Modelling of Hydrogen Embrittlement of Metals in Wet H2S containing Environments

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ABSTRACT: *Governing equations for elastic-plastic material describing the damage accumulation and fracture under hydrogen embrittlement (HE) conditions are presented. Scalar damage parameter and damage evolution equation is proposed. The proposed governing equations describe such features of HE as threshold stress, below which no failure occurs; the change of failure surface mode during HE; the delayed behavior of fracture, the existence of threshold stress intensity factor, etc. The determination of material constants from available experimental data is proposed.*

INTRODUCTION

The process of hydrogen embrittlement (HE) in metals is not completely understood yet despite the intensive experimental investigation that has been done all over the world. HE is manifested in time degradation of mechanical properties such as elongation to failure, yield and tensile strength, fracture toughness, etc. HE may also change the mode of fracture from ductile transgranular mode to brittle intergranular one.

HE in metals is usually caused by ions of hydrogen generated during the corrosion reaction in wet H_2S containing environments. It is assumed that hydrogen enters the metal continuously and interacts with defects of microstructure. This defect-hydrogen interaction results in trapping of hydrogen. The traps can be a single solute atom, carbide particles, grain boundaries, internal voids, microcracks and other types of single atom or multi-atom defects. Plastic deformation plays an important role in HE through the interaction between dislocations and hydrogen.

The exact description of all features of HE process is represented as a meaningless task. Instead of trying to reproduce all fine details of this process it is supposed to be more reasonable to introduce some internal variable (damage parameter) ω reflecting only the main features of damage accumulation. This approach for the creep of metals has been done by

Kachanov and Rabotnov [1,2]. The objective of this paper is to generalize the Kachanov-Rabotnov's idea for HE conditions and to analyze from this point of view some features of failure both in uniaxial and multiaxial cases.

CONSTITUTIVE EQUATIONS

Experimental facts of HE taken into consideration are follows [3]:

- there is some critical hydrogen concentration below which no hydrogen-induced cracking occurs;
- degradation of mechanical properties under HE increases with the increasing of hydrogen concentration;
- degradation of mechanical properties under HE is determined by the quantity of dissolved hydrogen and doesn't depend on the manner of hydrogen penetration in metal;
- there is the threshold stress as maximum applied stress below which no failure occurs;
- mechanical properties of material charged with hydrogen under HE can be restored during relaxation without stress as well as after removing the sources of hydrogen embrittlement.

Based on the above-mentioned experimental observations the following damage evolution equation has been proposed [3]:

$$d\omega/dt = A\, sign(\omega_* - \omega)\left|\omega_* - \omega\right|^m \tag{1}$$

where A, m are the material parameters, $\omega_*(\sigma_{ij})$ - the ultimate value for damage accumulated, which depends on stress state, environment, temperature, etc. The simplest approximation of the function $\omega_*(\sigma_{ij})$ has been proposed in the following form [3]:

$$\omega_* = \begin{cases} \alpha\sigma_0 + \beta, \sigma_0 > 0 \\ \beta, \sigma_0 \le 0 \end{cases} \tag{2}$$

where $\alpha > 0, \beta \ge 0$ are material parameters, $\sigma_0 = \sigma_{ii}$.

Material parameter α reflects the influence of stress level on damage accumulation process. Its value depends on hydrogen ion concentration, environment, temperature, and microstructure of material. The value of parameter α is connected with the adsorption of hydrogen at some critical sites within the material such as microvoids, microcracks and other defects in presence of stress. The hydrogen concentration in these critical sites exceeds the average hydrogen concentration in the bulk metal.

The value of parameter β coincides with the ultimate value of damage accumulated in material charged with hydrogen without load. This value is connected with such sources of hydrogen embrittlement as particles, impurities, dislocations, alloying elements, etc. Due to accumulated hydrogen these sources begin to transform with time at first to bubbles and then to three-dimensional hydrogen traps.

Let us postulate the yield surface under HE conditions in the following form:

$$\sigma_e = \sigma_*(\omega) \tag{3}$$

where $\sigma_e = \sqrt{3/2 s_{ij} s_{ij}}$ is the effective stress, $s_{ij} = \sigma_{ij} - (1/3)\sigma_0 \delta_{ij}$ is the deviator of stress tensor, $\sigma_*(\omega)$ is the yield strength, changeable under the action of hydrogen environment during the deformation process. The constitutive equations should be completed by some fracture criterion. For elastic-perfectly-plastic theory it is offered to use the deformation type criterion

$$\varepsilon^p_{\max} = \varepsilon_*(\omega) \tag{4}$$

where $\varepsilon^p_{\max}$ is the maximum plastic strain and $\varepsilon_*(\omega)$ is the ultimate plastic strain, changeable under the action of hydrogen environment during the deformation process.

