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STRESS CORROSION CRACKING AND FRACTURE TOUGHNESS OF HIGH STRENGTH STEELS

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Abstract: The stress corrosion cracking (SCC) process is at present a not fully elucidated mechanism of deterioration. It is a surface process that implies a corrosion and stress synergy, but the most practical consequence is that stress corrosion cracking can modify the mechanical characteristics of the metal causing brittle failure. Previously, we present some results about stress corrosion cracking, crack propagation rate or, even, crack arrest conditions in High Strength Steels. This kind of steels is usually used in prestressed and postensioned structures. These wires are of eutectoid composition and cold drawn. It is well established that failures occur when the wires are in contact with electrolytes of specific compositions while under stress. In the case of concrete, the electrolyte is its pore solution and the stress levels result from the different loads applied due to structural requirements.

In this work we suggest some improvements of the Mechanism of SCC based in the Surface Mobility of vacancies on the crack surface proposed by Galvele. Improvements consist in incorporating the electrochemical corrosion as one of the sources for the creation of vacancies and some mechanical effects, both produce synergic effect in the crack propagation rate and they are important for a more comprehensive explanation of the process.

On the other hand, the Fracture Toughness change when the steel corrodes, questioning the idea that is an intrinsic characteristic of the material. The reduction in the fracture toughness of steel wires when they are in contact to aggressive media involve that the material becomes less damage tolerant, which implies that it is necessary to detect defects of smaller size, as for example, small notch, pits or superficial cracks.

1 INTRODUCTION

Up to present the mechanism of SCC has not been explained satisfactorily. Numerous mechanisms have been proposed to explain the brittle failure of metals under stress, but only some of them, five specially, are considered to be relevant: i) Mechanism of Anodic Dissolution; developed by Parkins [1], ii) Film-induced Cleavage Model; whose theoretical aspects have been developed by Newman [2], iii) Surface Mobility SCC Mechanism; developed by Galvele [3], iv) Environmentally Enhanced Plasticity;

developed by Magnin et al. [4], and v) Hydrogen Embrittlement [5].

The Surface Mobility Mechanism (SMM) proposes a new perspective in which the crack advances, not due to anodic dissolution but to diffusion of atomic vacancies created in the lips of the crack towards its tip. SMM is the only mechanism that proposes equations enabling the prediction of crack propagation rate and that incorporates the effect of the hydrogen produced during the process, achieving to formulate an extension of the theory on SCC to hydrogen embrittlement.

Coherent with the lack of agreement in the type of mechanism that operates, an agreed testing method does not exist for the study of the susceptibility to SCC or to hydrogen embrittlement [6]. In the case of high strength steel wires for prestressed concrete, there are a standard tests where the aggressiveness is enhanced to accelerate the process. These tests enables to detect the susceptibility to hydrogen embrittlement of steel and serves as quality control test to detect faults [7]. Other authors suggest a test closer to concrete performance, which is based on the application of the theory of anodic dissolution [7-11] to specimens in alkaline solutions containing chlorides or of sodium bicarbonate [12] or in the use of pre-cracked specimens induced by fatigue [9, 13, 14] in whose studies the fracture toughness is calculated by fracture mechanics. None of these tests for prestressing wires can be generalized and give conclusive results. For the case of high strength wires, the existing test [7] has seemed not appropriate for other electrolytes and far from the chemical composition of the concrete pore solution. It has been then, necessary to try to develop a more suitable testing method for prestressing wires. The main conditions are: the test should be simple, able to be used for control of production and for making predictions of long term performance which should allow verifying the mechanism of progression of the SCC cracks.

In present work, profit is made on a more realistic testing methodology to propose the integration of the SMM to the fracture mechanics principles and to incorporate in them the Anodic Dissolution as part of the general process. The result is called the Fracto Surface-Mobility Mechanism, FSMM. Regarding the testing methodology (still needing optimization of the test conditions) it is used for the study of the mechanisms of SCC in prestressing wires and has been crucial to develop the proposed model. It consists in, having the wire under tension, to replace the generation of a fatigue's crack by the creation of a more natural crack made to growth it electrochemically from a notch and using a solution of sodium bicarbonate as electrolyte. When the crack reaches a certain depth, the wire is removed from the solution and it is tested in air. This methodology enabled to calculate the fracture toughness of the wire and to predict the crack propagation rate [6]. The fracture toughness is calculated by Fracture Mechanics (FM). Due the observations made in the tests, the theory of the SMM was modified to fit into the results obtained.

