SMALL PUNCH TEST METHODOLOGIES FOR THE ANALYSIS OF THE HYDROGEN EMBRITTLEMENT OF STRUCTURAL STEELS

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ABSTRACT

In the present study, a new small punch test (SPT) methodology has been used to analyse the effect of hydrogen embrittlement on the tensile properties of three different grades of CrMoV steel: the base metal (CrMoV-1), weld metal (CrMoV-2) and this same weld metal subjected to an intermediate heat treatment (CrMoV-3). SPT results were compared with those obtained in standard tensile tests carried out in a hydrogen environment. Moreover, a new SPT methodology was used to analyse the environmental effects on a CrNiMn steel under cathodic protection and cathodic charge.

Results obtained shows the usefulness of the SPT to estimate the grade of deterioration induced by hydrogen embrittlement, especially when a lack of testing material makes impossible the test of standard specimens.

KEYWORDS: Small Punch Test (SPT), Hydrogen Embrittlement (HE), Stress Corrosion Cracking (SCC).

1. INTRODUCTION

The effect of hydrogen is especially important in high-strength steels exposed to aqueous environments under cathodic protection (such as off-shore platforms) or those in which H_2S is present (as in gas transport pipelines). Both phenomena, Hydrogen Embrittlement (HE) and Stress Corrosion Cracking (SCC), are rather similar, resulting in brittle failures in the presence of an aggressive environment under maintained stress. Both phenomena are dependent on the loading rate, even disappearing for higher ones, but at very slow strain rates hydrogen has a significant embrittling effect. Different methodologies for testing HE have been investigated since the publication of the "ASTOH Selected Technical Papers" in 1947 [2].

There are particular situations where standards such as [3,4] can't be followed to perform characterizations on in-service components, mostly due to the impossibility to machine specimens fitting the required dimensions, [3]. One of those situations is usually present in welded joints of any type of structure. In other cases, it can be a harsh task to test virgin material due to the inherent operational difficulties and uncertainties characteristic of standard SCC and HE tests.

To find a solution to these types of scenarios, miniature tests were developed, the Small Punch Test (SPT) being the most notable. Although a reference standard that includes the tensile and fracture estimations from SPT is currently still not available, a European Code of Practice was developed in 2006 [5]. SPT allows to estimate parameters as the yield stress, ultimate tensile strength and even fracture toughness of metallic materials with high reliability [6]. Throughout the last years some authors have proved the validity of the SPT to be used in HE and SCC characterizations [7-9], having the advantage of being faster, easier and safer to perform than the standard tests.

This paper presents a review of the characterization of HE on a high strength steel by SPT using two approaches, which will be subsequently compared to conventional mechanic tests.

2. MATERIALS

Three CrMoV steels were used in this study: the base metal (CrMoV-1), with a high resistance to hydrogen embrittlement [9], a high strength weld metal (CrMoV-2), which is highly susceptible to this phenomenon [9], and this same weld metal after being subjected to an intermediate heat treatment (CrMoV-3). Figure 1a and Figure 1b shows the microstructure of CrMoV-1 (tempered martensite in Figure 1a) and CrMoV-2 (lath martensite in Figure 1b), for CrMoV-3 (CrMoV-2 after heat treatment) microstructure is not presented because the treatment is not strong enough to modify it (remaining the same as in Figure 1-b). A quenched and tempered (from ferritic base) CrNiMn high-strength R5 grade steel was also analyzed, having the tempered martensite microstructure showed in Figure 1c, Table 1 shows the mechanical properties of this steel.

3. EXPERIMENTAL METHODOLOGY

3.1. Tensile properties determination

The effect of hydrogen embrittlement on the tensile properties degradation of CrMoV steels was analyzed by means of a custom designed SPT device, which is depicted in Figure 2a and is thoroughly described in [9]. This device allows to test the specimens inside a hydrogen environment. A 1N solution of H_2SO_4 in distilled water with 10 drops of CS_2 and 10 mg of As_2SO_3 per litre was employed as electrolyte. The solution of As_2O_3 was prepared using Pressouyre's method [2]. Platinum was used as anode , and the reference electrode employed contained an Ag/AgCl solution. A current density of 20 mA/cm^2 was set at the beginning of the test. All the SPT specimens (10x10x0.5 mm) were mechanically polished (up to 1200 emery paper) and cleaned before testing. The tests were carried out at a cross-head speed of 0.2 mm/min.