Simple approximations for $\sigma_*(\omega)$ and $\varepsilon_*(\omega)$ vs. ω dependencies can be written in the following manner:

$$\sigma_*(\omega) = \sigma_*^0 (1 - k_1 \omega) \tag{5}$$

$$\varepsilon_*(\omega) = \varepsilon_*^0 (1 - k_2 \omega) \tag{6}$$

where σ_*^0 and ε_*^0 are the yield strength of specimen, ultimate plastic strain of specimen under air conditions, k_1, k_2 are the material parameters. Taking into consideration the dimensionless character of damage parameter ω one of parameters k_1 or k_2 can be equated to 1, i.e. $k_2 = 1$ and $k_1 = k$.

DETERMINATION OF HE - PARAMETERS

To obtain the values of material parameters β and k it is necessary to consider the results of tensile tests for specimens charged with hydrogen without stress. In this case $\omega_* = \beta$ and from Eq.3 and Eq.4 it is followed:

$$\beta = 1 - \varepsilon_*(0) / \varepsilon_*^0 \quad (7)$$

$$k\beta = 1 - \sigma_*(0) / \sigma_*^0 \quad (8)$$

where $\varepsilon_*(0)$ and $\sigma_*(0)$ are ultimate plastic tensile strain and yield strength.

Thus, the material parameters k and β reflect the change of strength and strain characteristics of specimens charged with hydrogen without stress in comparison with these characteristics of specimens in air conditions.

HE is examined usually by uniaxial tension load tests (UTLT) or slow strain rate tests (SSRT) in wet H_2S containing media. The results of UTLT include the experimental data for the threshold stress σ_{th}.

From theoretical point of view the failure under UTLT doesn't occur if $\sigma \le \min_{t>0}\left\{\sigma_*^0(1 - k\omega(t))\right\}$. Hence, the threshold stress σ_{th} can be written in the following form:

$$\sigma_{th} = \frac{\sigma_*^0(1 - k\beta)}{1 + k\alpha\sigma_*^0} \quad (9)$$

The value of material parameter α can be obtained from Eq.9 with already known parameters k and β as follows:

$$k\alpha\sigma_*^0 = \frac{\sigma_*(0)}{\sigma_{th}} - 1 \quad (10)$$

The SSRT are performed on cylindrical specimens using a tensile machine where specimens are loaded slowly to fracture at the constant strain rate. $\dot{\varepsilon}_0$. The fracture of specimen under Eq.4 occurs in the time t_f, when the condition $\varepsilon^p = \dot{\varepsilon}_0 t_f - \sigma(t_f)/E = \varepsilon_*^0(1-\omega(t_f))$. takes place. It can be shown that

$$\omega_f = \omega(t_f) \approx \omega_* = (\alpha\sigma_*^0 + \beta)/(1 + k\alpha\sigma_*^0) \qquad (11)$$

Hence, for the ultimate plastic strain ε_f accumulated under SSRT and for ultimate stress σ_f we have the following equations:

$$\begin{aligned} \varepsilon_f &= \varepsilon_*^0(1-\omega_f) \approx \varepsilon_*^0(1-\omega_*) \\ \sigma_f &= \sigma_*^0(1-k\omega_f) \approx \sigma_*^0(1-k\omega_*) \end{aligned} \qquad (12)$$

The value of parameter α can be estimated from Eq.11 using the already known parameters k, β as follows:

$$k\alpha\sigma_*^0 = \frac{\sigma_*(0)}{\sigma_f} - 1 \qquad (13)$$

The values of material parameters A and m can be found by means of the least squares method from experimental data for tensile stress vs. time to failure (UTLT) or for tensile stress vs. strain (SSRT) relations.

Unfortunately, the complete set of experimental data (the tensile tests for specimens charged with hydrogen without stress and UTLT, SSRT) which allow to determinate all HE material parameters α, β, A, m and k is not available. As a rule, the experimental data on the change of mechanical characteristics of specimens, charged with hydrogen without stress are not available and it is impossible to estimate the values of material parameters β and k.

When the experimental data both on UTLT and SSRT are known, one can estimate two parameters k and α (or β). Kaneko [4] investigated the influence of microstructure of AISI 4130 steel on the value of threshold stress σ_{th} and the value of the ductility loss I. The ductility loss determined as $I=1-L/L_0$, where L_0 is the elongation of specimen in the air tensile test and L is the same in SSRT can compare with ω_*. Using Eq.9 the expressions for σ_{th} and ω_* can be rewritten in the form

$$\begin{cases} \alpha\sigma_*^0 r + \beta = \omega_* \\ k\omega_* + r = 1 \end{cases} \tag{14}$$

Hence, the parameter k can be estimated on the experimental values ω_* = I and $r = \sigma_{th} / \sigma_*^0$, but the parameter α can't be found without the knowledge of material parameter β. The results of calculation for the parameter k that correspond to experimental data of Kaneko [4] are represented in Table 1.

The hydrogen influence on the change of mechanical properties of some Russian grade steel (38HNZMFA steel) charged under the high hydrogen pressure without external stress was investigated by Korchagin [5]. In this case the value of parameter β can be determined by means of Eq.7. For this steel quenched and tempered to various strength levels σ_*^0 and charged up to average hydrogen concentration C_H the values of parameter β are represented in Table 2.

