EFFECT OF HYDROGEN ON BRITTLENESS OF STRUCTURAL STEELS AND WELDS

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ABSTRACT

The effect of diffusible hydrogen on mechanical properties of structural steels Ст.3, 09Г2С, 08Х4Н2М and welds of the 09Х2Н2М type was experimentally studied. The presence of diffusible hydrogen was found to be associated with emission of negative secondary ions H^-. Diffusible hydrogen is shown to cause changes in the main strength characteristics of steels, as well as to decrease the minimum brittle fracture stress and toughness factor. The paper suggests explanation of the mechanism of hydrogen effect on metal brittleness based on the concept of variation of the submicrocrack specific surface energy under the influence of the hydrogen negative ion layer.

KEYWORDS

Welded joints, structural steels, mechanical properties, hydrogen embrittlement, secondary ion mass-spectrometry, mechanism of hydrogen embrittlement, negative ions, microcleavage.

The problem of hydrogen embrittlement of structural steels and welds draws attention of investigators for a long time. For the explanation of hydrogen embrittlement mechanism different hypotheses, analysed in detaild in a number of reviews and monographs, for example: Shapovalov (1982), were proposed. These hypotheses are based on a certain idea about the effect of the following factors: high pressure of molecular hydrogen inside micropores in volume of metal; decrease in interatomic bonds as a result of increasing concentration of dissolved hydrogen; decrease in surface tension by hydrogen adsorbtion; interaction of hydrogen with dislocations.

In (Karpenko et al.,1973) preference was given to hydrogen chemisorption on the surface of the growing crack, but in (Panasjuk et al.,1987) a dislocation-decohesion conception of hydrogen embrittlement was developed, according to which hydrogen is accumulated in cores of dislocations and its decohesive action stimulates destruction. Most of hypotheses have a common idea about the existence of the initial microcracks or other natural micropores in metal, which accumulate hydrogen, causing embrittlement.

Numerous hypotheses proposed show that, despite being investigated intensively, the complex phenomenon of hydrogen embrittlement still belongs to the unexplained ones, and its study remains an urgent task.

In this work we studied experimentally the effect of diffusible hydrogen on mechanical properties of steels, used widely for welded structures: Ст.3, 09Г2С, 08Х4Н2М. To study the behavior of welds, containing diffusible hydrogen, we tested the metal deposited with flux-cored wires intended for welding steels mentioned above. This deposited metal was obtained by welding according to recommendations (Pokhodnya et al.,1980).

Cylinder specimens for uniaxial tension tests and for a study by secondary ion mass-spectrometry were prepared from central part of welds. The base metal specimens were prepared similarly. The specimens were charged with diffusible hydrogen electrolytically in solution 5 % H_2SO_4 (with additions

of 0.05 % sodium tiosulphate) at current density 10 mA/cm^2.

In specimens for mechanical tests only the working part was charged with hydrogen, holder parts were isolated from electrolyte. For ensuring the same content of diffusible hydrogen in all specimens the whole series of specimens (16 items) of each steel were placed in the electrolyte simultaneously. After charging the specimens were held in liquid nitrogen up to the start of testing.

The content of hydrogen was controlled by chromatographic method and by vacuum melting. Secondary ion mass-spectrometry method was applied which allows to determine the composition of particles on the surface and in the volume of the solids, to analyze the surface, to study diffusion and other processes (Fogel,1967;Pokhodnya and Shvachko,1987). For these experiments the Riber LAS-2000 system was used. At obtaining the superhigh vacuum in this installation, contaminant was removed from the specimen surface by intensive ion bombardment. The degree of cleaning was controlled by spectra of secondary ions and, during ion etching, - by the Auger spectroscopy method.

The observation of the surface by scanning electron microscopy showed the relief formation resulting from ion bombardment which proved that the surface layer was scattered to the depth of tenth parts of a micrometre. To obtain the secondary ions, the primary beam of argon ions was used. Since hydrogen exists in metal in various forms: as a proton, an atom, a molecule, and within hydrogen combinations (Shapovalov, 1982) - it was necessary to study in detail the origin of particles, which were observed in secondary ion spectra and could be associated with the diffusible hydrogen presence. When studying the specimens before and after charging with hydrogen and using the well known method for separation of the surface and volume origin ions (Kozlov et al.,1968), it was found that the emission of H^-secondary ions was associated with the presence of diffusible hydrogen. Other particles in secondary ion spectra, for example, H^+, OH^+, $FeOH^+$et al. were knocked out from the adsorbed hydrogenous components of residual gas and the products of their interaction with the surface: the

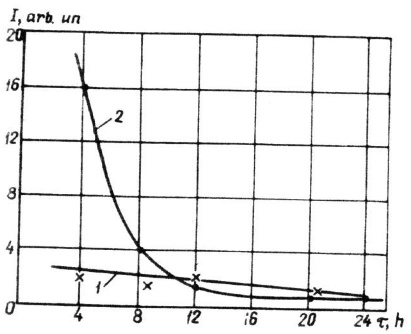

Fig.1. Time dependence of H^+(1) and H^-(2) secondary ions intensity (I) for hydrogenated specimens of steel.

superhigh vacuum in LAS-2000 system did not exclude this effect.

