EMBRITTLEMENT OF QUENCHED STEEL UNDER THE EFFECT OF ULTRA LOW CONCENTRATIONS OF DIFFUSION-MOBILE HYDROGEN

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ABSTRACT

The non-cathode hydrogen saturation effect on the mechanical properties of the 30ХГСА steel with the martensite structure of quenching was studied. It was ascertained that the critical concentration of diffusion-mobile hydrogen resulting in disastrous embrittlement of steel was ~0,02 ppm. Substantional changing of mechanical properties of the quenched steel (σ_N^{AE}, σ_F) was due to the change of the failure mechanism from intragrain to grain boundary.

KEYWORDS

Quenched steel, hydrogen embrittlement, non-cathode H-saturation, mechanical properties, stress of the crack nucleation σ_N^{AE}, breaking stress σ_F, lazer spectroscopy, acoustic emission (AE), grain boundaries failure.

INTRODUCTION

The aim of this paper is to determine critical concentrations of diffusion-mobile hydrogen (DMH) resulting in embrittlement of steel with a quenched martensite structure. The study of this problem is important in connection with an enhanced susceptibility of materials with a martensite structure to hydrogen embrittlement, as well as in connection with the problem of delayed failure of quenched steels (Velichko and Zabilsky, 1991; Zabilsky and Velichko, 1992). In the literature available the question of embrittling effect of ultra low concentrations of DMH has not been considered actually which is due to the lack of reliable techniques of hydrogen detection in metals in quantities less than 0,1 ppm.

EXPERIMENTAL PROCEDURE

The concentration of DMH in metal was determined by the quantity of hydrogen released from H-presaturated samples. The detection of hydrogen was accomplished by the technique of active spectroscopy in a laser installation developed in the Phis.-Technical Institute (Izhevsk) by G.M.Mikheyev and coauthors (Malyev et al., 1989). The H-saturated sample was kept in an optical measuring cell of this installation at room temperature and residual pressure of 1 kPa. The sensitivity of this technique is 10^{-5} ppm, a measurement error is 10%. The total content of hydrogen in the samples was determined by vacuum-melting in an a atmosphere of a gas-carrier (Ar) using Leco RH-1 device.

Mechanical testing was accomplished according to the scheme of three-points bending on prism-like samples with a section of 4x10 mm (the base of testing - 40 mm) on 30ХГСА steel of the following chemical composition: 0,30%-wt. C; 1,06% Mn; 1,07% Si; 0,006% S; 0,013% P. Quenching was carried out in oil from the temperature of 860°C which produced hardness of 48,5-49,5 HRC. Then using an electric sparc method a notch on the narrow side of the sample was made, the radius at the top being 0,1 mm and the depth being 2 mm. To detect the moment of a brittle crack nucleation the method of AE was used which is highly sensitive to the processes of microcracking. The stress of the crack nucleation σ_N^{AE} and the breaking stress σ_F were used as the main characteristics of mechanical properties. Mechanical testing was carried out using a universal testing machine 1958Y-10-1.

RESULTS AND DISCUSSION

At the first stage of investigations the saturation of the samples with hydrogen was carried out by the method of cathode polarization in 0,1 N H_2SO_4 with the addition of 1,5 g/l of stimulator of hydrogen saturation (thiocarbamide). Since a quick-quenched state is characterized by an enhanced tendency to crack-formation (Velichko et al., 1992) the H-saturation of the samples was carried out 5 days after quenching. The mechanical properties were determined in a wide range of current densities of hydrogen saturation - from $5\cdot10^{-7}$ to $5\cdot10^{1}$ mA/sm^2. The analysis of the kinetics of hydrogen release showed that more than 80% of DMH desorbed during first 24 h holding.

