Skin-effect of redistribution of dissolved hydrogen in metals under tension

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Abstract

Plastic deformation is accompanied by structural rearrangement of the material. Prediction and diagnosis of such adjustment is an important task, since for structural materials, the plastic deformation precedes the destruction.

One of the important features of plastic deformation is the redistribution of natural hydrogen that is inside metals. This process is associated with a number of mechanical phenomena, ranging from the diffusion of hydrogen into the zone of tensile stresses and ending with a change in the size of the structural elements of the metal and the appearance of new structural defects.

Studies show that there is a good correlation between the concentration of diffusively mobile hydrogen and the value of plastic deformation, in many cases they are linearly related.

The report describes a new effect, discovered by the authors in the process of investigating specimens broken with different degrees of plastic deformation. A careful study of the distribution of hydrogen concentrations shows that all changes that are associated with plastic deformation occur in the surface layer of about 1 mm in thickness. Thus, this result gives evidence submitted on the surface nature of the damage accumulation during plastic deformation. On the one hand, this is the basis for developing methods of technical diagnostics of damage by the state of a thin layer. On the other hand, the obtained data makes it possible to develop methods for reducing the damage in plastic deformation by treating the metal surface.

1 Introduction

The strong influence of hydrogen on the strength and other mechanical characteristics of metals was found approximately 150 years ago. In the cracks of cast iron castings, hydrogen gas has been found, and since then any new technology for the production of metals and many other materials has faced to the problem of the destructive effect of hydrogen at an increasingly low level of its concentrations in the solid material.

At the beginning of the 20th century, in connection with the mass production of rolled steel, we had to fight with flocken - discontinuities in the rolled steel.

Causing this disease mass relative hydrogen concentration in the steels of the order of 4 ppm. Then metallurgists faced the brittleness of aluminum alloys already at the concentration level of about 0.4 ppm. "Hydrogen problems" arose in the production of titanium, zirconium, heat-resistant nickel alloys.
Simulation is one of the main ways to find out the cause of hydrogen embrittlement. Hydrogen has a strong effect on the strength of metals, and so many works are devoted to modeling this effect.
Several basic approaches can be distinguished: taking into account the influence of hydrogen on the nucleation and movement of dislocations, taking into account the influence of hydrogen on the development of cracks, taking into account the internal pressure of hydrogen in the metal and "physical approaches" based on taking into account the potential energy of hydrogen interaction with the material matrix.
The motion and formation of dislocations and their influence on local plasticity near the top of cracks lead to local plasticity because of the very high concentration of dislocations. The mechanism of local hydrogen plasticity (HELP) was first described in the work of a scientific group from the University of Illinois [1]. Later, in [3] and [4, 5], on the basis of physical considerations on the potentials of hydrogen interaction with dislocations, the defining equations of the material were proposed that simulate local changes in material properties at the mouth of the microcrack.
At the same time, calculations performed by the authors of the model in [3] show that significant changes in mechanical properties in HELP occur at local relative mass concentrations of hydrogen of the order of 10000 ppm, which is an unattainably high concentration for most metals. Steel even at much lower concentrations independently crack up to complete failure without any external load.
The calculation of local plasticity in the theoretical examination of a crack with a spherical vertex shows that the local concentrations of hydrogen are only 100 times higher than the average [6]. Given that the averages are usually about ppm, the local concentrations do not exceed 100 ppm. Thus, the verification calculation does not confirm that under the influence of external mechanical loads, local accumulation of hydrogen is possible, which is necessary for triggering physical mechanisms of local plasticity.
There is still a whole series of uncertainties about which the authors of the model write, in particular, there is a nonlinear dependence of the internal potential on the magnitude of the stresses and hydrogen concentration, and since huge local concentrations that are many times larger than those observed in practice are considered, all the nonlinearities play a big role.
It was noted in [7] that the HELP model requires huge computational resources for solving any applied problem, therefore, the only way out is to use the continuum model of dislocation development. Such a replacement is often inadequate and the authors propose to use the growth criterion of the submicrocrack, that is, reduce all the hydrogen problems to modeling the development of a crack and to reduce crack resistance.
The peeling model (HEDE) [8] is a similar HELP. The difference lies in the fact that HEDE takes into account the decrease in the energy of formation of free fracture surfaces with increasing local hydrogen concentration.
Standard modeling of the development of hydrogen-induced cracks, taking into ac-

count the reduction in fracture toughness, is also a common approach. At the same time, the model does not relate to real physical mechanisms of hydrogen influence. In addition, it turns out that the consideration of the same model in problems of different dimensions yields strongly differing results [9, 10].

