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RESISTANCE OF CONSTRUCTIONAL STEEL TO FRACTURE
IN HYDROGEN IMPREGNATION AND HYDROGEN SULFIDE
CRACKING

É. A. Savchenkov

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At present definite successes have been attained in understanding the phenomenon of hydrogen embrittlement of steel [1-3 et al.]. However, only a qualitative relationship has been established. The greater the hydrogen concentration at the crack tip, the lower the failure stress intensity factor [4]. The concept of Troiano and Oriani [5, 6] of the critical hydrogen concentration as the limit at which the metal loses cohesion strength has not made it possible to completely clarify this question since neither theoretical nor experimental methods of determination of such a critical concentration have been proposed [2, 4]. The critical activity (concentration) is a thermodynamic parameter of hydrogen, and the hydrogen resistance of a steel is determined by its structure and is not subject to a thermodynamic description.

Absorbed hydrogen may be found in various structural conditions and does not have the same influence on the strength and plasticity of steel [7]. The variety and number of the effects of hydrogen influence have been responsible for conflicting opinions and hypotheses on hydrogen embrittlement.

Hydrogen in alloys is simultaneously a surface and a volumetric agent. However, normally only its adsorption or cohesion action is taken into consideration.

The study of hydrogen embrittlement involves method difficulties since the most "dangerous" is active hydrogen. The activity $a = \exp(\Delta\mu/kT)$ depends upon the difference in chemical potentials $\Delta\mu$ in the presence of which hydrogen is diffusion-mobile, which leads to the appearance of both flows and nonuniformity in the hydrogen concentration. Of the many works devoted to investigation of hydrogen in metals only in a few ([3, 8-11], for example) are the mechanical properties compared with the activity (fugacity) of hydrogen.

Earlier on specimens with stress raisers we [10, 11] obtained for the first time generalized empirical relationships of the strength S of steel (the characteristic of the metal which makes it possible to evaluate its average cohesion strength [12, 13, et al.]) to the concentration of the free C_1 and combined C_2 components of the absorbed hydrogen. Below are analyzed the basic results following from these relationships.

According to the data of [10, 11] the coefficient of hydrogen decohesion (loss of strength) $\beta = \Delta S/S$ in reversible hydrogen embrittlement is determined as

$$\beta_1 = \beta_e \exp(\gamma C_1)^{0.5} = \beta_e \exp a_1^{0.5} = \exp(a_1^{0.5} - a_1^0); \quad (1)$$

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TABLE 1

Steel	Chemical analysis, %									
	C	Si	Mn	Cr	Mo	Cu	Ni	Nb	S	P
20	0,22	0,31	0,55	—	—	—	—	—	0,04	0,04
Kh46	0,10	0,24	0,94	Tr.	Tr.	0,28	0,11	0,03	0,001	0,010
30KhMA	0,31	0,24	0,55	0,92	0,19	0,17	0,22	—	0,010	0,010
18Kh1G1MF	0,24	0,13	0,65	1,04	0,46	—	0,14	—	0,030	0,023

Note. In addition to the above elements Kh46 steel contained 0.029% Al and 18Kh1G1MF 0.14% V.

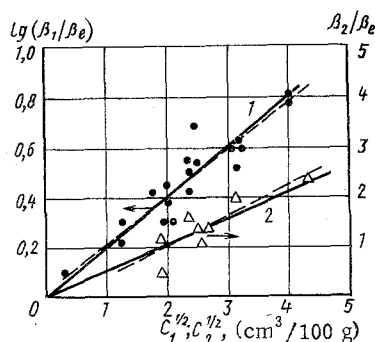


Fig. 1. Concentration relationship of decohesion (loss of strength of specimens with a notch) of 20 and 18Kh1G1MF steels in reversible (1) and irreversible (2) hydrogen embrittlement (hydrogen impregnation under different conditions in hydrogen sulfide containing electrolytes, start of measurement the level of hydrogen in the original steel): solid lines) the data of calculations using Eqs. (1) and (2); broken) empirical regression lines with correlation coefficients of 0.92 and 0.88 and dispersions of 0.08 and 0.3 for Eqs. (1) and (2), respectively; C_1 , C_2) the concentrations of the free and combined components of the absorbed hydrogen, respectively.

and in irreversible hydrogen embrittlement

$$\beta_2 = \beta_e (\gamma C_2)^{0.5} = a_2^{0.5} \exp(-a_1^{0.5}), \quad (2)$$

where γ is the activity coefficient of free hydrogen in metal (for steel $\gamma \cong 0.25$ ($\text{cm}^3/100 \text{ g}$)⁻¹ or $\gamma = 5000$ if the concentration is expressed in atomic (molar) portions), a_1^* is the critical activity (the concentration $C_{1*} = a_1^*/\gamma$) of free hydrogen in metal, C_1 is the concentration of diffusion-mobile (free, lattice) hydrogen extracted from the metal at normal temperature, C_2 is the concentration of residual (molecular) hydrogen, which is dependent upon the melting method, and β_e is an empirical structurally sensitive parameter of the alloy.

