Modeling the skin effect, associated with hydrogen charging of samples, within the framework of the HEDE mechanism of cracking

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Abstract. The article is concerned with finite element solution of hydrogen-induced brittle fracture of a metal cylindrical specimen with a semicircular groove. The study is based on the HEDE model of hydrogen brittleness and considers the skin effect of charging the samples with hydrogen. The results showed that taking into account the skin effect leads to the changes in the mechanisms of destruction of samples, and it can be the true cause of the experimentally observed dual fracture pattern.
Keywords: cracking; decohesion; skin effect; hydrogen diffusion; dissolved hydrogen; destruction

Introduction

The influence of hydrogen on various properties of iron and its alloys has been studied since the 19th century. It was found that saturation with hydrogen leads to a strong decrease in strength properties, plasticity, impact strength and crack resistance characteristics, metal products and structures fail at loads less than the calculated ones.

As a rule, hydrogen dissolved in the material is the cause of the brittle fracture of steel. It is the only element that has a significant effect on the properties of steel, even at ultra-low concentrations (at a mass concentration of the order of one hundred thousandths of a percent) that are beyond the sensitivity range of most analytical methods for determining alloy components. The problem is complicated by the fact that hydrogen is everywhere, either in the form of chemical compounds, the most common of which is water, or in a gaseous state. Therefore, even if insignificantly low concentrations can be achieved during the production of alloys, the subsequent processing and operation of metal parts inevitably leads to the fact that the concentration of hydrogen increases, and it begins to noticeably affect the properties of metals and alloys. This makes it impossible to exclude the influence of hydrogen using special technologies. Therefore, it is necessary to take into account the effect of hydrogen on the structure and strength of materials at the stage of production of structures, as well as during their operation.

Nowadays, one of the generally accepted and most developed approaches to describing the mechanism of hydrogen embrittlement is hydrogen enhanced decohesion model (HEDE) [1]. Its concept states the following. Hydrogen moves under the action of internal stresses and accumulates near the regions of maximum normal tensile stress. An increase in its local concentration leads to a decrease in the free energy required for the formation of a fracture surface, as a result of which decohesion or "delamination" occurs.

To date, many works devoted to modeling the HEDE mechanism have been carried out. A detailed review of the latest results from this approach is given in [2]. Most of them are oriented and based on experimental data obtained for samples artificially charged with hydrogen in an electrolyte solution using a cathodic current. It should be noted here that in all the studies performed, the authors considered the distribution of hydrogen concentrations inside the metal, which occurs during the charging of the samples with it, as uniform. All redistributions and changes in hydrogen concentration were conditioned by external loading or crack growth.

Most often, the value of the initial hydrogen concentration is established only based on the fitting of the model parameters to the experimental data. Therefore, in different works it varies from 0.0001 to 2 ppm. As a result, the authors, summing up the research results, point out the emerging problems with determining a large number of model parameters and not only the qualitative agreement of the simulation results with experimental data.

Actually, charging with hydrogen leads to a highly non-uniform distribution of concentrations of this substance [3–5]. As a rule, the hydrogen content in the surface layer with a thickness of about one grain size of the metal (60-100 μm) exceeds its value inside the sample by tens of times. This phenomenon is called skin effect [6]. And despite such prolonged and thorough investigation of the problems of hydrogen brittleness, the modeling of this phenomenon has so far been carried out without taking into account the influence of the skin effect.

Obviously, skin effect will significantly affect the result of the simulation research, as well as it can discover new effects and improve understanding the mechanisms of hydrogen brittleness. And this article is concerned with a numerical investigation of the influence of the skin effect of hydrogen charging of samples on a crack growth within the framework of HEDE mechanism of cracking.

The HEDE model of brittle fracture
The process of hydrogen transport inside a solid is traditionally considered within the HEDE model as a diffusion process. To describe it, Fick's law [7] is applied with the additional term that takes into account the thermodynamic (or chemical) potential V [8]:

$$\frac{\partial C}{\partial t} = \nabla \cdot \left[D(T,\underline{r}) \left(\nabla C + \frac{C \nabla V}{RT} \right) \right]. \tag{1}$$

Here C is the hydrogen concentration, D is the diffusion coefficient, R is the gas constant, T is the absolute temperature, $\underline{r}$ is the radius vector, and t is the time. Taking into account the effect of mechanical stresses, this equation can be rewritten as

$$\frac{\partial C}{\partial t} = D[T]\nabla^2 C - D[T]\frac{V_H \nabla C \cdot \nabla p}{RT} - D[T]\frac{C V_H \nabla^2 p}{RT}, \tag{2}$$

where p is the hydrostatic pressure determined by the spherical part of the stress tensor, $p = \frac{1}{3} I_1 \left(\underline{\sigma} \right)$, V_H is the partial molar volume of hydrogen.

