens

As a result the specimen could be divided into two groups. The first one deals with the samples No. 01 and 02 subjected to the tensile stress of the amplitude 140 and 160 MPa. In the case of greater number of cycles the hydrogen distribution is not so homogeneous. Figures 4 and 5 show the distribution for the specimens No. 01 for 10 mio cycles and No. 02 - for 5,44 mio cycles. The effect of the spatial redistribution of the hydrogen in the specimen is observed. The distribution is not so homogeneous for the lower load amplitude.

The second group of the specimens No. 03, 04, 05 under the tensile stress of amplitude 180 MPa and were broken. The hydrogen content exceeds considerably the contents in the neck of the non-broken specimens.
Figure 3 shows the diagram of hydrogen distribution in the neck of specimens No. 01 and No. 10.

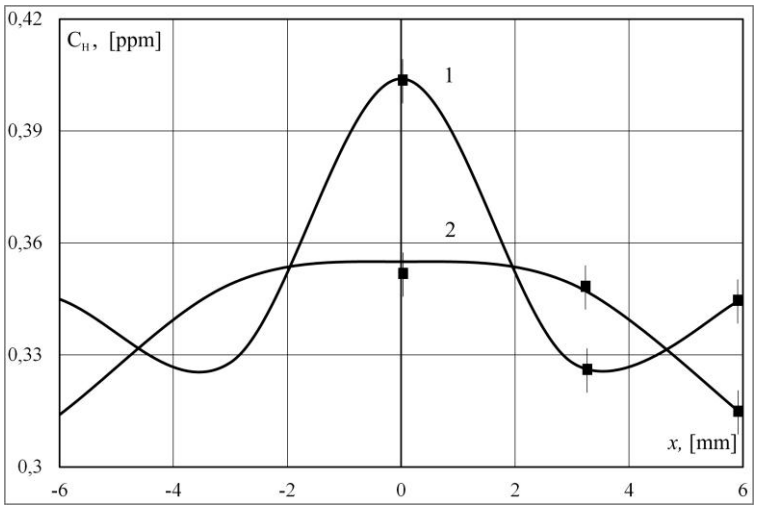


Fig.3. Diagram of the hydrogen concentration in the neck of specimens No. 01- 1 and No.10-2.

A characteristic feature of this group is the extraction curve shifted to side of mobile hydrogen. Fig.4 and 5 displays the extraction curves for the specimens made of the neck of No. 3 and 02 respectively.

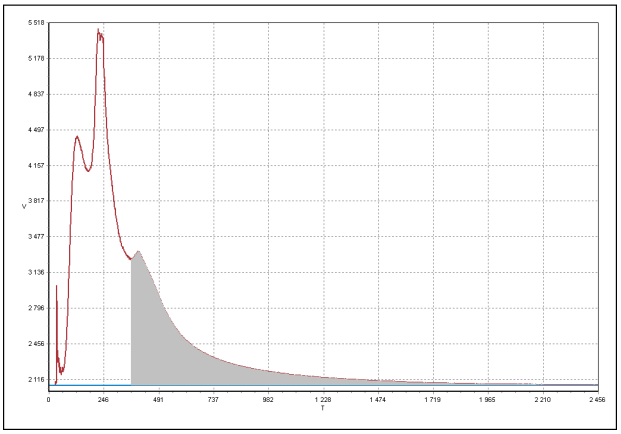


Fig.4. Extraction curve for the specimen made of the neck of No. 03.

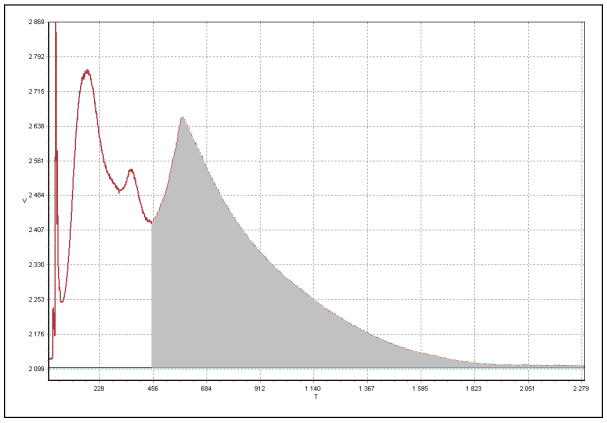


Fig.5. Extraction curve for the specimen made of the neck of No. 02.

The second peak of the extraction curve corresponding to mobile hydrogen is by several times higher than that in the non-broken one. The height of this peak allows one to estimate the number of cycles in the specimen No. 04 as 3-4 mio.