Fig.1 shows the plot of the dependence of the DMH quantity desorbing from the sample on the current density of H-saturation. From the figure it is seen that at the current density i=5 mA/sm^2 the quantity of DMH reaches its maximum value equal to 6 ppm. The increase of the current density above 5 mA/

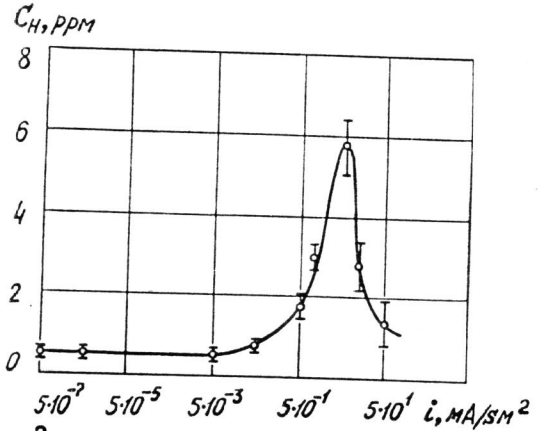

Fig.1. DMH content change in quenched steel 30ХГСА depending on current density of H-saturation.

sm^2 results in lowering the quantity of hydrogen which is accounted for by a screening effect of a gas cushion of hydrogen bubbles forming at enhanced current densities as well as by the possible formation of microdefects (voids) in the subsurface bulk of the sample-cathode. At i<5 mA/sm^2 the effectiveness of H-saturation is also reduced, the process stabilizes in the interval from $5\cdot10^{-3}$ to $5\cdot10^{-7}$ mA/sm^2; the content of DMH is kept on the level of 0,7 ppm. The low level of mechanical properties at this ($\sigma_N^{AE}\approx300$ MPa; $\sigma_F\approx600$ MPa) indicates the state of embrittlement.

To reduce the content of DMH to the level not less than 0,7 ppm and to determine the critical hydrogen concentration resulting in embrittlement further investigations were accomplished on the samples H-saturated without cathode polarization. The H-saturation of the samples was carried out in the electrolyte containing a small quantity of thiocarbamide (0,015 g/l). H_2SO_4 concentration C_A was varied in the interval from 0,0001 to 0,1 N of the solution. It should be pointed out that over the whole studied range of acid concentrations the traces of corrosion were not observed on the surface of the H-saturated samples.

Fig.2 (curve 1) illustrates the change of mechanical properties of the 30ХГСА steel depending on H_2SO_4 concentration. The DMH content in the samples (C_H) is illustrated by the curve 2. It is obvious that at H_2SO_4 concentration of 0,00068 N C_H=0,0035 ppm. The level of mechanical properties becomes lower by 3-4%. The increase of C_A from 0,00068 to 0,00125 N H_2SO_4 results in the rise of the DMH content from 0,0035 to 0,16 ppm, which is accompanied by a disastrous fall of σ_N^{AE}. The stress of the crack nucleation σ_N^{AE} and the bre-

aking stress σ_F decrease by 4,5 and 3 times, respectively.

Thus, the critical DMH concentration, at which the change of mechanical properties (embrittlement) of the quenched steel occurs, corresponds to ~0,02 ppm.

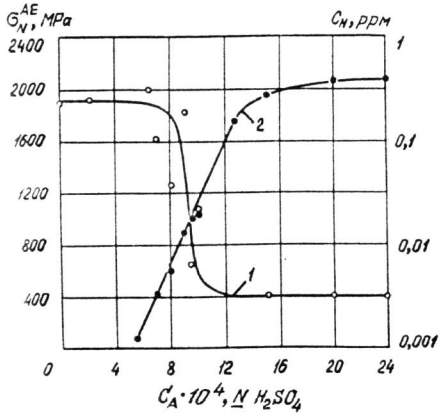

Fig.2. Changes of mechanical properties and DMH content in quenched steel 30ХГСА depending on H_2SO_4 concentration C_A: 1 - σ_N^{AE}; 2 - DMH content C_H.

Mechanical and AE diagrams of samples loading with a various DMH content are presented in Fig.3. It is seen that on reaching the DMH content of 0,019 ppm there occurs a stage of a pre-critical development of a brittle crack, which is proved by the appearance of AE signals in the macroelastic region of loading (diagram 2).

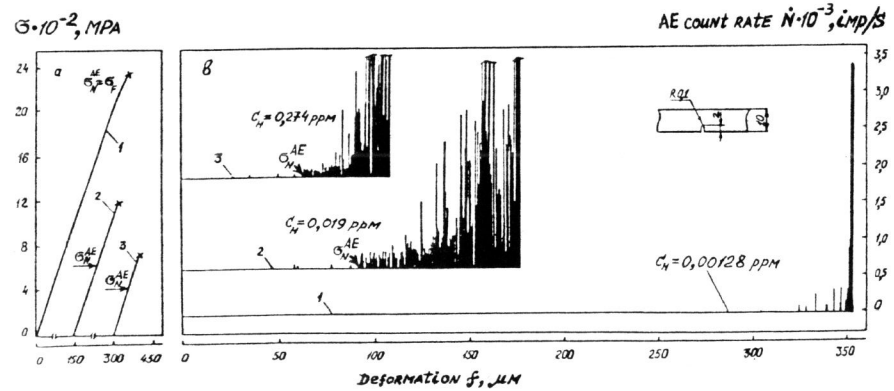

Fig.3.

