ON HYDROGEN INDUCED CRACKING IN PRESTRESSING STEEL WIRES

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ABSTRACT. The paper summarizes the results of an extensive research program to determine hydrogen embrittlement susceptibility of prestressing steels. It includes a theoretical approach to find expressions based on Linear Elastic Fracture Mechanics to relate times to rupture to stress applied and an experimental approach to check the validity of the model to explain the observed times to rupture and to show the influence of surface residual stresses and test temperature on hydrogen susceptibility.

INTRODUCTION

High strength steel wires (ultimate tensile strength > 1500 MPa) cold drawing eutectoid steels, are widely used for prestressing concrete. The importance of such steels may be reckoned from the world production, over 10^6 tonne per year.

In prestressed concrete structures steel tendons are always under tension. When protected by sound and uncracked concrete durability of steel tendons is good enough as evidenced by experience. When unstressed tendons are tested in an aggressive environment, like sea water, only local attack -like pitting- may appear. Nevertheless under the combined action of stress and an aggressive environment cracks may develop and grow for stress intensities well below the fracture toughness of the material. Such phenomenom is well known as stress corrosion cracking.

Stress corrrosion cracking (SCC) is one of the problems of much concern of prestressing steels and several failures have been attributed to SCC in the past. See for instance the published cases by CUR (1), Phillips (2), Schupack (3) and Nurnberger (4). Consequently, SCC has been the subject of many studies and three International Symposia have been organized by the International Federation for Prestressing (FIP) with the aim of investigating the mechanisms, test methods and protection procedures of SCC of prestressing steels (5, 6, 7).

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There is a general agreement that hydrogen embrittlement plays an important role in the environmental cracking of prestressing steels. Therefore, in 1978, the FIP proposed a test (8), the ammonium thiocyanate test, to determine the hydrogen embrittlement susceptibility of prestressing steels. In spite of some objections to this standard corrosion test proposal posed by Parkins et al. (9) the third International Symposium has recognized, that it is the best suited for steel control and acceptance (Ref. 7, Conclusions). Thus, any contribution to a better understanding of the meaning of the ammonium thiocyanate test, and especially of the influence of temperature and stress level on the times to rupture of various steels, should be welcomed both from the scientific point of view and for practical and economic reasons.

The authors, Elices et al. have proposed a model (10) for hydrogen induced cracking of prestressing steels, assuming that the controlling step is hydrogen diffusion towards regions of highest hydrostatic stresses. The model has been checked experimentally, by testing samples precracked by fatigue and comparing times to rupture predicted by the model with the experimental values.

The extension of the model to smooth samples, in the actual conditions of the FIP test proposal needed a previous explanation of the high scatter of the experimental results as well as the observed differences in times to rupture when testing smooth samples of steels whose K_{IHE} is however nearly coincident, see Elices et al. (11). Recently, Elices et al. (12) have shown that surface residual stresses can be the main cause of those experimental observations.

Now, the model can be extended to predict the behaviour of smooth samples tested in tension at constant load in a hydrogen embrittlement environment, such as the ammonium thiocyanate solution, by using the residual stresses together with the applied stress to initiate a crack at the surface.

THEORETICAL MODEL

The model is based on three basic assumptions:

a/ The mechanism controlling the time required to initiate a crack at the surface is the diffusion of hydrogen towards the region of maximum hydrostatic stress.

b/ The initiation time, i.e. the time required to initiate a crack, is the time required to produce a critical hydrogen concentration along a distance x_c; the "damaged zone", i.e. the region where the hydrogen concentration is higher than the critical one increases with time, and it will be assumed that a crack will be created when the damaged zone size is x_c, so that $K_I = 0.94 \sqrt{\pi x_c} = K_{IHE}$ where σ is the applied stress; K_I is the stress intensity factor when a crack of size x_c is created and K_{IHE} is the threshold stress intensity factor for the environment considered.

c/ The propagation time, i.e. the time required to propagate the crack from the initial size x_c up to a critical value to produce the final rupture of the sample will be neglected. That is, it is assumed that the initiation time coincides with the time to rupture.