The third group consists of four specimens № 06, 07, 08, 09 loaded by a tensile force of the amplitude 180 mp and were not broken , as well as a non-loaded specimen No. 10.
The comparison of the various characteristics of the hydrogen extraction from the specimen allows us to draw the following conclusions:

1. The hydrogen contents in the necks of specimens No. 08, 09, 10 is 0.36 ppm, whereas in the neck of specimens № 06, 07 is 0.414 ppm, that indicates a greater number of loading cycles for No. 06, 07 (about 1 mio). Besides, the hydrogen distribution along the neck is not homogeneous with a minimum

in the specimen No. 02 (analogous to specimen No. 01) which is explained by a hydrogen flow from the neighbouring regions to the zone of maximum tensile stresses.
2. Hydrogen distribution along the necks of specimens No. 08, 09, 10 is not homogenous, i.e. these specimens have a relative low number of cycles, less than 1 mio.

Therefore, in the process of defect accumulation under a cyclic loading there occur both volumetric and energetic redistribution of hydrogen in the zone of tensile stresses. One observes a correlation between the residue life and the character of this distribution. The hydrogen is accumulated in the fracture zone and pushed in the state with a lower bond energy. The broken specimens have another form of the extraction curves and the hydrogen concentration in the broken specimens is essentially higher.

Theoretical model

Taking into account the mutual effect of diffusion and deformation is relevant in studying of the processes that are accompanied with vibration and alternating loading–unloading cycles in the materials with hydrogen. Under the unsteady deformation of a solid, the motion of the hydrogen can be directed against the diffusion flax. It causes to the hydrogen localization and, as a result, to the irreversible deterioration of the material mechanical properties. For example, the embrittlement and fracture of metal occurs in the places of diffusion-mobile hydrogen accumulation [1, 2].
The study of the hydrogen flow which internal stresses caused by in addition to the diffusion flow was initiated [3, 4]. However, it was resulted in to no closed mathematical model of the impurity-transport process because the flax was expressed through the parameters of a microscopic model or through unknown internal forces acting on hydrogen atoms.
In this study, we present the closed system of coupled equations of hydrogen transport during deformation of the solid that follows from the general laws of continuum mechanics. On this basis, we derive the generalized diffusion equation. As an application, the hydrogen localization phenomenon is considered in a rod during its cyclic loading. The obtained numerical and analytical results are compared with experiments on the investigation of hydrogen redistribution after the deformation of metal samples.
Thus, within the two-component approach [5], we considered two interpenetrating media: the dynamically deformed basic structure of a solid (for example, the metal lattice) and mobile hydrogen in a solid.
We describe the joint motion and the relation between the two indicated media in the absolute system of coordinates by the following set of the equations:
the equation of motion of the basic structure

$$\nabla \cdot \boldsymbol{\sigma} = \rho_1 \frac{\partial \mathbf{v_1}}{\partial t} - \mathbf{R_{21}} \tag{1}$$

the equation of motion of mobile hydrogen

$$-\nabla p = \rho_2 \frac{\partial \mathbf{v_2}}{\partial t} + \mathbf{R_{21}} \tag{2}$$

the continuity equation for mobile hydrogen

$$\frac{\partial \rho_2}{\partial t} + \nabla \cdot (\rho_2 \mathbf{v_2}) = 0 \tag{3}$$

and the equation of state of the mobile hydrogen

$$p = p(\rho_2) \tag{4}$$

Here, σ, ρ_1, and v_1 are the stress tensor, the density, and the velocity vector of the material basic structure, respectively; t is the time; ρ_2, $\mathbf{v_2}$ and p are the density, the velocity vector, and the pressure of the mobile hydrogen; and $\mathbf{R_{21}}$ is the internal force of interaction between the material basic structure and the mobile hydrogen:

$$\mathbf{R_{21}} = \rho_2 \alpha(\varepsilon)(\mathbf{v_2} - \mathbf{v}_1) \tag{5}$$

where $\alpha(\varepsilon) = \gamma / d(\varepsilon)$ is the resistance coefficient, γ is the constant, and $d(\varepsilon)$ is the characteristic size of penetrability of the material basic structure dependent on the spherical deformation [6].
Let us pass to the mobile set of coordinates related to the solid basic structure and to the relative velocity $\vartheta = \mathbf{v_2} - \mathbf{v}_1$ of the hydrogen. Equations (2) and (5) give, respectively, (6)

$$\vartheta = \frac{1}{\rho_2 \alpha(\varepsilon)} \mathbf{R_{21}} \tag{7}$$

It is permissible to neglect the moving-space forces ρ_2 in Eq. (6) because they are much less than the resistance forces $\mathbf{R_{21}}$ in the dynamics. After the linearization of Eq. (4) of state and the substitution of Eq. (6) in Eq. (7) we obtain (8) where c is the speed of sound in hydrogen.
Equation (3) in the mobile system of coordinates takes the form

$$\frac{\partial \rho_2}{\partial t} + \nabla \cdot (\rho_2 \vartheta) = 0 \tag{8}$$