2 EXPERIMENTAL METHODOLOGY

The materials and equipments used were described in previous papers [6, 15, 16]. A steel of eutectic composition have been tested in two conditions: cold drawn steel (1510 MPa yield strength) and the modified parent pearlitic steel (1300 MPa yield strength).

The methodology was described by Sanchez et al [17, 18]. The aim of the methodology is to achieve a more realistic and controlled test conditions than those that generate the surface defect by a fatigue because in present case fatigue is not operating in the process. In the proposed test the crack is generated by electrochemical dissolution by nucleating a pit in a hole made in an epoxy applied to cover the surface. Then the wire is stressed and tested to induce the crack that nucleates in the bottom of the notch. The testing method consists then of several stages. Two types of steel were used. The methodology is based in the control of the following electrochemical and mechanical parameters:

1) Mechano-electrochemical generation of a crack in the wire:

- The zone of the steel exposed to the electrolyte is first covered by epoxy resin.
- In order to localize the attack, a notch is then produced in the middle of the epoxy covered zone.
- The specimen is thus strained to 80% of its yield strength.
- It is next immersed in a solution of sodium bicarbonate at constant temperature.
- A fixed potential is applied, during around 100 h, and the current is registered by a data logger simultaneously.

The specimens are then removed from the solution and dried.

2) Slow Strain Rate Test (SSRT): SSRT is performed in air at a rate of $3*10^{-7}s^{-1}$ in order to determine the fracture toughness.

3) Scanning Electron Microscopy (SEM) analysis: SEM is used to identify brittle zones, cleavage and the different zones of the fractured surface. The crack dimensions are measured and the reduction of area is accounted.

3 RESULTS

Several tests were carried out on modified parent pearlitic and cold drawn steels according the methodology previously described. Figure 1 shows the electrochemical parameters measured during the mechano-electrochemical crack generation test. The potential was fixed at $-275mV_{Ag/AgCl}$. The cell intensity remains anodic in all cases that the crack grows during the test. Figure 2 shows the mechanical behaviour after the crack generation test. The results indicate that the ultimate elongation and the ultimate load are reduced. The mechanical behaviour depends of crack shape and size, and on the initial fracture toughness of the steel in the aggressive media [16].

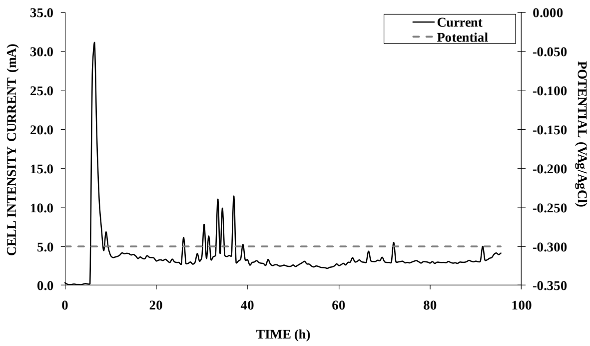

Figure 1: Evolution of electrochemical parameters during A06 SCC test.