Further, the fracture criterion associated with the magnitude of the crack opening comes into operation in the framework of the HEDE mechanism. According to Gorsky's law [9], the hydrogen is concentrated in the region of maximal spherical part of the stress tensor (i.e. hydrostatic tension) and reduces the adhesion of the crack faces which leads to the decohesion [10].

To describe these changes in the cohesion forces of grains one uses the parameter of the degree of filling the free surface of the crack with hydrogen atoms θ which can be represented as [11]:

$$\theta = \frac{C}{C + \exp\left(-\frac{\Delta g_H}{RT}\right)}, \tag{3}$$

where Δg_H is the difference between the Gibbs free energy for hydrogen between the state of being adsorbed inside the crystal lattice and the free state (taken from experiment). The equation (3) was obtained by Serebrinsky [11] by comparing the value with the filling parameter of hydrogen traps in the metal based on the McLean ratio, cf. [12].

The value of the parameter θ determines the change in the specific energy of the free surface $\gamma(\theta)$ which depends on the surface sorption of hydrogen [11]:

$$\gamma(\theta) = (1 - 1.0467\theta + 0.1687\theta^2)\gamma(0). \tag{4}$$

From the energetical identity $2\gamma(\theta) = \sigma_{Zc}(\theta)\delta_c(\theta)$, where $\sigma_{Zc}(\theta)$ denotes the maximal cohesive stress normal to the crack edges and $\delta_c(\theta)$ is the maximal separation displacement between them without breaking of bonds (decohesion), the law of hydrogen degradation follows in the form [11]:

$$\sigma_Z(\theta) = (1 - 1.0467\theta + 0.1687\theta^2)\sigma_Z(0), \tag{5}$$

under the assumption of a weak dependence of the value of the $\delta_c(\theta)$ from the parameter θ.

In this paper, we investigate the applicability of the HEDE model to the description of hydrogen-induced destruction of a corset sample taking into account the skin effect.

The numerical experiment

We considered the problem of the hydrogen-induced fracture of steel cylindrical specimen with a semicircular groove under the action of uniaxial tension. In order to monitor and control all dependencies and parameters used in the model, we have abandoned the analysis using standard finite element packages and developed our own finite volume program code written in the C++ in the Microsoft Visual Studio.

The calculation procedure consists of two successive stages: (i) solving the mechanical problem of the stress-strain state of the sample and (ii) analyzing the diffusion problem with the simultaneous calculation of the cohesive stresses σ_z.

On the stage (i) to calculate the equations of the linear theory of elasticity, we solved the system of equations (6). It consists of the equilibrium equation, definition of linear strain tensor $\underline{\varepsilon}$ and generalized Hooke's law:

$$\begin{cases} \nabla \cdot \underline{\sigma} + \underline{f} = 0, \\ \underline{\varepsilon} = \frac{1}{2}\left(\nabla\underline{u} + \left(\nabla\underline{u}\right)^T\right), \\ \underline{\sigma} = \lambda\vartheta\underline{E} + 2\mu\underline{\varepsilon}, \end{cases} \tag{6}$$

where $\underline{\sigma}$ – Cauchy stress tensor, $\underline{f}$ – volumetric force density, $\underline{u}$ – displacement vector, $\underline{E}$ –Young modulus, $\vartheta = \mathrm{I}_1\left(\underline{\varepsilon}\right)$, λ and μ – Lame parameters.

To solve the differential equilibrium equation in (6) numerically we used the establishment method, proposed by Wilkins [13]. It lies in the fact that the stationary problem solution is obtained by solving it as the non-stationary problem and reaching the stationary mode.