The dependences given in Fig.1 show that the current of H^- ions varies according to the variation of diffusible hydrogen content in the specimen. At the same time this variation did not effect the emission of H^+ secondary ions. These experimental results as well as the energy diagram of the metal-hydrogen molecule system (Kaminsky,1967), the quantum- mechanical analysis of the conditions of electron exchange between the metal surface and the hydrogen atom located nearby, and the results of calculating (Kishinevsky,1975) the probability of "survival" for negative ions, being removed from the surface at the rates, characteristic of secondary particles, enable to conclude, that the hydrogen atoms, diffusing from the metal, have the negative charge on the metal surface.

The mechanical properties of the mentioned steels were studied at the "Instron-1251" universal machine. The specimens were tested within the temperature range from +20 to -196°C. Using statistical treatment of the results, the temperature dependences of the strength and strain characteristics - $\sigma_{0,2}$, σ_b, ψ, δ and real fracture stress S_K, were plotted. Using these data for the hydrogenated and non-hydrogenated specimens the metal characteristics, proposed in (Mechkov,1981; Mechkov and Pakharenko,1985) were determined: Rmc is the resistance to micro cleavage, which is a minimal stress of brittle fracture, Kt = (Rmc/$\sigma_{0,2}$) is a toughness factor.

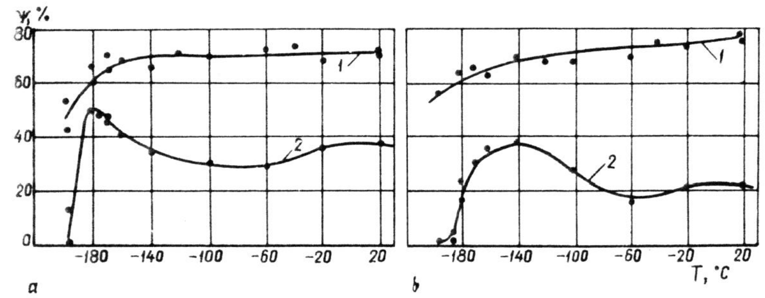

Fig. 2. Temperature dependences of the reduction of 09Г2С (a) and 08Х4Н2М (b) steels in the initial state (1) and after hydrogenation (2).

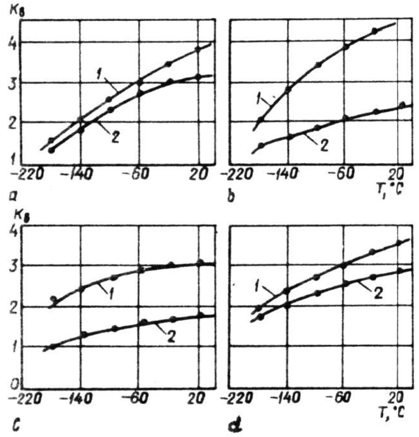

Fig.3. Temperature dependence of Kt toughness factor: a - for Ст.3 steel; b - for 09Г2С; c - for 08Х4Н2М; d - for deposited metal of 09Г2Н2М type (1,2 - see Fig.2)

As an example, the dependence Ψ (T) for hydrogenated and non-hydrogenated steels 09Г2С and 08Х4Н2М are given in Fig.2. These results confirmed the variations determined earlier for the above mentioned characteristics and also proved that due to the diffusible hydrogen charging the Rmc value decreases considerable. The Kt value is changed accordingly. The data given in the Table illustrate the Rmc changes caused by hydrogen saturation, and the curves in Fig.3 show the temperature dependences of Kt for the metals studied.

Table. Hydrogen content of specimen metals and microcleavage resistance

Metal	Hydrogen content in metal [H], cm /100g.				Rmc ,MPa	
	initial	after hydrogenation			initial	after hydrorenation
	[H]init	[H]dif	[H]res	[H]total		
09Г2С	0.9	7.2	1.8	9.0	1300	760
08X4H2M	0.9	4.3	1.3	5.6	1800	920
Weld in steel 08X4H2M	0.7	2.4	1.1	3.5	1420	1340