A

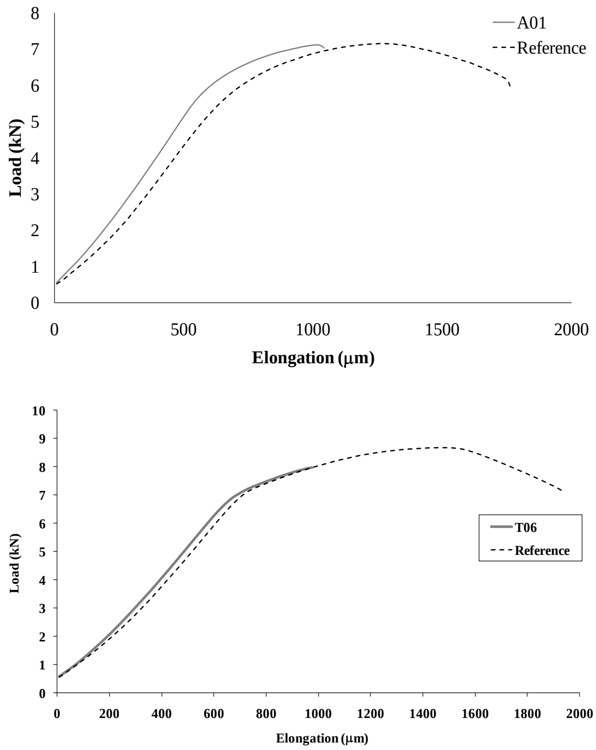

Figure 2: Mechanical behavior of steel after crack generation test.

Regarding the aspect of the fracture surface Figure 3 shows that of the modified parent pearlitic steel and cold drawn steels tested according to previous methodology. It is possible to distinguish the notch, stress corrosion crack and the brittle fracture surface in both steels. Oxides are observed at the notch in its external part while the lateral surfaces of the crack and its bottom are free of oxides. Another important observation is that the crack tip border is defined by a cleavage area at mechanical fracture section. Brittle zones appear in the whole interior of the surface of fracture. Table 1 summarizes the experimental results according to the testing methodology. It is shown there the geometrical, mechanical and electrochemical parameters obtained from the SCC test.

a
b
c

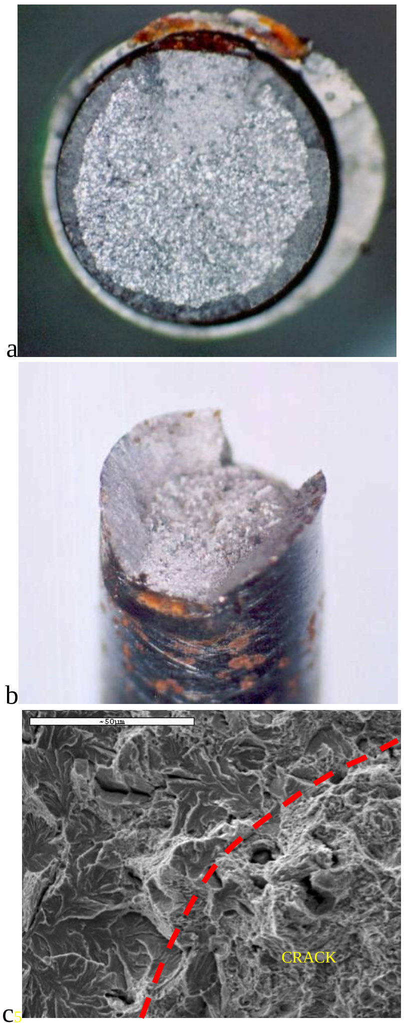

Figure 3: Surface of fracture: a) modified parent pearlitic steel, b) cold drawn steel and c) Crack tip.

Table 1: Experimental SCC results: a_f is the crack length, P is the mechanical load, t is the experiment time, I is the Faraday current and a_m is the notch length

Test		**a_f (μm)**	**P (kN)**	**t (h)**	**I (A)**	**a_m (μm)**
Parent pearlitic steel	A01	840	5.1	188.5	5.63E-7	160
	A02	1000	5.1	96	5.70E-07	160
	A03	600	5.1	96	1.20E-06	160
	A04	810	5.1	98.05	3.28E-07	170
	A05	260	5.1	22.75	5.50E-07	215
	A06	720	5.1	95.5	3.34E-06	80
	A07	760	7	49.5	3.22E-07	120
	A08	760	7	16	2.00E-05	160
Cold drawn steel	T01	800	5.93	96	1.03E-05	60
	T02	720	5.93	98	8.14E-07	200
	T03	680	5.93	170	5.57E-07	120
	T04	640	5.9	96	1.50E-07	160
	T05	800	5.9	96	1.37E-06	120
	T06	500	5.9	134.2	2.29E-5	230
	T07	730	5.9	97	5.47E-08	120
	T08	720	7.5	222.5	1.80E-6	120

4 DISCUSSION

It is important to start by mentioning that the SMM [3] is based in a set of assumptions which could not be verified in the observation of the fractures obtained and shown in previous figures. The aspects departing from the SMM are: i) the crack surface is free of oxides while the SMM is based in that there are the oxides in the walls of the crack which are the source of production of vacancies, ii) an anodic current is necessary to be registered in order the crack to grow while the SMM considers the growing only dependent on the vacancies movement towards the crack tip, and iii) the crack arrests when the current registered is cathodic, behaviour not considered by the SCC which assumes that the crack cannot arrest, but always progress.

