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Influence of structural changes in carbon steel surface layer while cycle deforming on hydrogen absorption

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Abstract

Fatigue tests were carried out with spring steel samples after they had been cathodically charged with hydrogen in a solution of sulfuric acid in the presence of selenious acid as hydrogen absorption promoter. The distribution of hydrogen across the depth of the surface layer is defined. It is suggested that the surface metal layer 40–50 μm thick accounts for the major concentration of hydrogen. The preliminary cyclic strain before cathodic charging with hydrogen increases hydrogen concentration in steel. In this case the thickness of the hydrogen rich layer remains the same. Fatigue tests with intermittent deformation have shown that such deformations decrease the durability of the spring steel. It is shown that the hydrogen concentration of the surface layer 5 μm thick in the area of fracture increased approximately twofold as a result of cyclic deformation of steel preliminarily charged with cathodic hydrogen.

Keywords: Metals; Strain

1. Introduction

The presence of impurities in metals decreases their resistance tensile strength, and consequently their fatigue resistance. One such harmful impurity decreasing the plasticity and strength of metals is hydrogen. Among the first to detect losses in the fatigue characteristics of mild iron and steel after cyanide zinc plating were Swange and France [1]. The larger the strength achieved by the treatment of steel, the more significant is the decrease in endurance limit. Gustafson [2] found that specimens from a spring steel after cyanide zinc plating have much less fatigue resistance at the lower values of area of dispersion than uncoated specimens. Loss in the fatigue characteristics of steel after chrome-plating have been observed by a series of authors [3–6]. Fewer results have been achieved in the case of cathode polarized steel samples in solutions of electrolytes without deposition of metal [7–11], but elastic deformation of specimens after cathodic charging was performed with the use of a different technique. For example, Beloglazov [8] used a rotated wire sample deformed by an arc to show promoters and inhibitors of hydrogen absorption. Low-cycle hydrogen fatigue has been investigated in more detail [12–22]. Absorption of hydrogen by steel is observed in many corrosive environments: in sour mine water and some kinds of ground-waters, in water from peat bogs and swamps, in wet hydrogen sulphide and in water saturated by the same, as well as in oxygen-deficient water, in sodium hydroxide solutions at elevated temperatures and in other environments [23], by deposition of electroplatings, chemical and electrochemical etching [24], and cathodic protection of steel against corrosion [25]. In some works [17–19], the cause of hydrogen fatigue of steel at low-cycle loading has been studied.

The present work is one of a series of papers [26–29] that deal with hydrogen embrittlement of steel, and is concerned with clearing up features of fatigue rupture of spring steel (composition, %: 0.62 C; 0.98 Mn; 0.32 Si and 0.2 Cr) electrolytically charged with cathodic hydrogen.

2. Experimental

Flat samples (0.8 mm thick) used in this study were heat treated to a hardness of 47–50 HRC. The charging of samples with hydrogen was performed by cathodic polarization with a direct current density of 50 A/m^2 for 60 min in a 0.05 M solution of sulfuric acid with the addition of 4

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kg/m^3 selenious acid as a promoter of hydrogen absorption. A platinum plate served as the anode. Untreated samples and those after a preliminary cyclic macroelastic (body of crystal exposed plastic deformation) deformation up to the state of hardening and up to the state of weakening were hydrogen charged. An increase in microhardness from ~740 up to 4630 MPa (number of cycles $7.8\cdot10^3$ at a stress of deformation of 4630 MPa) matched the state of hardening, and a decrease in microhardness up to 3060 MPa (number of cycles $8.1\cdot10^4$ at the same deformation stress) matched the state of weakening. The hydrogen content in the near-surface layer of steel was defined by the anode-photometric method [30]. The fatigue tests were carried out by sign-alternating bend by the machine of electromagnetic type [26] in conditions of resonance oscillations at a frequency of 90 Hz. The basis of comparative tests was $2\cdot10^6$ cycles. The intermittent cyclic deformation was carried out as follows: periods of deformation were preliminarily defined from the maximal magnitude of decrease of microhardness of the specimen surface. The periods of relaxation were defined by the time approximately (2.5 h) of complete reset of the microhardness of the original value. Consequent periods of deformation and strain-relief were equal to the initial periods described above.