Replacing ϑ with Eq. (8), we obtain the diffusion equation, which takes into account the effect of deformation and inertia forces:

$$\frac{\partial \rho_2}{\partial t} = \nabla \cdot (D \nabla \rho_2) + \nabla \cdot (\frac{D}{c^2} \rho_2 \frac{\partial \mathbf{v_1}}{\partial t}) \tag{9}$$

where $D = D(\varepsilon) = \frac{c^2}{\alpha(\varepsilon)}$. In the absence of deformation. Eq. (9) is reduced to the classical diffusion equation with the diffusivity $D_0 = D(0)$. Therefore, as the first approximation, D is determined by the experimental values obtained in statics [7].
Eqs. (1) and (9) enables us to determine the hydrogen-redistribution dynamics during the deformation of material. In most cases, the effect of the force R_{21} on the motion of the basic material structure in Eq. (1) can be neglected in the first approximation. Then the substitution of the velocity v_1 found from Eq. (1) to Eq. (9) gives the unified equation of the hydrogen diffusion in the deformed solid.
As an example, we study the dynamics of accumulation of hydrogen near the rod center $-l \le x \le l$ under the action of longitudinal forces $F_0 \sin \omega t$ on its ends. For the steady stage of the process of the rod vibrations, the solution of Eq. (1) in displacements has the following form:

$$u(x,t) = u_0 \sin \omega t \sin \frac{\omega x}{c_1}$$

We write the deformation field corresponding to it in the form

$$\varepsilon(x,t) = u_x(x,t) = u_0 \sin \omega t \cos \frac{\omega x}{c_1}$$

Here c_1 is the speed of sound in the basic material structure.

Let hydrogen be distributed uniformly at $t = 0$, and $D(\varepsilon) = D_0 - D_1\varepsilon$ [6]. We find the redistribution of the hydrogen density $\rho_2(x,t)$ under the condition of its constant mass in the rod.

In dimensionless variables Eq. (9) takes the following form:

$$\frac{\partial \rho_2}{\partial F} = \frac{\partial}{\partial X} \cdot \left((1 - \beta\varepsilon) \frac{\partial}{\partial X} \rho_2) \right) + \frac{\partial}{\partial X} \left((1 - \beta\varepsilon) \rho_2 W \right) \tag{10}$$

where $F = \frac{D_0 t}{l^2}$, $\beta = D_1 / D_0$, $X = x / l_0$, $\varepsilon(X,F) = \varepsilon_0 \sin \Omega F \cos \lambda X$, $W(X,F) = W_0 \sin \Omega F \sin \lambda X$,

$\Omega = \frac{\omega l^2}{D_0}$, $W_0 = -\varepsilon_0 \lambda \left(\frac{c_1}{c} \right)^2$, $\lambda = \frac{\omega l}{c_1}$.

Equation (10) describes two competing processes: on the one hand, the diffusion tends to the equating the hydrogen distribution in material; on the other hand, the hydrogen transport process takes place due to the moving-space forces are determined by the standing wave (the rod vibration form). The dimensionless frequency Ω, as a rule, is high. In this case, the dimensionless form of the equation enables us to search for the solution of the boundary value problem using the method of two time scales.

Due to the symmetry, it suffices to find the solution of Eq. (10) on $0 \le X \le 1$, with the initial condition $\rho_2(X,0) = \rho_0$, and the boundary conditions

$$\left. \frac{\partial \rho_2}{\partial X} \right|_{X=0} = 0, \quad \left. \left(\frac{\partial \rho_2}{\partial X} + \rho_2 W \right) \right|_{X=1} = 0$$

The use of the averaging method [8] to Eq. (10) enables us to obtain the following equation for the principal slowly evolving term $\rho(X,F)$ in the expansion of $\rho_2(X,F)$:

$$\frac{\partial \rho}{\partial F} = \frac{\partial}{\partial X} \cdot \left(\frac{\partial \rho}{\partial X} + \gamma \rho \sin 2\lambda X \right), \qquad \gamma = \frac{\beta\lambda}{4} \left(\varepsilon_0 \frac{c_1}{c} \right)^2$$

with the boundary conditions

$$\left. \frac{\partial \rho}{\partial X} \right|_{X=0} = 0, \quad \left. \left(\frac{\partial \rho}{\partial X} + \gamma \rho \ \sin 2\lambda \right) \right|_{X=1} = 0$$

and the initial condition $\rho(X,0) = \rho_0$.