Therefore, either the mechanism is not valid or operating in present types of steels or the theory should be modified to fit into the observations. This is what is tried in present discussion: the proposal of modification of the SMM mechanism and its coupling to the principles of fracture mechanics in order to complete the mechanical aspects of the model.

We propose to change some hypothesis of the SMM to be coherent with the experimental observations: i) the source of vacancies are not lying on the crack surfaces but in the notch at the metal surface where the oxides are observed, ii) consequently, the path length of the vacancies is the crack depth and not the atomic distance, iii) the diffusion cannot be in steady state conditions but the process is clearly non stationary, and iv) the stress influences the vacancy rate towards the crack tip and a new formulation of the influence of the mechanical conditions in the crack progression is necessary. We proposed that the vacancy generation is due to the anodic dissolution in the surface defect. Then, according to Faraday's Law it is possible to estimate the vacancy flux (Jv) from the cell current intensity:

$$J_v = C*I \qquad (1)$$

where, C is a constant which depends on geometry conditions and I is the anodic intensity.

In order to apply a non-steady state diffusion coefficient it is necessary first to analyse the literature on the subject that is not very numerous. The aspects that influence the surface diffusion coefficient, Ds: the self-diffusion, the type of electrolyte which induce a precise electrochemical potential and the stress level. We propose the hypothesis that the diffusion barrier depends on the strain, thus, it is explained that the activation energy decreases for tensile stress and vice-versa. The atoms diffuse to lower energy states (less strained areas) while the vacancies diffuse to high energy areas and relax the material. According to this hypothesis, the stress gradient change the surface diffusion coefficient and it is possible to apply the Stress Intensity Factor (K) to define this stress gradient. Following Irwin theory [19] it is possible to estimate the mechanical energy created by a stress concentration. We propose to change the diffusion coefficient expression of Galvele by adding the square of the Stress Intensity Factor to the activation energy parameter, as is shown in the following equation:

$$D_S = D^0 exp\left[\frac{-Q^{act}}{RT} + \beta K_I^2\right] = D_{S,\sigma=0} exp[\beta K_I^2] \qquad (2)$$

where: $D_{S,\sigma=0}$ is the surface diffusion coefficient without stress, β is a constant, K_I is the mode-I stress intensity factor

Equation 2 includes the three main factors of SCC process: the material, the environment and the stress conditions. This way it is possible to merge the Fracture Mechanics and the Surface Mobility Mechanism to aim into a Fracto-Surface Mobility Mechanism.

Until now we have not taking into account the role of the hydrogen evolution, According to present theoretical frame, the corrosion anodic current generates the vacancies at the notch and they diffuse to the crack tip by the stress gradient. Our proposal is that it is necessary to change the activation energy reducing it according to the hydrogen interaction-vacancy (Q_H):

$$D_{S,\sigma=0} = 0.014 * 10^{-4}\, exp\left[\frac{-13Tm + Q_H}{RT}\right] \qquad (3)$$

Where Tm is the melting point.

This means that the hydrogen role is also to drive the vacancies to the crack tip and it also can penetrate the metal at the crack tip. Therefore, hydrogen seems to have a double effect: i) it enhances the surface diffusion, and ii) it penetrates in the metal at the crack tip leading into the noticed hydrogen embrittlement which reduces the mechanical properties [16, 20-24].

Table 2 summarizes the main aspects of the SMM mechanism that we propose to modify from present observations and after the application of FSMM with the corresponding equations.