The characteristics of the stress-strain state of the sample obtained at this step were transferred to the next stage (ii). It included solving the system of foregoing Eqs. (2), (3), (5):

$$\begin{cases} \frac{\partial C}{\partial t} = D[T]\nabla^2 C - D[T]\frac{V_H \nabla C \cdot \nabla p}{RT} - D[T]\frac{C V_H \nabla^2 p}{RT}, \\ \theta = \frac{55.85 \cdot C \cdot 10^{-6}}{55.85 \cdot C \cdot 10^{-6} + \exp\left(-\frac{\Delta g_H}{RT}\right)}, \\ \sigma_Z(\theta) = (1 - 1.0467\theta + 0.1687\theta^2)\sigma_Z(0). \end{cases} \tag{7}$$

The numerical solution of Eq. (2) was also carried out based on the establishment method of Wilkins [13]. The value of stress $\sigma_Z(0)$ was taken equal to $4.5\sigma_Y$ following the recommendations of [14].

A schematic representation of the specimen that we studied is shown in Fig. 1 (right side). The diameter of a cylinder is $d = 16$ mm, the radius of a semicircular groove is $r = 0.6$ mm. We solved the problem in a two-dimensional axisymmetric formulation. Considering the symmetry, we modeled a quarter of the longitudinal section of the cylinder that is also shown in the Fig. 1. The tensile load $\sigma = 500$ MPa acting along the horizontal axis Ox was applied to

the right edge of the sample. Mesh nodes on the right edge of the simulated area were unable to move along the horizontal direction Ox, nodes on the lower edge - along the vertical direction Oy. The physical properties of the considered material are shown in Table 1.

Table 1. Physical properties of the PSB1080 steel

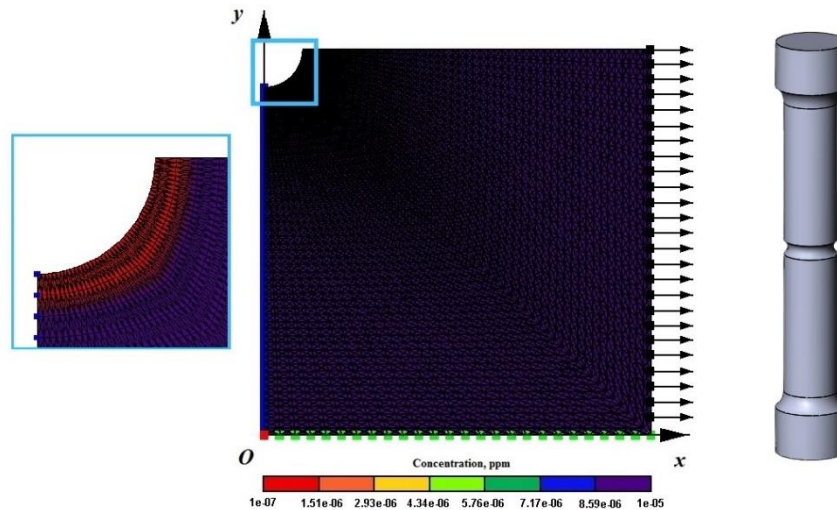| Tensile strength σ_B, MPa	Yield strength σ_Y, MPa	Density ρ, kg/m³	Bulk modulus K, GPa	Shear modulus μ, GPa
1498	1276	7800	160	79.3

Fig. 1. Finite element model: initial and boundary conditions

The skin effect was represented by the established initial hydrogen concentration $c_0 = 10\ ppm$ in a thin surface layer of the specimen with a thickness of one element (Fig. 1, zoom). At the same time in the entire volume of the cylinder the initial substance concentration was equal to the background value $c_{bg} = 0.1\ ppm$, usually observed in experiments.

It was assumed that the crack would consistently propagate along the left edge of the simulated area, starting from the groove surface. The criterion for the destruction, that is, the breaking of the bond between the atomic planes of the material, was the elastic stress obtained from the solution of the static problem exceeding the magnitude of the cohesive stress. As soon as this relationship was fulfilled, the restriction on displacement along the vertical axis Oy was removed at the mesh node. This node was able to break away from the bottom face or, taking into account the symmetry, from the opposite nodal point and move upward under the action of the tensile load.

Simulation results

One of the values monitored during the simulation was the time elapsed between the fulfillment of the fracture criterion at two successive mesh nodes. It was found that the dependence of this value as the crack propagates deeper into the sample is strongly non-monotonic (Fig. 2).

The fracture criterion at the first mesh node was fulfilled instantly, at the very first integration time step. This is conditioned to the high hydrogen concentration in the surface layer of the sample. The same was observed for the second mesh node. The concentration of hydrogen in the sample remained almost unchanged.

