Modeling of Hydrogen Embrittlement of Metals in Wet H_2S containing Environments

VLADIMIR ASTAFEV
Department of Strength of Materials
Samara State Aerospace University
34, Moskovskoe Shosse, Samara, 443086
RUSSIAN FEDERATION
vladimir.astafev@mail.ru, http://www.ssau.ru

Abstract: - Governing equations for elastic-plastic material describing the damage accumulation and failure under hydrogen embrittlement (HE) conditions are presented. Scalar damage parameter and damage evolution equation are 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 failure, the existence of threshold stress intensity factor, etc. The determination of material constants from available experimental data is proposed.

Key-Words: - hydrogen embrittlement, damage, metals, tensile strength, delayed fracture

1 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 [1-4]. HE is manifested in time degradation of mechanical properties such as elongation to failure, yield and tensile strength, fracture toughness, etc. (Fig. 1 and Fig. 2). When hydrogen is present, materials change also the mode of fracture from ductile transgranular mode to brittle intergranular one. Failure of materials can occurs unexpectedly, sometime after many times of service (delayed fracture).

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 [1-4]. 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 [5].

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, like Sofronis at etc. [5-6], it is supposed to be more reasonable to introduce some internal variable (damage parameter) ω reflecting only the main features of damage accumulation under hydrogen embrittlement. This approach for the failure of metals under creep conditions has been done by Kachanov and Rabotnov [7, 8].

The objective of this paper is to generalize the Kachanov-Rabotnov ís idea for HE conditions and to analyze from this point of view some features of failure both in uniaxial and multiaxial cases.

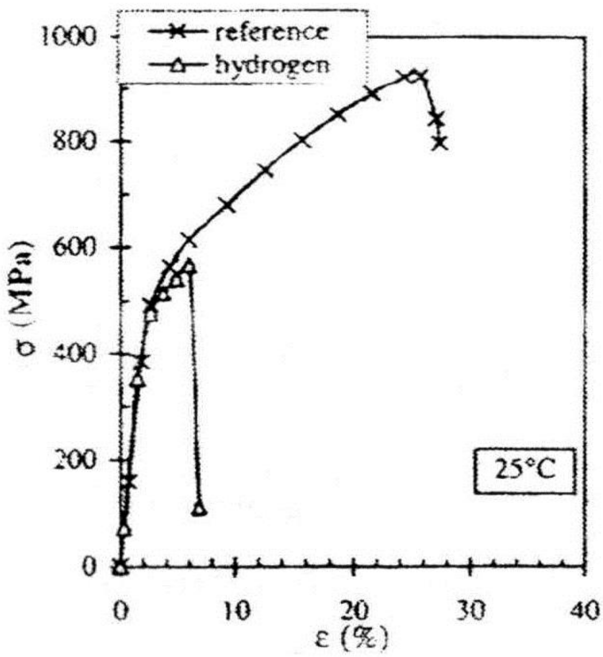

Fig. 1. Tensile curves of mill-annealed alloy 600 for reference and pre-hydrogenated specimens at 25 °C (from Delafosse and Magnin [9])

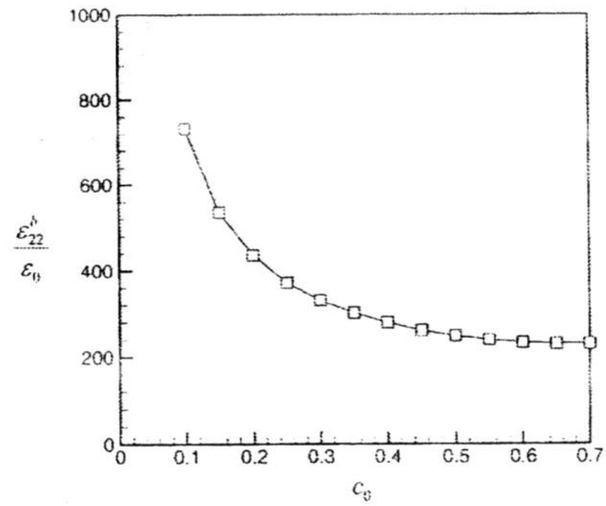

Fig. 2. Critical normalized macroscopic strain at various initial hydrogen concentrations c_0 (from Liang, Sofronis and Aravas [10]).