From Eq. (1) with $\beta_1 \rightarrow 1$ (which designates rupture of a polycrystal by hydrogen) follows the parametric equation — the condition of decohesion of a hydrogen impregnated metal in reversible hydrogen embrittlement:

$$n_e = 1/\beta_e = \exp(\gamma C_{1*})^{0.5} = \exp a_1^{0.5}. \quad (3)$$

From Eq. (3) it may be seen that in essence β_e is a new structural parameter characterizing the tendency toward hydrogen embrittlement of an infinitely dilute solution of hydrogen in metal ($n_e = 1/\beta_e$ is the hydrogen resistance). The value of β_e depends upon the composition and structure of the steel and is calculated from Eqs. (1) and (2) using the experimental values of β and C . A physical analog of the structural parameter β_e is the equivalent electrical conductivity of infinitely dilute solutions [14]. From Eq. (3) and knowing β_e it is possible to calculate the critical concentration of free hydrogen in the given steel. As

may be seen from Eqs. (1) and (2) the critical activity (concentration) of free hydrogen is the saturation point of the steel in reversible hydrogen embrittlement and determines the intensity of cracking (sensitivity to a crack) in irreversible hydrogen embrittlement.

From Eq. (3) it follows that the parameter β_e has the sense of the probability of the decohesion of steel in hydrogen embrittlement. Actually, according to the general theory of fluctuations Eq. (3) may be represented in the form of the change in the corresponding potential $\Delta\theta$ as the probability of the condition of decohesion:

$$\beta_e = \exp(-a_1^{0.5}) = \exp(-\Delta\Phi/RT). \quad (4)$$

From Eq. (2) with $\beta \rightarrow 1$ it is possible to obtain the condition of decohesion in irreversible hydrogen embrittlement:

$$n_e = 1/\beta_e = a_2^{0.5}, \quad (5)$$

where a_2^* is the critical pressure (activity) of molecular hydrogen necessary for advance of a microcrack. From Eq. (5) it may be seen that the index of hydrogen resistance of steel n_e is equal to the critical pressure (activity) of molecular hydrogen at cracks. Therefore the resistance of steel to reversible or irreversible hydrogen embrittlement is determined by the single parameter $\beta_e = 1/n_e$. The critical hydrogen concentration is the thermodynamic equivalent of the structural parameter of hydrogen resistance and may be expressed through the concentration of either free lattice or combined molecular hydrogen. The ratio between them is found from Eqs. (3) and (5):

$$a_2^* = \exp 2a_1^{0.5} \cong 1 + 2a_1^{0.5}. \quad (6)$$

Figure 1 presents graphically relationships (1) and (2) and experimental data obtained for 20 and 18Kh1G1MF steels in hydrogen impregnation using five methods in hydrogen sulfide containing media (pH = 0.6-3.5) [10, 11]. It may be seen that Eqs. (1) and (2) adequately describe the experimental results. Tables 1 and 2 present the chemical composition, heat treat cycles, mechanical properties, and values of S, β_e , and C_{1*} for certain steels obtained experimentally according to the methods of [9, 11] and Eqs. (1) and (3). From Table 2 it may be seen that the values of the critical concentrations of free hydrogen for plastic and high-strength steels are close to the known values [2, 15]. It should be noted that the hydrogen resistance n_e (the pressure of rupture of the bonds) or its reciprocal, the probability of decohesion β_e , as follows from Eqs. (1) and (2), is equal to the ratio of the "current" values of the loss in strength (tensile strength of specimens with a notch) and the corresponding hydrogen activities. These ratios are constant for each structure of a steel, that is, in evaluating the hydrogen resistance of a steel it is necessary to compare the action and its result (the selection of deformation indices instead of force ones apparently is not of value). The author of [16] was close to such an understanding of the tendency of a steel toward hydrogen embrittlement. He proposed assuming as critical that concentration of hydrogen at which the properties of the steel become quasiconstant. All of the existing methods of evaluation of the tendency of a steel toward hydrogen embrittlement take into consideration either the hydrogen concentration or the change in properties of the materials.