Table 2: Integration the Fracto-Surface Mobility Mechanism: FSMM

Surface Mobility Mechanism		Fracto-Surface Mobility Mechanism	
Aspect to be modified	**Equation**	**Modification proposed**	**Equation**
The source of vacancies	$C = C^0 \exp\left(\frac{\sigma a^3}{kT}\right)$	Corrosion as source of vacancies	$J_V \approx I$
Diffusion Coefficient	Exchange Current Density, i_0 $D_S = 7.40 * 10^{-4}\, exp\left[\frac{-30Tm}{RT}\right] + 0.014 * 10^{-4}\, exp\left[\frac{-13Tm}{RT}\right]$ $D_S = \frac{i_0\, N_A\, AF\, n^2\, a^2}{6F}$	Fracture Mechanic and electrochemical integration	$D_S = D_{S,\sigma=0} \exp\left[\beta K_I^2\right]$ $D_{S,\sigma=0} = 0.014 * 10^{-4}\, exp\left[\frac{-13Tm+Q_H}{RT}\right]$
The path length of the vacancies	$L \approx 10^{-8} m$	Crack length	$L \approx a$
Crack propagation rate by steady state diffusion	$cpr = \frac{D_S}{L}\left[exp\left(\frac{\sigma a^3+\alpha E_b}{kT}\right) - 1\right]$	Non stationary diffusion	$J_V = D_S \frac{\partial^2 C_V}{\partial L^2}$

We have estimated the β parameter of equation 3 by iteration method considering the experimental results. The values of β parameter get the same for both materials. These results are coherent with the theoretical model because the β parameter depends only from the elastic properties and both materials have the same elastic behaviour and the same chemical composition. For enabling predictions it is necessary to also consider the crack propagation rate. From the theoretical model proposed it is also possible to estimate several parameters from the experimental conditions: crack tip position, crack propagation rate and stress intensity factor. However, three main aspects have been varied for a correct estimation of the crack velocity: i) a crack growth rate is not constant (Figure 4a), ii) the possibility that the crack arrests (Figure 4b), and iii) the occurrence of a failure of material during the test (Figure 4c). For SCC growth to be sustained, it is a necessary, but not sufficient, condition that the current in the potentiostatic test remains anodic. Notable results are the crack stops. The crack propagation rate also increases with the remote load, but the crack arrests when the yielding is reached at the crack tip. Finally, the growing of the crack is affected by the crack geometry. This has been analyzed using FEM calculations and verified with the compliance method [15, 17]. Both conditions are related with the stress gradient on the crack walls.

In other cases the steel reaches the failure during a SCC test and then it enabled to analyze the fracture toughness in the particular environment-electrochemical conditions. This is an important material characteristic that also influences the crack rate and it has to be emphasized the interesting observation that the toughness did not remained constant as was previously stated [6, 16, 17]. This result calls for the need to review the damage tolerance of prestressed structures in contaminated atmospheres and under hydrogen evolution.

Present paper shows previous calculations about stress intensity factor for a bar with crack geometry similar to that generated by stress corrosion, from solving the Integral J by finite element calculations [6, 16].