TABLE 1: HE-parameters for AISI 4130 steel

σ_*^0 (MPa)	σ_{th} (MPa)	r	ω_*	k	$\alpha\sigma_*^0$
650	530	0,815	0,89	0,21	1,09-1,24β
700	560	0,8	0,89	0,22	1,12-1,25β
750	600	0,8	0,91	0,22	1,14-1,25β
800	600	0,75	0,96	0,26	1,28-1,33β
850	500	0,588	0,97	0,42	1,65-1,70β
900	400	0,444	0,98	0,57	2,21-2,25β

TABLE 2: HE-parameters for quenched and tempered 38HNZMFA steel

σ_*^0, (MPa)	ε_*^0	C_H, cm^3/100 g	$\sigma_*(0)$, (MPa)	$\varepsilon_*(0)$	β
1620	0,1	5,7	1420	0,0	1
730	0,185	5,4	810	0,16	0,14
640	0,18	5,2	660	0,17	0,06

MULTIAXIAL FAILURE CONDITIONS

The governing equations Eq.1-Eq.6 allow to describe HE process both in uniaxial and multiaxial stress state. In the case of multiaxial stress state under the constant stress tensor σ_{ij} the threshold stress corresponds to the threshold surface, i.e. some surface in the stress space within which no failure occurs, $\sigma_e \le \min\limits_{t \ge 0}\left\{\sigma_*^0(1-k\omega(t))\right\}$. Hence, the equation for the threshold surface is

$$\sigma_e = \begin{cases} \sigma_*^0(1-k(\alpha\sigma_0+\beta)),\ \sigma_0 > 0 \\ \sigma_*^0(1-k\beta),\ \sigma_0 \le 0 \end{cases} \tag{15}$$

Thus, the failure occurs if the stresses are out of the threshold surface, Eq.15. For example, the failure occurs under any shear stress if the hydrostatic stress σ_0 satisfies the following condition $\sigma_0 > (1-k\beta)/k\alpha$. For the plane stress conditions Eq.15 can be written as follows:

$$\begin{cases} \sqrt{\xi_1^2 - \xi_1\xi_2 + \xi_2^2} + \alpha k\sigma_*^0(\xi_1+\xi_2) = 1,\ \xi_1+\xi_2 > 0 \\ \xi_1^2 - \xi_1\xi_2 + \xi_2^2 = 1,\ \xi_1+\xi_2 \le 0 \end{cases} \tag{16}$$

where $\xi_1 = \sigma_1 / \sigma_*^0(1-k\beta)$, $\xi_2 = \sigma_2 / \sigma_*^0(1-k\beta)$ are the dimensionless principal stresses. The schematic form of threshold surfaces, represented by Eq.15 and Eq.16 are shown on the Figure1 and the Figure 2.

$\sigma_1 = \sigma_2 = \sigma_3$

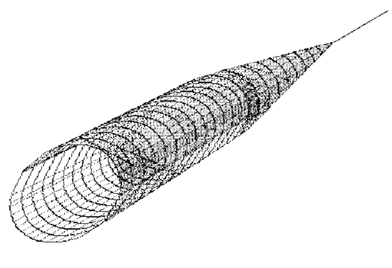

Figure 1: Schematic form of threshold surface.

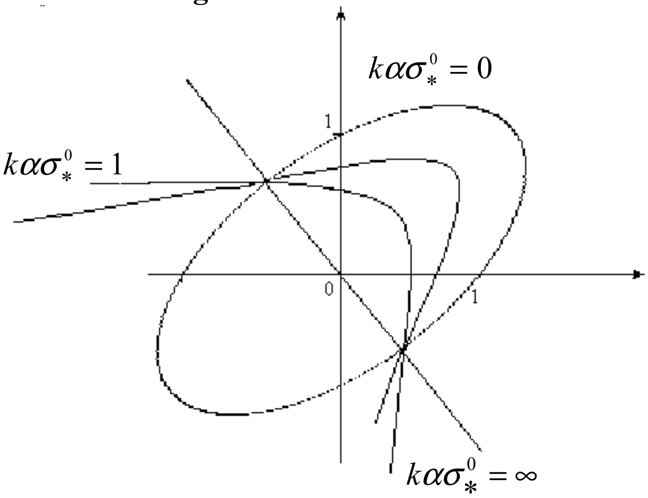

Figure 2: The threshold surface for the plain stress.

We can see that the value of $2k\alpha\sigma_*^0$ influences on these surfaces. For $2k\alpha\sigma_*^0 << 1$ the threshold surface changes weakly and keeps the elliptical form that is typical for ductile transgranular failure mode. For $2k\alpha\sigma_*^0 \geq 1$ the threshold surface changes from elliptical form to parabolic and hyperbolic ones. In this case the value of σ_0 plays the prevailing role that is typical for brittle intergranular failure mode.

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