The last assumption has been proved experimentally by a threefold procedure: by testing in tension degasified samples discharged after 90% of the expected time to rupture no changes in the tensile strength were observed by Piñero (13), acoustic emission measurements in the ammonium thiocyanate test show no signals until few minutes before the final fracture of the samples (8); finally direct measurements of the compliance of the sample show no variations along the test until few minutes before the final fracture (13).

The hydrogen concentration under equilibrium conditions $C(x,\infty)$ at any point x is given by Gerberich and Chen (14):

$$C(x,\infty) = C_0 \exp \{\sigma_H V_H/RT\} \tag{1}$$

where C_0 is the equilibrium hydrogen concentration provided by the ammonium thiocyanate solution in the absence of stress, V_H is the partial molar volume of hydrogen, R is the gas constant, T the absolute temperature and σ_H the hydrostatic component of the stress field. In the case considered, it will be assumed that the stress field is a constant tension σ given by

$$\sigma = \sigma_{ap} + \sigma_{res} \tag{2}$$

if $\sigma_{ap} + \sigma_{res} < \sigma_y$

where σ_{ap} is the applied stress, σ_{res} is the average surface residual stress and σ_y is the yield stress.

For $\sigma_{ap} + \sigma_{res} > \sigma_y$, it will be assumed that

$$\sigma = \sigma_y \tag{2a}$$

or

$$\sigma = \sigma_{ap} \tag{2b}$$

whatever will be greater.

Hence

$$\sigma_H = \frac{1}{3} \sigma \tag{3}$$

Under transient conditions the hydrogen concentration at time t for a plane infinite source of hydrogen diffusing into a plane infinite specimen is given by Doig and Jones (15):

$$C(x,t) = C(x,\infty) \{1 - \operatorname{erf} x/2(Dt)^{1/2}\} \tag{4}$$

where D is the diffusion coefficient of hydrogen in the steel and erfz is the error function given by the integral

$$\mathrm{erf}\,z = 2\pi^{-1/2} \int_0^z \exp(-y^2)\,dy$$

For the geometry under consideration, a cylindrical wire in tension, the use of the exact solution instead of eq. 4 would not affect the results significantly for x values small compared with the diameter of the wire and it would require a much elaborated calculations. Therefore, eq. 4 will be used throughout the model since the degree of approximation involved is enough.

From eqs. 1 and 4 the hydrogen concentration is

$$C(x,t) = C_0 \exp\{\sigma_H V_H/RT\}\{1 - \mathrm{erf}\ x/2(Dt)^{1/2}\} \qquad (5)$$

According to the basic assumptions of the model, the time to fracture t_R, coincident with the initiation time, is the time required to exceed a critical hydrogen concentration along a distance x_c given by

$$K_{IHE} = 0.94\ \sigma\ \sqrt{\pi x_c} \qquad (6)$$

where σ is the stress given by eq. 2 and K_{IHE} is the threshold stress intensity factor for the environment considered.

Eq. 6 has been derived recently by Elices (16) for the stress intensity factor in a round bar of diameter D with a semielliptical crack of depth x_c subjected to a tension σ, if $x_c/D < 0.15$.

Thus, the time to rupture t_R can be obtained from the following equation:

$$C_C = C_0 \exp\{\sigma V_H/3RT\}\{1 - \mathrm{erf}\ x_c/2(Dt_R)^{1/2}\} \qquad (7)$$

where x_c is given by eq. 6.

If initial and critical concentration values C_0 and C_c were known, eq. 7 would give t_R for each stress σ. Although C_0 may be measured, C_c must be assumed. The method followed in this research has been, thus, to derive C_c/C_0 values from experimental t_R measurements and, after checking the constancy of the C_c/C_0 values, use a mean value of C_c/C_0 to achieve the curve σ vs. t_R.