In order to have information about the tensile properties of standard specimens tested in a hydrogen environment, a sample and device sketched in Figure 2b was designed. The same conditions as described for the SPT were employed to perform these tensile tests. Plane specimens, with a 0.5 mm thickness were employed, in order to achieve similar hydrogen concentrations as those achieved in the small punch specimens.

Expressions (1)-(3) were used for estimating the tensile properties by means of SPT, in both air and hydrogen environment. P_y was calculated as the intersection between the SPT curve and a straight line running parallel to the initial elastic slope with an offset of t/10, where t is the initial specimen thickness [9,10]. P_m is the maximum test load and d_m the displacement at maximum load.

$$\sigma_{ys} = \alpha \cdot \frac{P_{y\_t/10}}{t^2} \quad (1) \qquad\qquad \sigma_{ut} = \beta_1 \cdot \frac{P_m}{t^2} \quad (2)$$

$$\sigma_{ut} = \beta_2 \cdot \frac{P_m}{(d_m \cdot t)} \quad (3)$$

3.2. Fracture mechanics

For conventional fracture mechanics tests, an analysis was carried out obtaining the stress intensity factor, K_{EAC}, employing the methodology based on the GE-EPRI procedure [12].

For small punch tests, Lacalle's methodology [6] was employed in order to obtain the fracture toughness of the embrittled material, J_{Ith}. It consists on the determination of the CTOD value, δ_{SPi}, that marks the initiation by means of SPT tests on notched specimens, from which the value of J_{IC} is determined and transformed into the crack initiation intensity factor, K_{Jth}. After that, as stated in [8], in order to compare this value with the results of K_{EAC} obtained from conventional tests in 25 mm CT specimens, K_{Jth} was expressed into its equivalent factor obtained from 25 mm samples, K_{Jth25}, following the expression (6) [13]. Due to the lack of literature to obtain equivalent stress intensity factors in function of the sample thickness the expression (6), even if [13] had just been evaluated for ferritic steels up to 825Mpa of yield strength, is considered accurate enough for the present high-strength steel that had a ferritic base before being heat treated.

$$J_{Ic} = \frac{\delta_{SPi} \cdot \sigma_{ys}}{d_n} \quad (4)$$

Being d_n an adimensional factor [6].

Being δ_{SPi} the CTOD value that marks the crack initiaion on a SPT notched sample [6].

$$K_{Jth} = \sqrt{J_{Ic} \cdot E} \quad (5)$$

Being E the Young Modulus.

$$K_{Jth25}\left(MPa \cdot m^{1/2}\right) = K_{min} + \left(K_{Jth} - K_{min}\right) \cdot \left(\frac{0.5mm}{25mm}\right)^{1/4} \quad (6)$$

Being $K_{min} = 20\ MPa \cdot m^{1/2}$

In order to apply Lacalle's model [6], yield stress is necessary. It doesn't differ much from the value of the as received material [8], but accurate values can be estimated using the expression (7) also proposed in [6], or the previously presented expression (1):

$$\sigma_{ys}(MPa) = 5.75 \cdot P_y\ (N) \quad (7)$$

Being P_y the first inflexion point of the Load - Punch displacement record [6].

The analysis was carried out in two different environmental conditions: cathodic protection and cathodic charge. For each one, two different levels of aggressiveness were studied. Cathodic protection, is usually applied in the accessible parts of the platforms or the off-shore structures. The second one, known as cathodic charge or anodic polarization, reproduces local aggressive environments impossible to avoid, an sometimes to predict, that can seriously affect the structural integrity of the component exposed. Figure 3 shows an schema of the two main methods used to study Hydrogen influence in steels, used in this work [1].

The technique of cathodic protection is used to avoid corrosion phenomena for marine water environments. Basically, it involves the use of a sacrificial anode of aluminum (more active than steel), which in presence of seawater is connected to the steel structure, which is the cathode that will be protected from corrosion [1] due to the imposition of a fixed potential, which will maintain the stability of the process. For cathodic protection the solution was consisting of marine water simulated having a 3.5% in weight dissolution of NaCl in distilled H_2O. Aluminum was used as an anode, and the reference electrode employed contained an Ag/AgCl solution. The pH was controlled at the range 5.5 – 5.7 during the whole tests, at room temperature. Two levels of cathodic protection (aggressiveness) were analyzed: -950 mV and -1050 mV of fixed potential.

