

## IDENTIFICATION OF CORROSION-MECHANICAL FRACTURE MECHANISM OF STRUCTURAL STEELS

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The paper research results on damage incubation in a low strength steel under the conditions of fatigue and cavitation, and also discusses temperature dependent subcritical crack growth in a high strength steel under the influence of proton-donor environments and after preliminary hydrogenating. The effect of aqueous medium content on the rates of electrolytic reactions on the deformed metal-environment interface has been investigated. Correlation dependencies between repassivation characteristics of the deformed steel surface and its fracture due to fatigue and cavitation have been determined. The reasons for a scatter of experimentally determined subcritical crack growth activation energies with taking into account the fracture micromechanisms are considered.

INTRODUCTION

Mechanisms of corrosion-mechanical fracture (CMF) of steels can be considered both from the side of the microstructural aspects of material fracture and from the side of the nature of environmental effects, e.g. local anodic dissolution, hydrogen embrittlement. It is a common practice to draw the important role of environmental condition in protective film fracture and repassivation of the juvenile surface for interpretation of the effect of the corrosion medium content on corrosion-mechanical fracture. However, in general, the effect of the surface repassivation processes is considered in the analysis of corrosion-mechanical fracture controlled by local anodic dissolution (Logan (1) and Akid and Miller (2)). The surface effect is often ignored when investigating the hydrogen-induced corrosion-mechanical fracture, assuming that the fracture rate is controlled by hydrogen diffusion into the pre-fracture zone. This point of view usually is based on the evaluations of temperature dependence of subcritical crack growth in high strength steels under the effect of the aqueous environments. Since the rate of the process and thus its activation energy,  $\Delta H$  is controlled by its slowest part, one can determine the controlling CMF stage by comparing  $\Delta H$  values (Van der Sluys (3) and Romaniv et al (4)). In particular, it was found (3) that

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the experimentally measured value  $\Delta H = 37$  kJ/mol coincides with that for penetration of electrolytic hydrogen through a steel membrane.

The role of electrochemical repassivation reactions on the stage of corrosion-mechanical fracture initiation (incubation period) during fatigue and cavitation of the low-strength steel, when local anodic dissolution is the leading mechanism of environment effect and also on the subcritical crack growth stage in stress corrosion cracking of the high strength steel, when aggressive effect of the environment is determined by its hydrogenating ability, is analysed.

#### EXPERIMENTAL DETAILS

Initiation of corrosion-mechanical damage was investigated in 0.4C-1Cr steel (0.41%C, 0.91% Cr, 0.60% Mn,  $\sigma_{YS} = 540$  MPa) undergoing fatigue and cavitation in the aqueous solutions containing 0.05 mol/l NaCl at ambient temperature. Aggressiveness of the environment was changed by introduction of corrosion inhibitors - morpholine, KORSOL (based on pyrophosphates) and piperidine in concentration of 1.0 g/l. Fatigue tests were carried out on 6x18x160 mm single-edged-notched beam specimens cyclically loaded by the stresses of 350 MPa with a frequency of 10 Hz and a load ratio of 0.05. The cavitation tests were performed by using vibration method with a frequency of 20 kHz and an amplitude of 36  $\mu\text{m}$ . In fatigue tests, the duration of the incubation time was assumed to be the number of cycles  $N_i$  required for the crack to extend to 0.05 mm. In cavitation, it was the time  $\tau_i$  when the mass of a specimen was decreased by 0.0001 g.

The characteristics of relaxation of electrochemical processes on juvenile surface were investigated using the reverse torsion specimens. Such load technique provides high plastic deformation (and thus large juvenile area) without fracture. Before the torsion the specimen was put into a chamber coaxially to an auxiliary reference silver chloride electrode. The electrochemical measurement were performed with a potentiostat.

Subcritical crack growth at stress corrosion cracking was investigated for the 0.45C-1Cr-2Ni-1Mo steel (0.46%C, 1.02% Cr, 0.61% Mn, 2.2% Ni, 0.45%Mo,  $\sigma_{YS} = 1720$  MPa), which has been exposed to thermal treatment to form a martensite structure with different average sizes of former austenite grains, 8 and 140  $\mu\text{m}$ , respectively. In the last case, grain boundaries had "tooth" shape. Experiments were performed in the temperature range of 25-100°C on beam specimens with fatigue cracks, subjected to 4-point bending. The tests were carried out in the proton-donor media, namely water and dimethylsulphoxide (DMSO) with addition of 0.1 mol/l  $\text{HClO}_4$ , as well as in air after the preliminary hydrogenation by electrolytic charging for 1h in 26%  $\text{H}_2\text{SO}_4$  solution with a current density of 0.1 A/cm<sup>2</sup>, cadmium plating and holding 2h at 100°C. This specimen treatment helps in uniform hydrogen distribution in a specimen and keeping the constant hydrogen concentration during experiments.