EXPERIMENTS

The model has been checked through the ammonium thiocyanate test proposed by the FIP. Testing procedures are described elsewhere (8). In this research program tests have been carried out at different stress levels and temperatures of 35 and 50°C. The potential of the wire with respect to the standard calomel electrode is fairly constant about -760mV and the pH of the solution is about 3.9.

Four commercial prestressing steel wires have been tested. Their chemical composition are shown in table 1 and their mechanical properties are summarized in table 2. All them are eutectoid cold drawn steels, produced by patenting 12 mm. diameter rods in a molten lead bath to produce fine pearlite, after which the rods were cold drawn to achieve 7 mm. diameter wires. Finally, the drawn wires were stress-relieved at 425°C for a few seconds and cooling in water (steels A, B and D) or in oil (steel C).

TABLE 1.- Chemical Compositions

Steel	%C	%Mn	%Si	%P	%S	%N
A	0.82	0.60	0.18	0.010	0.024	0.007
B,C,D	0.81	0.60	0.27	0.014	0.029	0.011

TABLE 2.- Mechanical Properties

Steel	0.1% Proof Stress,MPa	0.2% Proof Stress,MPa	U.T.S. MPa	Elong. under max. load (%)	Reduc. of Area (%)	Fracture Tough K_c^* MPa m1/2
A	1421	1455	1700	6.0	30	98
B	1436	1460	1581	5.5	29,5	98
C	1387	1410	1553	5.6	27,2	98
D	1433	1460	1682	5.5	27	98

K_c^* is an average critical value from compliance measurements.

Specimens used for testing were smooth round wires with their surface in the as-delivered condition. Samples were degreased with 3 chloro-ethylene and loaded at constant load by means of levers. If no fracture ocurred after some time, the specimen was unloaded and that time recorded, in order to obtain a threshold stress value. This was never before 600 hours. For each stress level, at least four tests were performed, and in many cases eight tests were carried out.

The results are shown in Figs. 1, 2, 3 and 4 for the four steels tested and the two temperatures used. For each stress level the average time to rupture and the interval corresponding to the standard deviation are plotted, showing the high scatter obtained with this kind of tests.

On the other hand, surface residual stresses have been also measured. The method used, by X-ray diffraction, as well as the experimental results have been previously published (12). For the steel considered in this research, the measurements showed tensile residual stresses between 50 and 90 MPa. Since the crack will be created at the point where the residual stress is maximum the value to be used in the calculation will be varied between 40 and 200 MPa. For checking of the model, the following values of the constants and parameters involved will be used:

$V_H = 2\ cm^3/mol$, according to the value quoted for steels by Hirth (17).

$D = 10^{-11}\ m^2/s$ at 50°C and $D = 4.99 \cdot 10^{-12}\ m^2/s$ at 35°C, values used previously by the authors (10) and by Doig and Jones (15), when an activation energy for hydrogen diffusion of 9000 cal/mol is used (13).

$K_{IHE} = 0.27\ K_{IC}$, as was previously shown by the authors for all commercial prestressing steels in the ammonium thiocyanate solution (11).

RESULTS AND DISCUSSION

Figures 1, 2, 3 and 4 show the theoretical curves σ_{ap} vs. t_R predicted by the model for the four steels tested and the two temperatures used. The C_c/C_0 values used in the obtention of the curves are average values for all steels tested: C_c/C_0 = = 1.18 for 50°C and $C_c/C_0 = 1.24$ for 35°C. This means a ratio C_0 at 50°C/C_0 at 35°C of 1.05.

As can be seen in the figures, a good agreement between the experimental results and the theoretical curves has been achieved, showing the validity of the model to predict the hydrogen embrittlement behaviour of prestressing steel wires. Moreover, the model predicts the threshold stresses (applied plus residual) for no rupture; from eq. 7 and the values of C_c/C_0 quoted, the threshold stresses are 826 MPa for 35°C and 666 MPa for 50°C.