Further, as can be seen in Fig. 2, starting from the third node, the value of calculation time increases and reaches its maximum at the sixth mesh node (at 0.85 mm from the sample surface). This is associated with the fact that now it takes some time in solving the diffusion problem, which is necessary for hydrogen to redistribute under the action of the internal stresses

and can accumulate near a new stress concentrator - the current crack tip. At the same time, it should be noted that undoubtedly the level of normal stresses acting in the horizontal direction near the concentrator is constantly increasing. The critical hydrogen concentration, at which the fracture criterion was fulfilled, at the third mesh node was 0.375 ppm, and at the sixth its value decreased to 0.226 ppm.
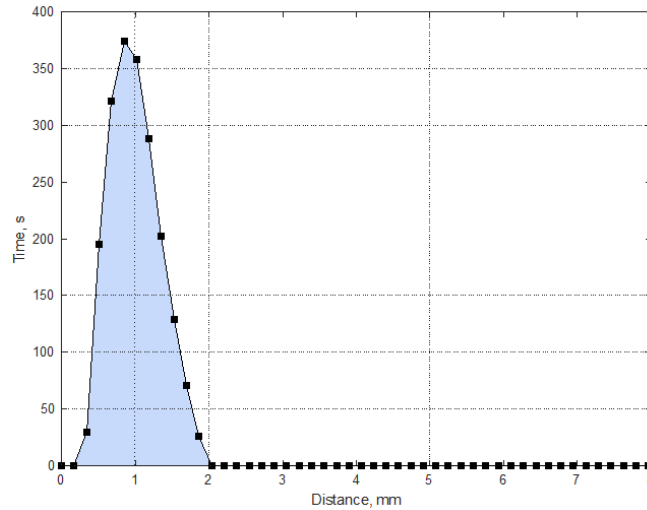

Fig. 2. Dependence of the time interval between the fulfilment of the fracture criterion in two successive nodes

After that, the value of the stresses acting near the concentrator begins to play a key role. Its value becomes more and more, that makes it possible to accumulate a lower content of hydrogen at the crack tip to fulfill the fracture criterion. Therefore, in Fig. 2, we observe a section of decreasing dependence up to the twelfth mesh node, that corresponds to 1.86 mm from the sample surface. The critical hydrogen concentration at this node was 0.112 ppm.

Hereafter, the level of the acting stresses becomes sufficient for the fracture criterion to be fulfilled even at the background hydrogen content. Therefore, the further propagation of the crack will occur instantly, at the very first integration time step.

The distribution of hydrogen concentration along the radius of a specimen is shown in Fig. 3. There are dependencies for different points in time - from the initial distribution, that we have established, to the propagation of a crack to a quarter of the cylinder thickness.
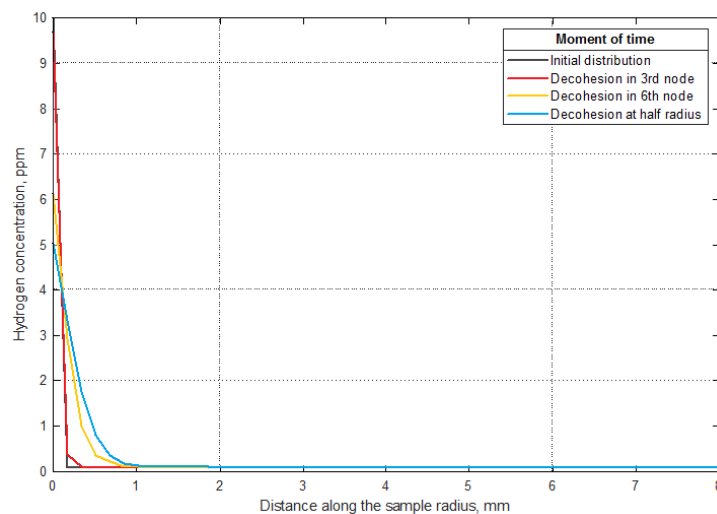

Fig. 3. The distribution of hydrogen concentration along the cylinder radius

It was found that, as the crack propagates, the increased hydrogen content, clearly limited by the surface layer and associated with the skin effect, gradually smooths out, it propagates deep into the material under the action of applied stresses. But at the same time, it does not penetrate deeper than a certain value, in this case 1.86 mm from the sample surface. Further crack propagation occurs at the background concentration without being accompanied by hydrogen diffusion. This is due to the high level of internal stresses acting near the crack tip.