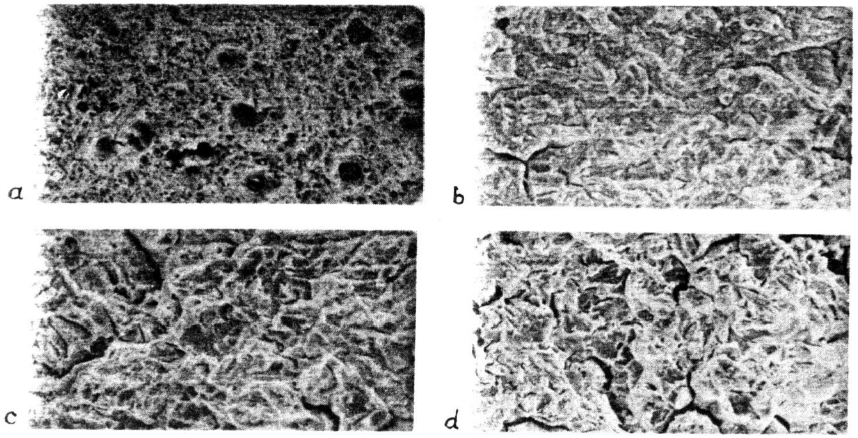

Fig.4. Surface fracture of 08X4H2M steel specimens (x 800): a,b - at 20°C; c,d - at -180°C; a,c - in the initial state; b,d - after hydroganation.

Using scanning electron microscopy it was found that at the variation of the mechanical properties of steels caused by hydrogen saturation, the fracture surface relief of the specimens, tested at different temperatures, is also changed. As it is seen in Fig.4a, the non-hydrogenated specimens of the 08Г2С steel, tested at 20 C, have the dimple surface relief, which proves the tough fracture mechanism. The brittle fracture zones with numerous microcracks were releaved on the surface after testing the hydrogenated specimens at the same temperature (Fig.4b). The fracture of ~~of~~ the specimens at low temperature causes the formation of the relief, which has all characteristics of the brittle fracture (Fig. 4b), but the hydrogen charging results in the increase in the microcrack number (Fig.4c).

The observed effect of diffusible hydrogen on the mechanical properties of metal, on resistance to microcleavage in particular, and the above mentioned conclusion that the hydrogen atoms exists in the form of negative ions on the surface of steel, enable to assume the following. According to the modern ideas, it is possible to apply the Griffiths model in its classical form for the micromechanism of metal microcleavage fracture (Mechkov,1981; Meshkov and Pakharenko, 1985). In this model the critical stage is the loss of of the submicrocrack stability. It is just at this stage, that the effect of negative charged layer of hydrogen atoms on the juvenile survace of submicrocrack must be maximum: the decrease in the density of free electrons near the surface will cause the reduction of surface energy and, hence, will facilitate the crack transition to the accelerated autocatalytic propagation, i.e. the resistance to brittle fracture, defined in the experiment as the Rmc value, will decrease.

The analytic equation for Rmc, which enables its quantitative calculation (Meshkov and Pakharenco,1985) is well known:

$$R_{MC}=4(\gamma E/\pi)^{1/2}G\sqrt{b}\,d^{-1/2}/\alpha\pi(1-\nu)K_T \tag{1}$$

where γ is specific surface energy; E is Young's modulus; b is Burgers vector modulus; G is shear modulus; α is the fraction of dislocations, entered in the cavity of the crack nucleous, from their total number in the cluster; ν is Poisson coefficien; Kt is the parameter in Petch-Hall equation, depending on the material constants (G, b, ν), crystall lattice type and strain deviator type; d is the grain size.

If we assume, that diffusible hydrogen does not influence the material constants in equation (1), then the γ value is the single parameter, which can be changed due to hydrogen saturation. Since, as it was mentioned above, it is possible to apply the Griffiths scheme in its classical form for the micromechanism of metal microcleavage fracture, the value for pure metal, determined experimentally or calculated theoretically (Mechkov and Pakharenko,1985) on the basis of the thermodynamic parameters, can be used in calculations, and the γ change caused by hydrogen can be determined by combining the Gibbs, Lengmuir isoterm and Siverts law equation. In this case the equation for will have the following form (Garafalo et al.1960):

$$\gamma = \gamma_0 - 2N_s kT \ln[1 + (Af)^{1/2}], \qquad (2)$$

where γ is the specific surface energy for the pure metal; N_S is the number of hydrogen particles adsorbed before saturation per unit of the crack surface area; A is the constant; f is the fugacity, which can be determined by Siverts law for hydrogen in iron.

The appearence of H^-layer on the surface of submicrocrack can not only lower the surface energy, but also hamper the recovery of metallic bond between the crack sides when it loses the elastic equilibrium state. As a result of this, the initiation of Griffiths crack will become more probable.

Thus, the experimental results, obtained in this work, allow to present the mechanism of hydrogen effect in structural steels and welded joints on mechanical properties of metal in a new way. This does not exclude other mechanism, analyzed earlier.

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