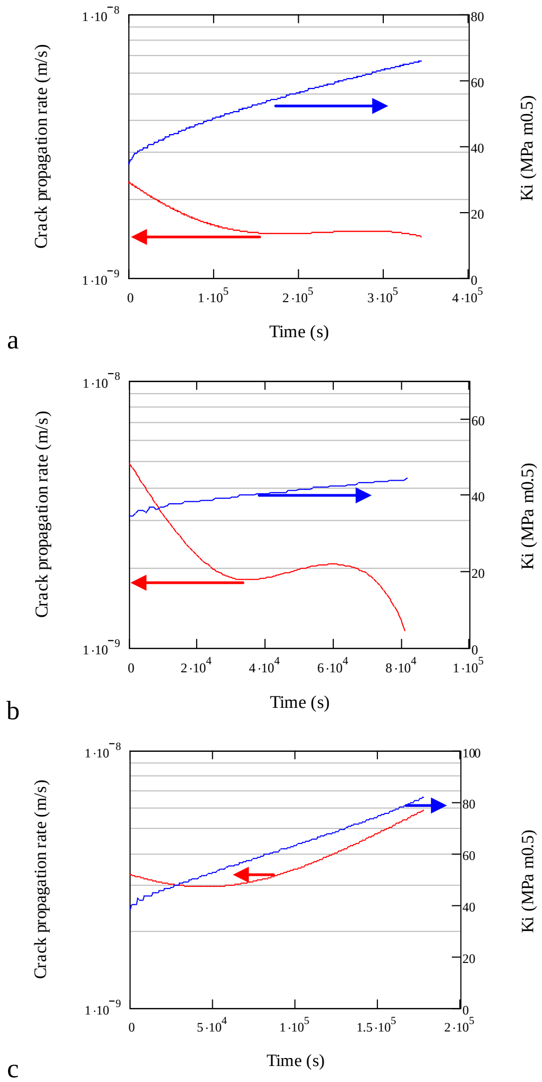

Figure 4: Crack Propagation Rate calculated from the model and test reference in table 2: a) crack growth rate of T04 test, b) crack arrest of test A05, and c) fracture of A07 specimen during the test.

Figure 5 show the values of the fracture toughness for cold drawn and parent steel. The fracture toughness of the cold drawn steel is higher than parent steel one, although it can be distinguished a large variation of the fracture toughness in both materials. In all cases it is achieved very smaller values, around 50 MPam$^{0.5}$ or less than the nominal ones. This means that the damage tolerance is reduced dramatically by the media, because when the crack grows up by stress corrosion cracking, the fracture toughness can be reduced around 40%. This reduction indicates the need to reconsider the crack depth needed to develop a brittle failure in the case of corroding high strength steels and therefore, to reduce the expected dam-age tolerance of these steels when they develop cracks by stress corrosion.

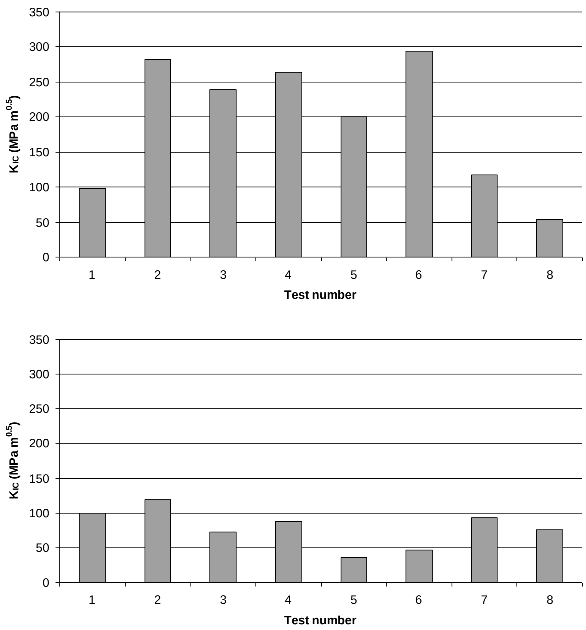

Figure 5: Fracture toughness of cold drawn steel (top) and parent steel (down) after stress corrosion cracking test.

5 CONCLUSION

In present paper, we try to contribute to surface mobility theory by presenting several modifications which complement it and serve to justify several experimental observations in high strength steel wires used for prestressing concrete. According to the extended SMM, that we call “fracto-SMM”, FSMM, in order to visualize the integration with fracture mechanics, it is possible to estimate the crack propagation rate or mechanical behaviour from the electrochemical, geometrical and material conditions according table 2. The main contribution consists in the integration of fracture mechanics into the Surface Mobility theory. Other integrating concepts to Surface Mobility Mechanism are the vacancies are generated by anodic dissolution and they are driven by a stress gradient to the crack tip in non-stationary conditions. By these integrations, the Stress Corrosion Cracking phenomenon is explained from the material, environment and mechanical point of view.

The hydrogen changes the activation energy of vacancies diffusion which means that the hydrogen role is to enhance the surface diffusion, and to penetrate in the metal at the crack tip leading into the hydrogen embrittlement which reduces the mechanical properties. We point that this methodology should be applied to safety and durability studies of prestressed structures in contaminated atmospheres.

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