To model hydrogen fragility, molecular dynamics is also used [11, 12], but because of the smallness of the modeled ensembles, it allows us to describe only micromechanisms at the apex of a microcrack or dislocation. The same disadvantage is possessed by the quantum mechanical approach [13, 14] because of the large heterogeneity of real metals, it can be used only to describe the behavior of cracks in ideal crystals or to model the behavior of individual microcracks and dislocations.

A new approach to modeling materials containing hydrogen was proposed in [15]. Experimental studies have shown that under the influence of external loads hydrogen changes its binding energy [16]. Therefore, a separate description of hydrogen transport inside the material in isolation from its stress-strain state is too crude. In [15] proposed a model of a continuous medium, which takes into account the mutual influence of hydrogen on the mechanical properties of the medium and the stress-strain state of the medium on the binding energy and hydrogen transfer.

In all models, a uniform concentration of hydrogen is considered throughout the entire volume of the material, with the exception of defects.

It remains an open question whether artificial saturation with hydrogen can be used in carrying out experimental studies. With the help of this method, practically all the experimental results were obtained. But modern manifestations of hydrogen embrittlement are of a complex nature and are observed under conditions when there is no hydrogen or its ions in the medium surrounding the material. Moreover, in welded joints it is observed in the purest form, and in other cases (for example, when turbine blades are destroyed) they speak of "hydrogen-induced destruction". Experimental data show that, due to the limited capacity of hydrogen traps, it is difficult to expect that its distribution along internal traps does not depend on the way it enters the solid.

Thus, clarifying the effects associated with the redistribution of hydrogen under the action of loads is an important task for both mechanics and technical diagnostics.

2 Experimental research

Model experiments were carried out on samples of aluminum alloy AMC. The choice of metal was made in such a way that the diffusion of hydrogen had practically no effect on its distribution. It is known that at room temperature there is practically no hydrogen diffusion in aluminum alloys. The diffusion coefficients are very small and the initial concentrations of hydrogen persist for years.

We have specially chosen a conventional plate 15 mm thick, obtained by rolling from a casting. The surface of the plate was not previously processed. Samples were prepared from the plate for mechanical testing. The drawing, which is presented in Fig.1.

Samples were subjected to low cycle fatigue tests on a tensile machine. The loading cycle was not symmetrical from 0 to $1.05\sigma_{0.2}$. As a rule, the samples were kept for 3-10 thousand cycles before failure.

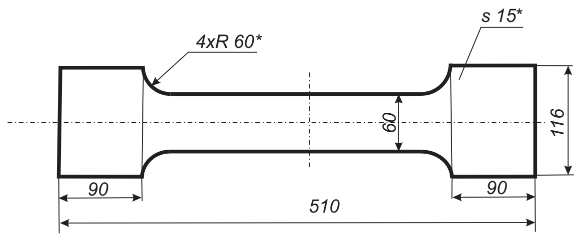

Figure 1: Samples of the AMC alloy for mechanical testing

After the destruction, the volume distribution of hydrogen in the samples was studied. Onlynatural hydrogen was studied. We did not any hydrogen charging or saturation. The sources of hydrogen were: the atmosphere of the laboratory and internal natural hydrogen, which was redistributed under the influence of mechanical loads.
Samples were cut from the broken samples in order to analyze the hydrogen content, had the form of parallelepipeds with a height of 8-15 mm and a section of 6x6 mm^2. The cutting scheme is shown in Fig.2.

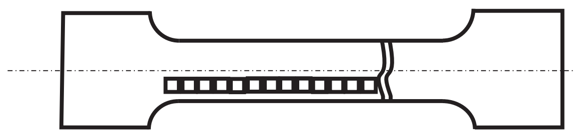

Figure 2: Scheme cutting specimens for measuring the concentration of hydrogen

Samples were cut in two ways:
1. With a portion of the flat rolling surface;
2. With the removal of 1 mm from the outer surface
Cutting was done with a manual saw to prevent overheating of the samples. The cut samples were investigated by hot vacuum extraction using the industrial hydrogen analyzer AV-1.
The procedure for measuring, sample preparation and the principle of operation of the analyzer is described in detail in [Pol1, Pol2, Pol3].
The results of measurements, hydrogen concentration depending on the removal of samples from the line of rupture are shown in Fig.3 and Fig.4. In Fig.3. The results for samples with part of the rolled surface are given. In Fig.4. The results for samples with the removed surface of rolled products are given.
A comparison of the graphs shows that there is a purely surface effect of the uneven distribution of hydrogen as a result of cyclic loading and plastic deformations [16]