CORRELATION BETWEEN CHARACTERISTICS OF REPASSIVATION OF THE  
DEFORMED SURFACE AND CMF UNDER FATIGUE AND CAVITATION

Addition of corrosion inhibitors has a strong effect on the incubation period of corrosion-mechanical fracture in steels. The effect of pipyridine was the maximum among the inhibitors considered. It increases the duration of corrosion-mechanical fracture incubation by the order in comparison with tests in pure water and is efficient both against fatigue and cavitation. Corrosion of the steels was inhibited most effectively by KORSOL. It turns out that the steel corrosion rate in an environment can not be used as an indicator of its aggressive effect at corrosion-mechanical fracture.

Plastic deformation by torsion of the steel causes a big shift of the electrolytic potential to a more negative value. This shift increases with the increase of plastic strains and decreases by addition of inhibitors. The rates of anodic and cathodic reactions are sharply increased on the deformed surface (Fig. 1). They depend on the exposure  $\tau$ , the polarisation potential and the presence of inhibitors. Polarisation curves for the deformed surface are characterised by linear Tafel parts, which indicate the activation nature of overvoltage of electrolytic reactions. Relaxation of the polarisation current, including the exchange current  $i_0$ , is described by the straight lines in the coordinates  $\log i_0 - \log \tau$ . Values  $i_0$  for different  $\tau$  were calculated from experimental polarisation curves (Fig. 1). The inhibitors retard the electrolytic reactions on the deformed surface. This effect is observed already at  $\tau = 10^{-2}$  s. It means that initial adsorption of the inhibitors starts rather early and their protective effect under the stationary and nonstationary (on the deformed surface) conditions can differ substantially.

The efficiency of this influence on the rate of nonstationary electrochemical processes, i.e. the activity of juvenile surface in the different environments can be evaluated from the amount of charge  $g_0$  spent in the oxidation of the deformed surface during the repassivation time. The value of  $g_0$  was determined by integration of the relaxation curves (Fig. 2). The calculated value  $g_0$  well correlates with the duration of the incubation period in fatigue  $N_i$  and cavitation  $\tau_i$  (Fig. 3). The correlation dependencies obtained prove the dominant role of the steel repassivation parameters in determination of the resistance against various kinds of corrosion-mechanical fracture and show, that fracture initiation is controlled by the nonstationary electrochemical processes on the deformed surface. The proposed approach allows to evaluate not only the inhibitor efficiency against corrosion-mechanical fracture in steels, but also to rate various media according to their corrosion activity in relation to their pH, presence of an activating or inhibiting additions.

IDENTIFICATION OF THE LIMITED STAGE OF CRACK GROWTH IN  
STEEL AT STRESS CORROSION CRACKING

Temperature dependencies of the subcritical crack growth rate in the investigated steel-environment systems are in general linear (Fig. 4). The nonlinearity appears in aqueous environments at a temperature above 80°C. However, the linearity remains till 100°C if the specimens were prehydrogenated. The  $\Delta H$  values, which are calculated from the linear parts of the subcritical crack growth temperature dependencies, scatter in a very wide range

(Table). The dependence of the subcritical crack growth activation energy in aqueous environments on the temperature and also its difference from the  $\Delta H$  for prehydrogenated specimens from the first sight disagree with the domination of the hydrogen mechanism at stress corrosion cracking. Let's consider the causes of the  $\Delta H$

TABLE - Energy Activation for Different Systems Steel-Environment.

	Steels Structure	Tests Conditions	$\Delta H$ (kJ/mol)
1	Fine Grain	Water	31.4-38.1
2	Fine Grain	DMSO + 0.16 mol/l HClO <sub>4</sub>	52.3-58.6
3	Fine Grain	After Hydrogenating	24.7-26.8
4	Coarse Grain	Water	62.8-73.3
5	Coarse Grain	After Hydrogenating	24.3-25.5

scatter at subcritical crack growth in investigated systems "steel-environment". We can argue that hydrogen diffusion in metal is the one who controls the subcritical crack growth in the preliminary hydrogenated specimens. Although the subcritical crack growth rates and fracture micromechanisms in fine grain and coarse grain steel to which correspond intergranular and transgranular fracture, respectively, are different, the  $\Delta H$  values are nearly equal. They are similar to the energies of hydrogen - dislocation interactions at this temperature range, 25 kJ/mol reported by Kikuta and Sugimoto(4).

In aqueous solutions,  $\Delta H$  in the coarse grain steel is considerably higher than in the fine grain steel. However it is proved that subcritical crack growth in the fine grain steel is occurs intergranularly, irrespective to the test temperature, but in the coarse grain steel the fracture occurs by mixed micromechanism. Moreover, energy-free intergranular cleavage mechanism becomes dominant by increasing temperature. Hence the transition to other subcritical crack growth micromechanisms is affects its rate and the measured  $\Delta H$  values, though the mechanism of the environment effect remains the same. Thus, the calculated  $\Delta H$  values mean the activation energy of the fracture process only if the fracture micromechanism does not sustain significant changes within the considered temperature range.