The high scatter observed in the experimental results obtained with the ammonium thiocyanate test can also be explained by the model. As can be seen in the figures, changing the residual stress value used in the calculations within the interval expected by the X-ray measurements, different theoretical curves are obtained covering the majority of the empirical results.

Finally, assuming an exponential relationship of C_0 on temperature:

$$C_0 = A\ e^{-B/T}$$

where A and B are constants, and knowing that

$$\frac{C_0 50}{C_0 35} = 1.05$$

it is quite easy to derive this ratio for room temperature:

$$\frac{C_0 50}{C_0 20} = 1.11$$

and thus to obtain the C_c/C_0 value for 20°C, which is 1.31 and

the corresponding threshold stress, which is 988 MPa. In fact a sample stressed at that level and kept at room temperature has not ruptured after 600 hours and the test is still running.

CONCLUSIONS

A theoretical model of hydrogen embrittlement has been developed. The model is based on the assumption that the mechanism controlling the time to rupture is the diffusion of hydrogen towards the region of maximum hydrostatic stress.

The model has been checked through an extensive experimental program, showing the validity of the model to explain the observed times to rupture as a function of the applied stress as well as the influence of surface residual stresses.

The model gives an explanation of the scatter of test results, considering the expected variations of residual stresses along the surface of the specimen.

Finally, the model predicts the threshold stresses for no rupture and the influence of the test temperature on the experimental results.

In a next future, the research may be directed to measuring the equilibrium hydrogen concentration C_0 for different temperatures and environments. In such a way the constancy of the critical hydrogen concentration C_c could be checked directly and times to rupture in a realistic environment could be predicted.

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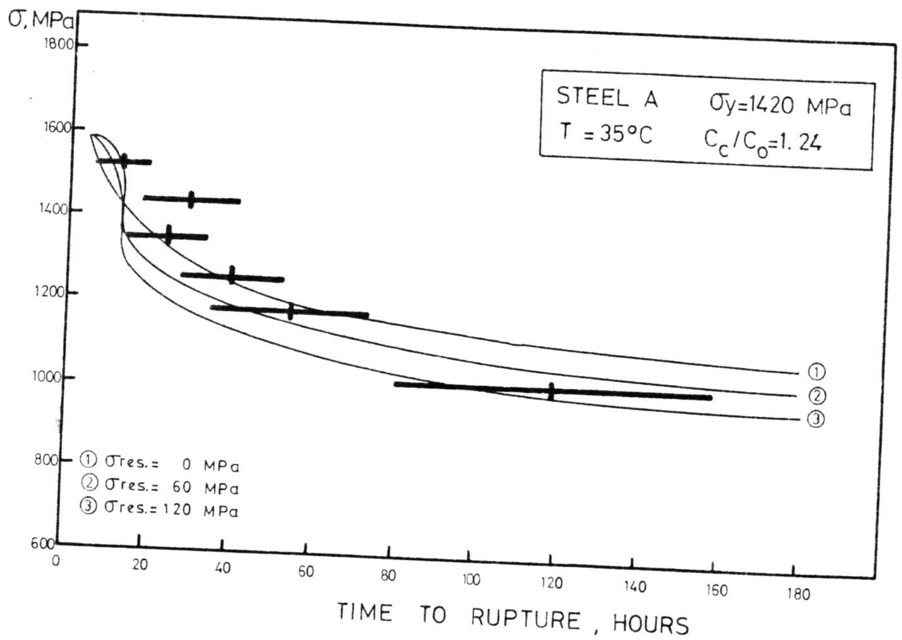