2 Constitutive Equations

Experimental facts of HE taken into consideration are follows [1-6, 9-11]:

• there is some critical hydrogen concentration below which no hydrogen-induced cracking occurs;

• degradation of mechanical properties of metals under HE conditions, that means the decreasing of these properties with the increasing of hydrogen concentration (Fig. 1 and Fig. 2);

• 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 metals charged with hydrogen under HE conditions can be partly 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 [11]:

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

where A and m are the material parameters, $\omega_*(\sigma_{ij})$ is 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 [11]:

$$\omega_* = \begin{cases} \alpha I_1 + \beta, I_1 \geq 0, \\ \beta, I_1 \leq 0, \end{cases} \qquad (2)$$

where $\alpha>0$ and $\beta\geq 0$ are the material parameters, $I_1=\sigma_{ii}$ is the first invariant of the stress tensor σ_{ij}.

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 form of modified von Mises type plasticity model [5]:

$$\sigma_e = \sigma_Y(\varepsilon^p, \omega) = \sigma_0(\omega)(1+\frac{\varepsilon^p}{\varepsilon_0})^{1/n}, \qquad (3)$$

where $\sigma_e=\sqrt{(2s_{ij}s_{ij}/3)}$ is the von Mises equivalent stress, $s_{ij}=\sigma_{ij}-(1/3)\sigma_0\delta_{ij}$ is the deviator stress tensor, $\sigma_0(\omega)$ is the yield stress in the presence of hydrogen, that decreases with increasing hydrogen concentration, ε^p is the plastic strain, $\varepsilon_0=\sigma_0(0)/E$ is the initial yield strain in uniaxial tension in the absence of hydrogen, n is the hardening exponent, that is assumed unaffected by hydrogen.

The constitutive equations should be completed by some failure criterion. For elastic-plastic theory, it is offered to use the deformation type criterion [12]

$$\varepsilon^p_{\max} = \varepsilon_0(\omega), \qquad (4)$$

where ε^p_{max} is the maximum plastic strain and ε_0 is the ultimate plastic strain, changeable under the action of hydrogen environment during the deformation process (Fig 2).

Simple approximations for $\sigma_0(\omega)$ and $\varepsilon_0(\omega)$ vs. ω dependencies can be written in the following manner:

$$\sigma_0(\omega) = \sigma_0(1 - k_1\omega) \tag{5}$$

$$\varepsilon_0(\omega) = \varepsilon_0(1 - k_2\omega) \tag{6}$$

where $\sigma_0=\sigma_0(0)$ and $\varepsilon_0=\varepsilon_0(0)$ are the yield strength of specimen and ultimate plastic strain of specimen under tension in air conditions in the absence of hydrogen (i.e. under condition $\omega=0$), k_1 and 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 $k_1=k$.

3 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 (i.e. under condition $\sigma_{ij}=0$). In this case $\omega_*(0)=\beta$ and from equations (5) and (6) it is followed, that

$$\beta = 1 - \varepsilon_0(\beta)/\varepsilon_0 \tag{7}$$

$$k\beta = 1 - \sigma_0(\beta)/\sigma_0 \tag{8}$$

where $\varepsilon_0(\beta)$ and $\sigma_0(\beta)$ are the ultimate plastic tensile strain and yield strength under condition $\sigma_{ij}=0$.

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 by 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 $\sigma \le min\{\sigma^0_*(1-k\omega(t)\}$ under $t>0$. Hence, the threshold stress σ_{th} can be written in the following form:

$$\sigma_{th} = \frac{\sigma_0(1-k\beta)}{1+k\alpha\sigma_0} \tag{9}$$

The relationship between threshold stress σ_{th} and yield strength of material σ_0 is schematically shown in the Fig. 3.