The solution of the indicated problem for $F \to \infty$ converges to the following solution of the corresponding steady problem:

$$\rho = \frac{\rho_0 \exp(\kappa \cos 2\lambda X)}{\int_0^1 \exp(\kappa \cos 2\lambda x)dx}, \qquad \kappa = \frac{\beta}{8}\left(\varepsilon_0 \frac{c_1}{c}\right)^2$$

From here, it can be seen that the accumulation of hydrogen in the rod center takes place for $D_0,\ D_1 > 0$.

It should be noted that $\lambda << 1$ in the case of low-frequency loading, therefore, $\cos 2\lambda x \approx 1 - 2\lambda^2 x^2$. Then the ultimate solution takes the form

$$\rho = \frac{\rho_0 \exp(-2\kappa\lambda^2 X^2)}{\int_0^1 \exp(-2\kappa\lambda^2 x^2)dx} = \frac{2a\rho_0 \exp(-a^2 X^2)}{\sqrt{\pi}\, erf(a)}, \qquad a = \sqrt{\beta}\varepsilon_0 \frac{\omega l}{c}$$

The original boundary value problems for Eq. (10) were solved by numerical methods for various $\beta, \varepsilon_0, \Omega, \lambda, W_0$, and $\rho_0 = 1$. In Fig. 6, we show the characteristic calculated hydrogen distributions $\rho(X, F)$ along the rod length for the consecutive moments of the dimensionless time *F* (curves *1–5*).

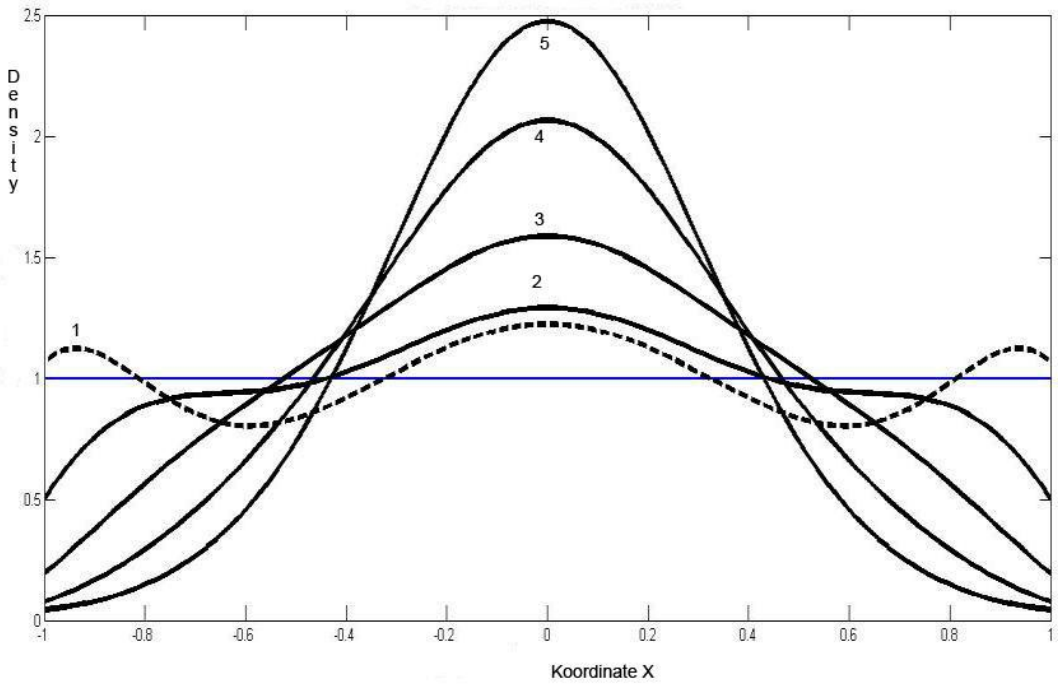


Fig.6. Hydrogen distribution for the consecutive moments of time (1-5) .

The obtained theoretical results were compared with the data of experiments carried out for ten rod samples from an aluminum–copper–magnesium alloy (Fig.3). Thus, the accumulation of hydrogen in the central part of the rod that was detected experimentally agrees well with the above results.

Summary

In the original model the internal interaction forces having a dynamic character were described. On the other hand, the hydrogen accumulation, which is quite non-uniform on the coordinate, in the central rod section was revealed with a number of tests of the samples under quasi-static loading. In this case, it is necessary to descript the forces of internal interaction between the hydrogen and the material basic structure in the form of elastic potentials. In other words, taking into account the effect of tension stresses in the hydrogen-redistribution energy balance is necessary, which requires additional investigation.

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