Let us compare the strength of specimens and the hydrogen resistance of the steel (Fig. 2). It may be seen that on the basis of the criterion n_e the investigated steels are distributed along the two branches of a dome-shaped curve close to the tip of which (or directly at it) is located the ferritic-pearlitic steel 20. According to Fig. 2 an increase in hydrogen resistance with an increase in cohesion strength of the steels relative to 20 steel is observed after structural strengthening or hardening and tempering with obtaining of a sorbitic structure. With other methods of strengthening (in our case low-temperature tempering of martensite) the hydrogen resistance of the steels is lower than of 20 steel. In addition a known paradox is observed. With an increase in cohesion strength in the absence of hydrogen the fracture resistance in the presence of hydrogen decreases. The explanation of this may be found in [17, 18] on the basis of the influence of internal adsorption of impurities on the strength of the bond of polycrystals. Determination of the parameter n_e makes it possible to make on a single figure a distribution by rule of steels with different structures and levels of strength and plasticity and to determine which factors cause their hydrogen resistance.

It should be noted that the universality of the tensile strength curves as limiting curves of plasticity and their dependence on the structure of the steel were established in fatigue tests [19]. Relationships similar to the "volcanic" type presented in Fig. 2 are

TABLE 2

Steel No.	Type of steel, treatment	σ_t	$\sigma_{0,2}$	σ_n^*	S^{**}	$\beta_e, \%$	$C_1^{***}, \text{cm}^3/100 \text{g}$
		MPa					
1	20 steel, normalized from 910°C	430	300	960	1104	5	36
2	Kh46, controlled rolling	540	380	1150	1322	2.8	51
3	30KhMA, hard, from 880°C and tempered at 580°C	800	670	1630	1874	2.6	53
4	18Kh1G1MF, norm. from 1040°C & temp. at 740°C	850	650	1500	1725	18	12
5	30KhMA, hard, from 880°C and tempered at 400°C	1100	870	2200	2530	30	6

*The tensile strength of a specimen with a sharp notch (tested according to the method of [9]).

†According to literature data $S \approx 1.15\sigma_n$ is the resistance to direct tension.

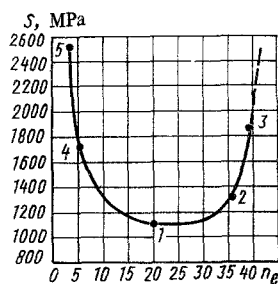


Fig. 2. Relationship between the strength of specimens with a notch (S) and the structure parameter of hydrogen resistance ($n_e = 1/\beta$) of different steels: 1-5) numbers of the steels in Table 2.

also observed for the hardness of metals in relation to the potential of the surface and for the catalytic, adsorption, and reaction properties of the surface in relation to the corresponding energy parameters [20, 21]. This makes it possible to propose that the parameter n_e of the cohesion strength of hydrogen impregnated steel depends upon the surface properties and the condition of the grain boundaries, that is, the internal and external adsorption activity of the steel.

Equations (1) and (3) make it possible to present in clear form the criterion of failure of constructional materials in hydrogen embrittlement:

$$S_H/S = 1 - \beta_1 = 1 - \beta_e \exp(\gamma C_1)^{0.5} = 1 - \exp(a_1^{0.5} - a_1^{0.5}), \quad (7)$$

where S_H is the strength of a steel in which the concentration of free hydrogen is equal to C_1 , determined on specimens with a notch. With the use of the criteria of linear fracture mechanics and assuming that $S = K_{IC}/\sqrt{\rho}$ (here ρ is the structural element or notch radius and K_{IC} is the critical stress intensity factor [12]), Eq. (7) acquires the form

$$K_{IH}/K_{IC} = 1 - \exp(a_1^{0.5} - a_1^{0.5}), \quad (8)$$

where K_{IH} is the failure stress intensity factor with the hydrogen concentration C_1 . In the general case in determining S and K_{IC} it is necessary to take into consideration the irreversible hydrogen embrittlement according to Eqs. (2) and (5). Earlier [4, 6] attempts were made to present the criterion of fracture of steel in hydrogen embrittlement in the form of a power function expressing the relationship of the hydrogen content to the stress intensity factor with an unknown exponent. In this case the "current" values of hydrogen concentration C_1 and the factor K_{IH} were assumed to be critical. From Eq. (8) it may be seen that failure of steel

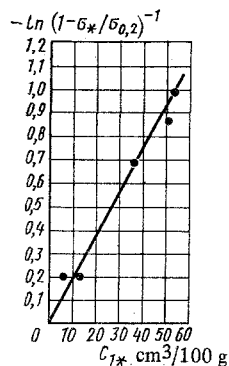


Fig. 3. Correlation between the critical hydrogen concentration and the threshold (critical) stresses for hydrogen sulfide cracking of steels: 1-5) the same as in Fig. 2.