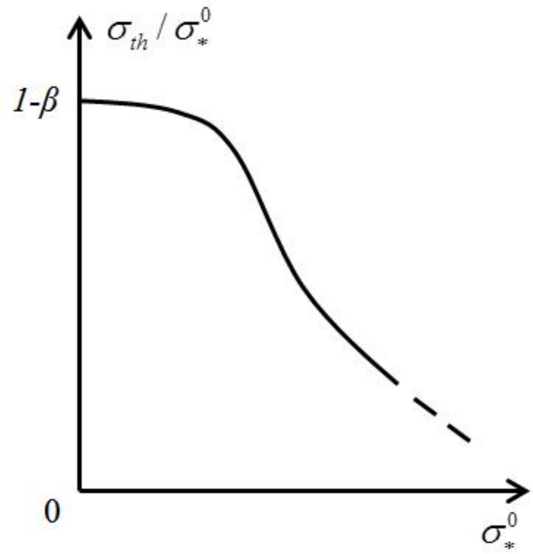

Fig. 3. The schematic relationship between threshold stress σ_{th} and yield strength of material σ_0.

So, the third parameter or the material parameter α can be obtained from (9) with already known parameters k and β as follows:

$$k\alpha\sigma_0 = \frac{\sigma_0(1-k\beta)}{\sigma_{th}} - 1 \tag{10}$$

The SSRT are performed on the previously hydrogen charged cylindrical specimens using a tensile machine where specimens are loaded slowly to failure at the constant strain rate $d\varepsilon_0/dt=v_0$. The failure of specimen at SSRT occurs at the time t_f, when the condition (4) will be performed. The condition (4) can be written in the following form:

$$\varepsilon^p(t_f) = v_0 t_f - \sigma(t_f)/E = \varepsilon_0(1-\omega(t_f)), \tag{11a}$$

where

$$\omega(t_f) = \omega_f \approx \frac{\alpha\sigma_0 + \beta}{1+k\alpha\sigma_0} \tag{11b}$$

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

$$\varepsilon_f = \varepsilon_0(1-\omega_f) \approx \varepsilon_0 \frac{1+(k-1)\alpha\sigma_0 - \beta}{1+k\alpha\sigma_0} \tag{12a}$$

$$\sigma_f = \sigma_0(1-k\omega_f) \approx \sigma_0 \frac{1-k\beta}{1+k\alpha\sigma_0} \tag{12b}$$

Thus, like the UTLT conditions the value of parameter α can be estimated from (12b) with using the already known parameters k and β as follows:

$$k\alpha\sigma_0 = \frac{\sigma_0(1-k\beta)}{\sigma_f} - 1 \qquad (13)$$

Unfortunately, the complete set of experimental data (the tensile tests for specimens charged with hydrogen without stress and UTLT or SSRT) which allow to determinate all HE material parameters α, β, A, m and k is not usually 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 only two parameters – materials parameters k and α (or β).

The experimental data on the influence of microstructure of AISI 4130 steel on the value of threshold stress σ_{th} and on the value of the ductility loss I have been presented in the paper [13]. 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_f. The relationship between ductility loss I and yield strength σ_0 is schematically shown in the Fig. 4.

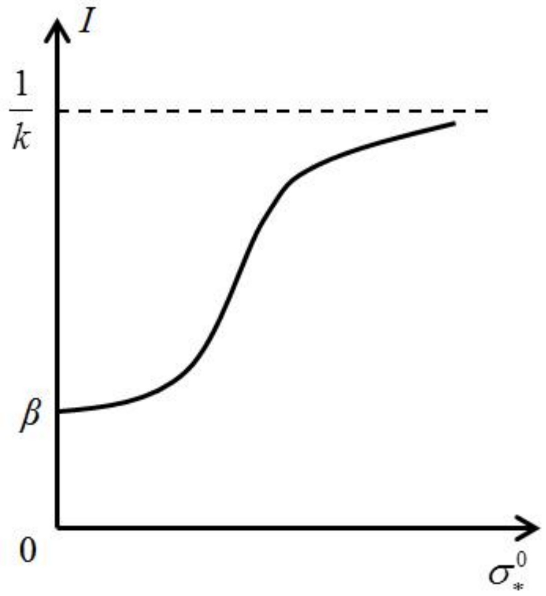

Fig. 4. The schematic relationship between ductility loss I and yield strength of material σ_0.