In our opinion, the subcritical crack growth in steel occurs due to hydrogen embrittlement, but the rate of hydrogen penetration and the fracture itself is controlled by the surface processes. The following experimental results confirm this conclusion. Different  $\Delta H$  values at subcritical crack growth in steel were obtained in such environments as water and acid solution of DMSO, which have different physical and chemical properties (replacement of one proton-donor environment with another one can change only the conditions of flow of the surface processes); non-linear temperature dependencies of the

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corrosion crack growth rate at a temperature over 80°C, at which oxygen solubility in aqueous solutions decreases sharply (it is only possible because of the change of the controlled stage of hydrogen embrittlement on the metal-environment interface, since the temperature dependence remains linear for prehydrogenated specimens till 100°C).

### SYMBOLS USED

$da/dt$	= crack growth rate (mm/s)
$\Delta H$	= activation energy of subcritical crack growth (kJ/mol)
$E$	= electrode potential (V)
$\sigma_{YS}$	= yield stress (MPa)
$N_i$	= incubation period of fatigue (cycle)
$g_o$	= charge of oxidation process (C)
$i_0$	= exchange current of electrochemical reaction (A)
$\tau_i$	= incubation period of corrosion-erosion wear (s)
$T$	= temperature (°C)

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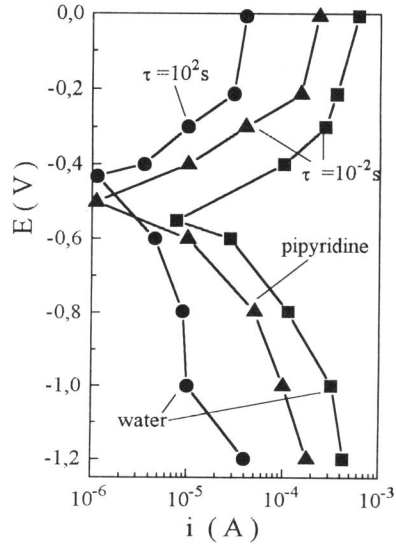


Fig. 1 Polarization curves for water and pipyridine at different expositions

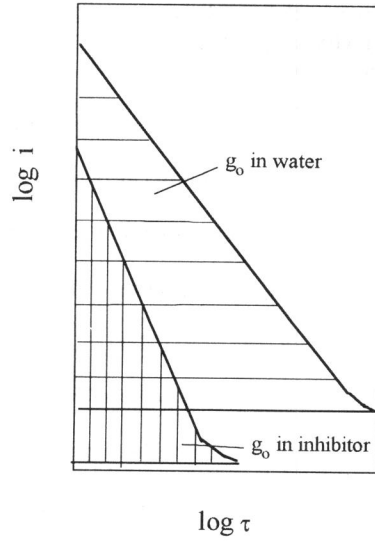


Fig. 2 Calculation method of charge  $g_0$

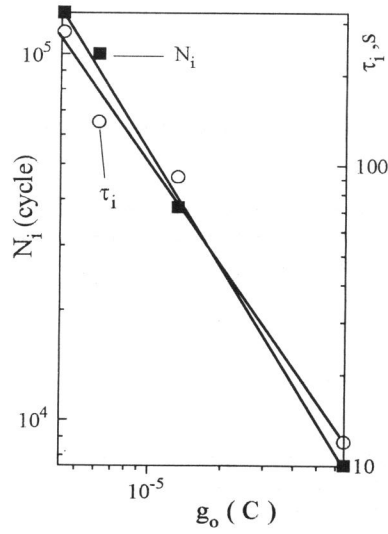


Fig. 3 Correlation dependencies  $g_0-N_i$  (fatigue) and  $g_0-\tau_i$  (cavitation)

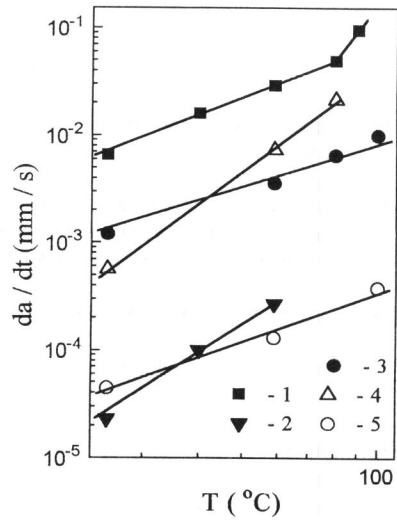


Fig. 4  $da/dt-T$  dependencies for different environments (numbers in Table)