Discussion
We carried out a numerical simulation of the hydrogen-induced brittle fracture of a cylindrical specimen with a semicircular groove based on the HEDE mechanism and considering the skin effect of charging the sample with hydrogen.

Of particular interest is the final distribution of hydrogen over the cylinder, obtained by solving the problem, taking into account such a non-uniform initial content of hydrogen. It is shown schematically in the Fig. 4.

While the crack is small and a relatively low stress acts near the tip, its growth will be provided by a high level of hydrogen concentration present in the surface layer and subsequently penetrates a little deeper into the bulk of the sample. This area corresponds to the zone of hydrogen-induced brittle fracture of the specimen. At the same time, when the crack propagates to the central part of the specimen, the level of internal stresses near the concentrator is high. Therefore, its growth will occur instantly, without the need for an increase in the background hydrogen concentration and without enough time for its further redistribution. This will correspond to the areas of the ordinary decohesion mechanism of crack growth. In this way, the fracture pattern becomes inhomogeneous.
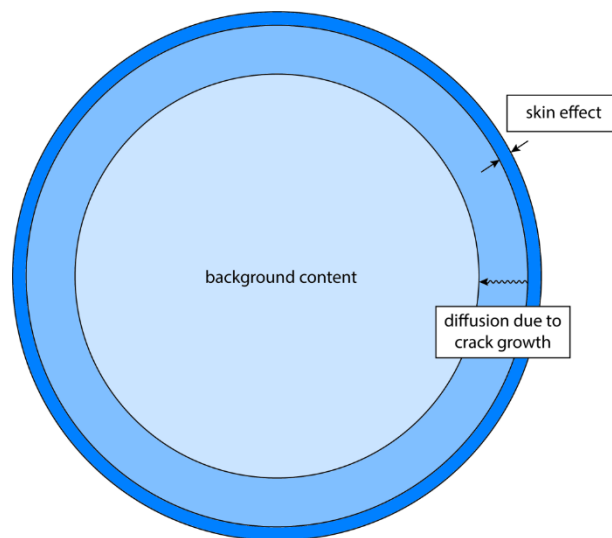

Fig. 4. The distribution of hydrogen content along the cylinder radius

Such a dual character of destruction is often observed in experiments [15,16]. This is usually explained by the successive action of two mechanisms of hydrogen-induced destruction – the HEDE model, that we used, and the HELP model (hydrogen enhanced localized plasticity) [17,18]. One or the other is chosen depending on the local concentration of hydrogen.

The main idea of the HELP is that hydrogen is concentrated at the crack tip under the action of internal stresses and reduces the energy required for the nucleation of dislocations, which are formed and accumulate near the stress concentrator. It produces the areas of localized plasticity, thereby the material "softens" at the crack tip.

Almost all studies on the HELP and HEDE models use the assumption of an initial uniform hydrogen concentration. As it follows from the calculations performed by the authors of the model [19] within the framework of HELP, a significant effect of hydrogen on the mechanical properties of the material begins at local relative mass concentrations of hydrogen of the order of 10^{-2} ppm. This level of content is unattainable high and is not observed in most metals. At the same time, according to the theoretical calculation of the plasticity of cracks [20], local concentrations of this substance at the crack tip are about 100 times higher than average. From this, it follows that if the experimentally observed average values of mass hydrogen concentration are 10^{-6} ppm, local concentration cannot be greater than 10^{-4} ppm. In this way, it is impossible to achieve such an accumulation of substance caused by the application of an external load, that can start the physical mechanisms of HELP model.

The presence of such contradictions and inaccuracies in the approaches existing nowadays allows us to state that the highly uneven distribution of hydrogen over the specimen, associated with the charging of the samples with substance, is the true reason for the dual nature of the destruction observed in practice.

Conclusions

The finite element solution of the destruction of a hydrogen-charged steel cylindrical specimen with a semicircular groove was obtained. The modeling was performed based on the HEDE model of hydrogen brittleness, considering the experimentally observed skin effect of charging the samples with hydrogen.

The simulation results showed that at the sample surface, hydrogen-induced brittle fracture is observed, while crack propagation in the central part of the specimen occurs at background substance concentration.

Such a change in the destruction mechanism confirms that skin effect of charging samples with hydrogen has a significant effect on the fracture of metal samples despite its very shallow depth and can be the main reason of the experimentally observed dual nature of destruction.

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