3 Discussion of results

Skin effect of the distribution of hydrogen under the influence of external mechanical loads, which we found, is not described in the literature
As a rule, special saturation with hydrogen in solutions of electrolytes is used for research. There are four main ways of saturation:
1. In gaseous hydrogen [20]

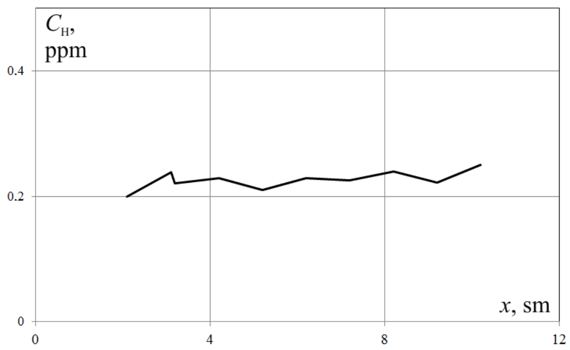

Figure 3: Distribution of hydrogen for samples with a surface layer of rolled metal

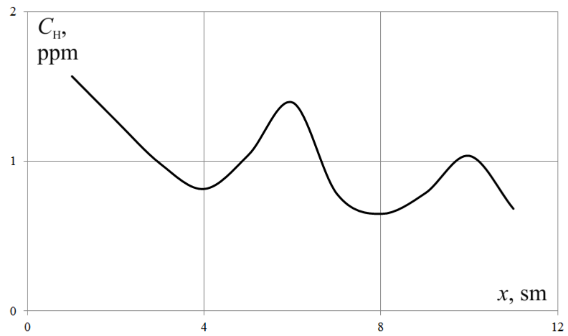

Figure 4: Distribution of hydrogen for samples with a removed surface of rolled products.

2. In acid solution due to corrosion or stress corrosion [20] 3. Cathodic hydrogen charging [20]
4. In electrolyte associated with near-neutral pH SCC, simulating sea or ground water or the environment of transported natural gas [21]. For example, [21] - test Standard set of test conditions for a consistent evaluation of the pipeline and pressure vessel steels and compares test results from different laboratories pertaining to the results of the treatment of H_2S.
At such a saturation, the hydrogen concentration is tens of times higher than the natural one, therefore in all ref.([22, 23], etc.) the skin effect of hydrogen distribution under the influence of external mechanical loads did not manifest itself.
The unevenness of the concentrations that we detected in the case when the surface layer of rolled metal was not removed is due to the well-known effect of Portevin-Le Chatelier. This effect leads to inhomogeneity in the appearance of plastic deformations and this is often found in aluminum alloys.
New in this experiment is the skin nature of the changes that occur with this effect. Concentrations of natural hydrogen in metals are related to their structure. The limiting saturation with hydrogen is characteristic for aluminum alloys. That is, the natural concentration of hydrogen, with a given alloy structure, is extremely saturated. This is due to the fact that the solubility of hydrogen during crystallization of aluminum alloys falls approximately 4 times and hydrogen expelled from the melt is concentrated in various structural defects.
A significant increase in the average hydrogen concentration observed by us (see

Fig. 3,4) can be associated only with the appearance of a large number of defects (microcracks, pores, bundles).
It follows from our results that these defects are localized in a thin layer of thickness less than 1 mm as a result of a significant (35%) plastic deformation. The rest of the volume of material does not experience similar devastation.
Thus, the skin effect of the distribution of hydrogen concentration is related to the skin effect of plastic deformation. We managed to find work that describes the skin effect of plastic deformation [24].
On the one hand, this is an important result for the mechanics. It explains the large influence of surface tension forces on plastic deformation [25], on the other hand, it is still not discussed and is not modeled either in the theory of mechanics of solid or in the numerous hydrogen embritlements models that was described in the introduction.
Accounting for the skin effect in modeling and strength calculations can significantly increase the accuracy of calculations and the adequacy of mechanical models.

4 Conclusions

As a result of the carried out experimental studies, the skin effect of the distribution of natural hydrogen concentrations for plastic deformation under the action of cyclic loading was first discovered.
The observed effect agrees well with the skin effect of residual stresses during plastic deformation, which was discovered 100 years ago but did not receive a theoretical description.
Modeling the skin effect will make it possible to obtain more adequate results when calculating the strength of metal structures and machine components.

Acknowledgements

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