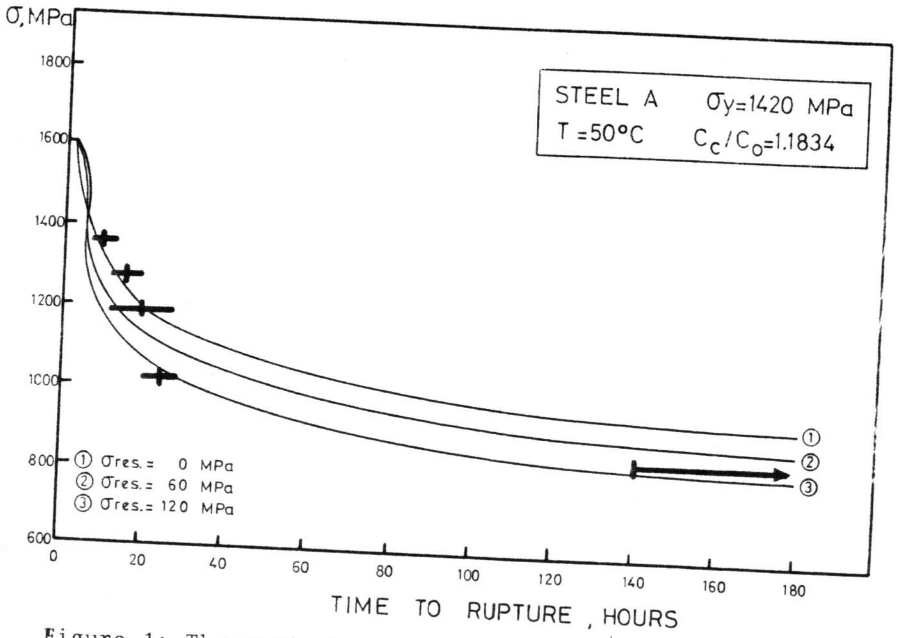

Figure 1: Theoretical curves and experimental results of steel A.

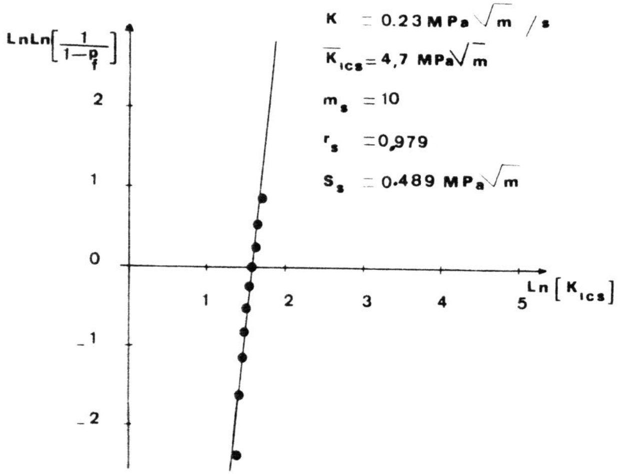

Figure 4.a : Weibull diagram for static fracture toughness tests on ceramics

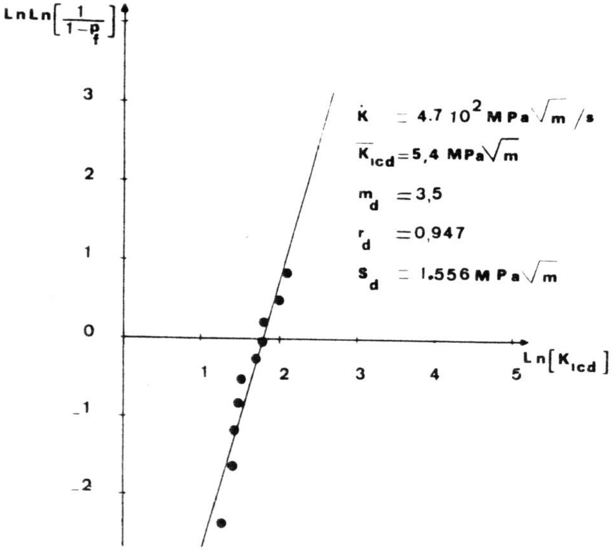

Figure 4.b : Weibull diagram for dynamic fracture toughness tests on ceramics

Photo N°1 : Fractography of static specimen

Photo N°2 : Fractography of dynamic specimen