3. Results and discussion

It is known [31], that it is the surface layer up to 50 μm thick that is responsible for metal fatigue. On the other hand, we have shown [32] that at electrochemical hydrogen charging of spring steel, hydrogen is absorbed preferentially by a surface layer 40–50 μm thick. Comparison of these two facts makes their relation evident. Hydrogen, as a consequence of its heightened concentration, modifies the crystal lattice chiefly in the near-surface layer. The cyclic deformation most greatly changes the structure in the same volumes of metal. Hence, structural changes determine the diffusive mobility of hydrogen in the layer responsible for the failure of the metal.

For the study of diffusion of hydrogen in steel subjected to cyclic deformation, we investigated its distribution in the surface steel layer after cathodic hydrogen absorption by initial specimens, and also after hardening and weakening of specimens by cycle deformation. The preliminary cyclic deformation up to any state of metal, either hardening or weakening, leads to an increase in the hydrogen content in steel, as shown in Fig. 1. It is possible to explain such a course of distribution curves of hydrogen in steel as follows. First, on the metal surface, a set of activated sites as shear bands appears as a result of cyclic plastic deformation of crystal the body. Second according to the data [33], cyclic deformation loosens interatomic links in the crystal lattice of the metal due to an increase in the density of imperfections from the instance of loading. In other words, the metal density is decreased. Thirdly, the cyclic deformation is accompanied by an increase in dislocations density, which may play a role in the accelerated hydrogen migration [34–36].

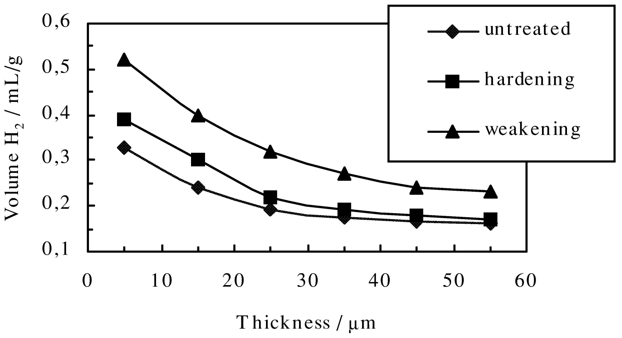

Fig. 1. Distribution of hydrogen across the depth of the surface layer of spring steel after preliminary cyclic strain and cathodically charged with hydrogen.

It is necessary to note that the thickness of the metal most filled by hydrogen as a result of cathodic polarization, does not depend on the degree of a preliminary cyclic deformation of the steel. However the hydrogen content in this layer has has increased (Fig. 1). Hence it is possible to state that at a cyclic deformation of spring steel, the basic changes in the structure of the metal occur in a layer 40 μm thick, i.e. in the same volume of metal which is most strongly charged with hydrogen. An increase in a cyclically deformed metal's ability to absorb hydrogen has an effect on the results of fatigue tests (Fig. 2), from which it follows that the increase of hydrogen concentration in the near-surface layer results in a decrease of fatigue limit. Thus, the obtained results allow to make the following conclusions: first, duting cyclic deformation of steel, its surface layer about 40 mm thick is responsible for fatigue failure. Second, the diffusive mobility of hydrogen in this layer is facilitated.

For explaining the role of hydrogen in the decrease of fatigue resistance of steel, examination of the influence of intermittent (with a 'rest' deformation on fatigue endurance) was carried out. The results of fatigue tests (Fig. 3) have shown that intermittent deformation of steel charged with hydrogen decreases its longevity as compared to continuous deformation. For untreated specimens, such an effect was not observed. Similar regularity was found

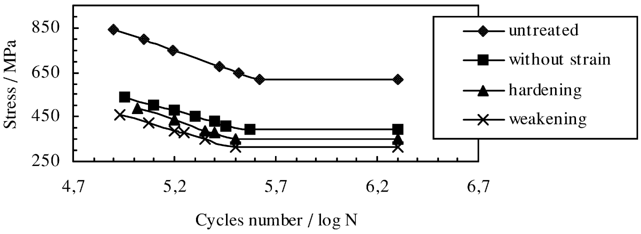

Fig. 2. Curves of fatigue of spring steel after preliminary cyclic strain and cathodically charged with hydrogen.