Both in the UTLT and SSRT conditions the expressions for σ_{th} (equation (9)) and ω_f (equation (11b)) can be rewritten in the form

$$r\alpha\sigma_0 + \beta = \omega_f \qquad (14a)$$

$$k\omega_f + r = 1 \qquad (14b)$$

Hence, the parameter k can be estimated on the experimental values $\omega_f=I$ and $r=\sigma_{th}/\sigma_0$ as $k=(1-r)/I$, 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 the paper [13] are represented in Table 1.

TABLE 1: HE-parameters for AISI 4130 steel

σ_0 (MPa)	σ_{th} (MPa)	r	ω_f	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

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 [14]. In this case the value of parameter β can be determined by means of equation (7). For this steel quenched and tempered to various strength levels σ_o and charged up to average hydrogen concentration C_H the values of parameter β are represented in Table 2.

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

σ_0 (MPa)	ε_0	C_H, $cm^3/100g$	$\sigma_0(\beta)$, (MPa)	$\varepsilon_0(\beta)$	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

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

4 Multiaxial Failure Conditions

The governing equations (1)–(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, if $\sigma_e \leq min\{\sigma_0(1-k\omega(t)\}$ under $t>0$.

Hence, the equation for the threshold surface is

$$\sigma_e = \begin{cases} \sigma_0(1-k(\alpha I_1+\beta)), I_1>0, \\ \sigma_0(1-k\beta), I_1<0. \end{cases} \quad (15)$$

Thus, the failure occurs if the stresses are out of the threshold surface (equation (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 equation (15) can be written as follows:

$$\xi_1^2 - \xi_1\xi_2 + \xi_2^2 = (1-k\alpha\sigma_0(\xi_1+\xi_2))^2, \xi_1+\xi_2>0 \quad (16a)$$

$$\xi_1^2 - \xi_1\xi_2 + \xi_2^2 = 1, \xi_1+\xi_2<0 \quad (16b)$$

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 equations (15) and (16) are shown on the Fig. 5 and Fig. 6.

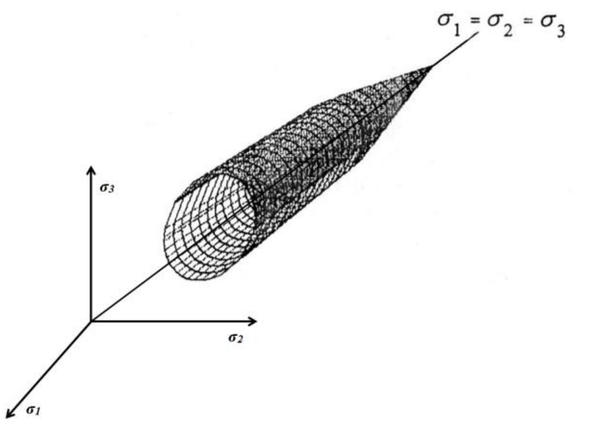

Fig. 5 Schematic form of the threshold surface.

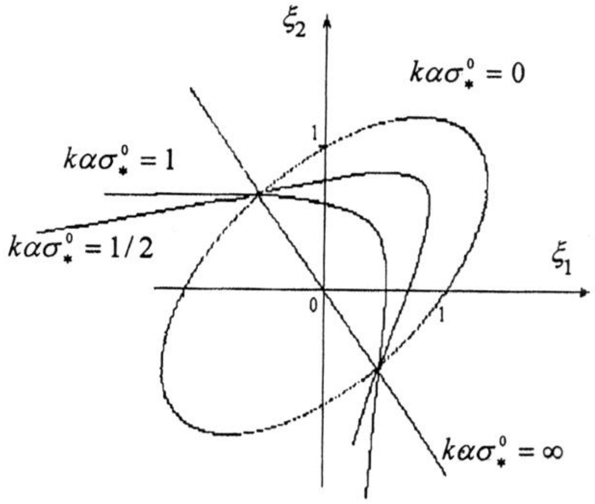

Fig. 6. The threshold surface for the plain stress.

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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