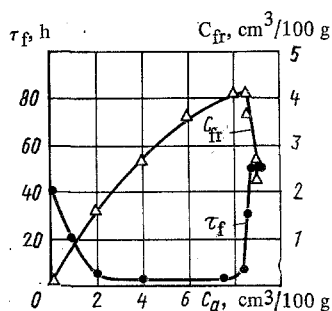


Fig. 4. Change in the time of hydrogen sulfide cracking (τ_f) and the concentration of the free (active) component (C_{fr}) of interstitial hydrogen vs the content of absorbed hydrogen (C_a). Nominal stress 420 MPa, medium a saturated solution of hydrogen sulfide in distilled water with the addition of hydrochloric acid to pH 0.6, and steel 18Kh1G1MF.

in hydrogen embrittlement is controlled by the parameters K_{IC} and β_e (or α_{1*}). The influence of the medium and the force action lies in the change in the combination of values of K_{IH} and α_1 .

It may be assumed that rules (1)-(8) established for the steel-hydrogen system are universal and do not depend upon the alloy or method of hydrogen impregnation, which will be verified subsequently.

The relationship of the new parameter of hydrogen resistance and the equations of decohesion of the hydrogen impregnated metal was revealed in analysis of the threshold stresses of hydrogen sulfide cracking. Hydrogen sulfide cracking tests[†] of the steels the chemical analyses of which are given in Table 1 were made on unnotched cylindrical specimens with a diameter of 6 mm in hydrogen sulfide saturated distilled water with 5% sodium chloride and 0.5% acetic acid, a base time of 700 h, and daily hydrogen sulfide bubbling of the cells, which were held at a constant temperature of $23 \pm 2^\circ\text{C}$. The load was recorded with standard Tokar' system dynamometers. The threshold (critical) stresses σ_* for hydrogen sulfide cracking were determined from the stress-rupture curves. Tests were made of 5-10 specimens per

[†]The tests were made in the laboratory of A. Ya. Tret'yak.

point. The threshold stresses for hydrogen sulfide cracking were represented in the form $1 - \sigma_*/\sigma_{0.2}$.

Figure 3 shows the relationship of the threshold stresses for hydrogen sulfide cracking to the parameter of hydrogen resistance (critical hydrogen concentration), which confirms the clear relationship of σ_* and C_{1*} .

The quantitative rules and criteria of fracture of hydrogen impregnated steel established show that the activity of hydrogen, creating "hydrogen stresses" [22] and adsorption effects, has primary significance. In the case of a reduction in the activity itself the concentration of interstitial hydrogen may not influence the life in retarded failure and hydrogen sulfide cracking of the steel [23]. Figure 4 presents the relationships of the time of hydrogen sulfide cracking and the concentration of active (lattice) hydrogen to the concentration of absorbed hydrogen in 18Kh1G1MF steel. In conducting these experiments, before loading, the steel was first hydrogen impregnated without stress [23]. It may be seen that the life changes antiprobably to the hydrogen activity. With combining of the absorbed hydrogen the interaction of the surface with the external medium acquires primary significance. The results presented in Fig. 4 show that the harmful influence of hydrogen may be neutralized by selection of appropriate alloying and methods of treatment of the steel to reduce the activity of hydrogen and under certain conditions to even obtain a positive effect from hydrogen impregnation.

Conclusions. 1. The tendency of steel toward hydrogen embrittlement is clearly characterized by the structure parameter, which has the sense of the probability of decohesion (loss of strength determined on specimens with a notch) of an infinitely dilute solid solution of hydrogen. The reciprocal, the index of hydrogen resistance, is proportional to the critical pressure of molecular hydrogen at the cracks.

2. The relationships of the "current" values of loss of strength of specimens with a notch to the corresponding hydrogen activities are constant and tend toward the value of the probability of decohesion (a value characterizing the resistance of the steel to the physicochemical action of hydrogen) of the steel with the given structure.

3. The limiting hydrogen concentrations in reversible and irreversible hydrogen embrittlement are the thermodynamic equivalents of the structure parameter of hydrogen resistance. Their relationship is expressed by the equations of decohesion, which made it possible for the first time to determine the values of the critical hydrogen concentrations in steels.

4. The critical (threshold) stresses for hydrogen sulfide cracking depend linearly upon the product of the hydrogen resistance and the yield strength of the steel.

5. The criterion of failure of constructional steels in hydrogen embrittlement may be represented in clear form through the probability of decohesion, the hydrogen activity, and the original crack resistance.

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