Fractographic examination showed that the fall in mechanical properties was due to the change of the mechanism of failure. With the DMH content below the critical value of 0,02 ppm, the failure proceeds according to an intragrain mechanism. With higher C_H the failure becomes intergrain, which is the

evidence of DMH accumulation on interfaces - grain boundaries.

Presented in Fig.2 (curve 2), the dependence of the quantity of DMH on concentration at $C_A \leq 0{,}00125$ N H_2SO_4 has a linear section in a half-logarithmic scale. Therefore, the content of DMH on grain boundaries changes according to the exponential law:

$$C_H = \alpha_1 \cdot \exp(\alpha_2 \cdot C_H), \qquad (1)$$

where α_1 and α_2 are the coefficients determined by the method of least squares: $\alpha_1 = 2{,}1 \cdot 10^{-5}$, ppm; $\alpha_2 = 7{,}1 \cdot 10^{-3}$, $(\text{N } H_2SO_4)^{-1}$. The deviation of the curve 2 from the exponential dependence (exit to the plateau) occurs at $C_H \approx 0{,}15$ ppm and it is the absorption volumes. If one assumes that DMH mostly segregates on grain boundaries in the process of electrolytical H-saturation, the evidence of which is the grain boundary failure, then the absorption capacity of grain boundaries is ~0,15 ppm of DMH.

Apart from the testing of the quenched samples the H-saturation experiments where accomplished on the samples after tempering. The tempering temperatures studied were 200, 400 and 650°C. As a result, an anormalous effect of the tempering temperature on hydrogen embrittlement was found out. The highest hydrogen brittleness was observed on the samples after tempering at 400°C (Fig.4).

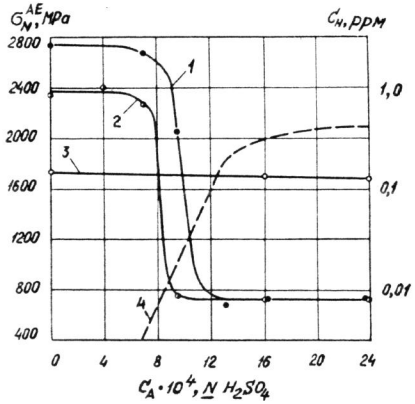

Fig.4. Changes of mechanical properties and DMH content C_H in quenched steel 30ХГСА after tempering depending on H_2SO_4 concentration C_A: 1 - tempering at 200°C; 2 - at 400°C; 3 - 650°C; 4 - C_H.

This result can be accounted for by the additive influence of the processes of one-step temper embrittlement (inhomogenious carbidies formation) and hydrogen effect.

CONCLUSION

Thus, the experimentally detected change of the mechanical

properties of the quenched steel 30ХГСА (σ_N^{AE}, σ_T) occurs under the effect of very small contents of DMH of 0,003-0,005 ppm. The critical concentration of DMH, at which one observes a disastrous embrittlement of the quenched steel, is~0,02 ppm.

REFERENCES

Velichko V.V., Zabilsky V.V. Delayed failure of quenched steel.1. The history of the problem, different factors effect, modern ideas (review). M., 1991.- 58 p.- Dep. in VINITI 01.04.91, No. 1526-V91.

1992, On the nature of recovery of quenched steels. In: Intercristalline brittleness of steels and alloys, (Trapheznicov V.A. and Zabilsky V.V.) p.p.36-42, Ural Branch of RAS, Izhevsk.

Zabilsky V.V., Velichko V.V. (1992), On the nature of the phenomenon of delayed failure of quenched steel, МiТОМ, No.9, p.p.28-34.

MaleyevD.I., MikheyevG.M., Mogilyova T.N. Lazer with modulation and active sinchronization of modes, developed on low volt modulators for high frequency quantum resonance spectroscopy of molecular hydrogen.- M., 1989.- 30 p.- Dep. in VINITI 06.03.89, No.1507.