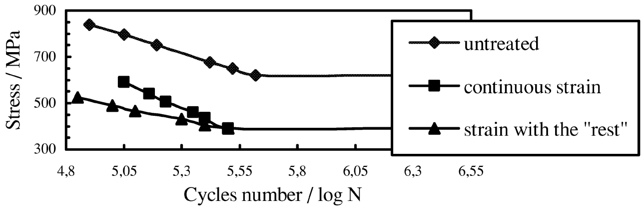

Fig. 3. Influence of ‘rest’ on the fatigue of spring steel cathodically charged with hydrogen.

previously by Rak and Beloglazov [37] for a titanium alloy. The hydrogen content measurement in the failure zone of the specimen (Fig. 4) has shown that its concentration in the near-surface steel layer does not depend on the technique of specimen deformation. The hydrogen concentration increases equally in metals, deformed continuously or deformed with a ‘rest’. Hence, it is possible to explain the decrease in longevity by the fact that during the ‘rest’ time, hydrogen distributed in the lattice of the metal prolongs to fill microcavities. The atomic hydrogen forms molecules, increasing gas pressure in pores and thus inducing further cracking of the metal. The increase in hydrogen concentration in the failure zone is conditioned by its diffusion in the area of maximal stress [26]. Moreover the molecular hydrogen in microcavities may be adsorbed on the surface of their walls and then split into atoms with a much smaller dissociation energy than in the gas phase [38]. Therefore, on the surface of microcavities hydrogen will necessarily be chemisorbed. It is apparent that with the increase in pressure, the chemisorbed hydrogen concentration will increase, which in turn causes strengthening of the following effects. The presence of chemisorbed hydrogen, as is known [39,40] results in a decrease in the surface energy of a metal which facilitates exit of dislocations out to the surface. Therefore, the surface of a microcavity will be activated during cyclic deformation, and it will strengthen hydrogen chemisorption. The hydrogen chemisorption on the surface of the formed crack leads to weakening of the interatomic links of the metal, accelerating its fracture. Thus results or fatigue test in terms of deformation with a ‘rest’ and data on the content of hydrogen suggest predominance of the adsorption mechanism of failure of the steel charged with hydrogen at a cyclic deformation.

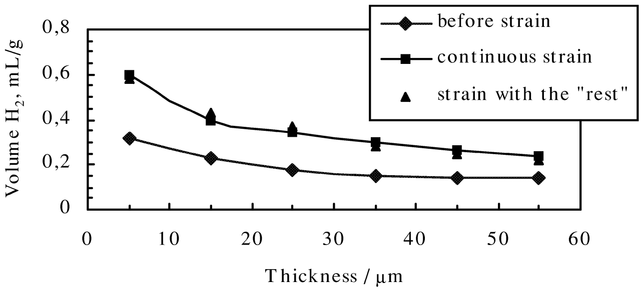

Fig. 4. Distribution of hydrogen after cyclic strain across the depth of the surface layer of spring steel in the area of fracture. Preliminary sample is charged by cathodic hydrogen.

The fatigue failure of metal is observed in the moment when the volume of the metal responsible for failure absorbs energy of a limiting value defined by the binding forces of the given metal [33]. Thus, absorbed energy continues formation of imperfections, and in particular, dislocations which promote the formation of cracks. We have noted [28] that close to the surface of the metal is the maximum dislocations density blocked by hydrogen. Hence, it is possible to guess that in steel saturated by hydrogen, a crack arises under the surface of the metal at a depth of 10–15 µm that is, in the areas having the greatest hydrogen concentration and dislocation density. Formation of complexes similar to hydrides of iron in the presence of a non-uniform field of tensile stresses made for a development microdeformation [41]. The possibility of a microcrack forming under the surface is proved also by results of work [42]. The arisen microcrack will be strongly filled by hydrogen thus accelerating failure of the metal for the above listed reasons.

4. Conclusions

It is confirmed that the cyclic alternating strain of a spring steel is accompanied by structural changes preferentially occurring in the near-surface layer with a thickness of 40–50 µm. Diffusive mobility of hydrogen in the near surface layer is increased during cyclic deformation of spring steel as result of an increase of dislocations density which may play a role in accelerated hydrogen migration. It is suggested that the adsorption mechanism of hydrogen fatigue is one of the causes of steel fracture in the process of cyclic alternating strain.

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