The technique of cathodic charge is used against the phenomena that occurs in more aggressive environments (hydrogen transport infrastructures), or to reproduce local situations where a huge amount of hydrogen is present. It consists in the interconnection, via an acid electrolyte, of a noble material (platinum in this case) and the steel, which will passivate and receive protection due to the fixed current interposed [1]. For cathodic charge, environmental conditions were simulated by using the same electrolyte described in section 3.1. A platinum grid was used as anode , and the reference electrode employed contained an Ag/AgCl solution. The pH was controlled at the range 0,65 - 0,80 at room temperature 20ºC - 25ºC. Two levels of charge (aggressiveness) were analyzed, $1mA/cm^2$ and $5mA/cm^2$.

In each case, two different loading rates were employed in conventional fracture mechanics tests, $6 \cdot 10^{-9}$ m/s (the lowest rate of the machine employed) and $6 \cdot 10^{-8}$ m/s (10 times higher in order to study the rate effect). For SPT tests specimens were embrittled during 2 hours, and then tested under two different approaches in displacement control. The first one is a simplified method, consisting of extracting the samples and testing them in air under two different standard load rates [5], 0,01mm/s (standard rate recommended by [5]) and 0,002mm/s (5 times lower in order to study the rate effect). The second approach, more accurate in terms of H_2 steady state and low rate to allow its damage to the crack tip, consisted of testing the samples inside the hydrogen environment at a low punch displacement rate of $5 \cdot 10^{-5}$ mm/s.

4. RESULTS AND DISCUSSION

4.1. Tensile properties

Figure 4 shows a comparison between the true stress – true strain curves obtained in both air and hydrogen, while Table 2 shows the obtained results. All the steels exhibited a decrease in the mechanical properties due to hydrogen embrittlement. In the case of both CrMoV-1 and CrMoV-3, no significant differences were found in the yield strength and ultimate tensile strength. However, a great decrease in ductility (elongation at failure) was observed when testing in hydrogen, especially in the case of CrMoV-3, which broke just above the yield strength. CrMoV-2 was highly affected by hydrogen, and all the specimens failed at a stress level lower than the yield strength (60% approx.).

While in the case of tensile tests carried out in air, all the specimens exhibited ductile behavior, with a 45º crack path, as depicted in Figure 5a, a competition of ductile and brittle fracture mechanisms was observed in the tests carried out in hydrogen. Figure 5b shows the failure pattern of CrMoV-2, the most embrittled material, which exhibited a horizontal crack, where wide zones of cleavage were observed.

Figure 6 shows the SPT curves obtained in both air and hydrogen for the CrMoV steels. Some tests were arrested at displacement levels close to P_y, in order to perform fractographic observations by SEM. Table 3 shows the obtained SPT parameters.

The same trend observed in conventional tensile tests was observed in the SPT ones: all steels exhibited hydrogen embrittlement, in terms of loss of ductility. In the case of CrMoV-1, the obtained SPT curve was the characteristic of a ductile steel. Thus, its analysis should be in terms of P_y/t^2 and $P_m/(t\ d_m)$ [10]. In this sense, results were in total agreement with those obtained in the standard tests, since no significant differences were found between the SPT parameters related with σ_{ys} and σ_{ut}, and only the parameter related with ductility, d_m, experimented a clear decrease.

It should be noted that the behavior of CrMoV-2 and CrMoV-3, tested in hydrogen, was not conventional. In this two cases, the specimen was observed to be totally cracked at a displacement level beyond P_y, and very close to it. In fact, the flat shape of the curve from this point on is indicating no bearing resistance of the specimen, but only friction between the testing components and a fully cracked specimen [14]. Figure 7 shows a SEM image of a CrMoV-3 specimen after a test interrupted at 500 N, corroborating this observation. Thus analysis of these steels should be performed only in terms of P_y, as the material broke under elastic behavior. This fact is in agreement with the results obtained in the standard tensile tests with CrMoV-2 and CrMoV-3. Nevertheless, a disagreement was observed in the case of CrMoV-2: while the yield strength decreases approximately by 40% when uniaxial tensile tests were performed in hydrogen, no significant differences were found between P_y/t^2 in air and hydrogen. This fact might be explained in the different test conditions. In the tensile test, the specimen contour is totally submerged in hydrogen, and more aggressive conditions are developed. Moreover, it was observed in a previous work [9] that CrMoV-2 is very sensitive to hydrogen embrittlement, due to its microstructure (virgin lath martensite), and a less aggressive environment should be used for the analysis of this steel (i.e. reducing current density).

Figure 8a shows the fractography of a CrMoV-1 SPT specimen tested in air. This fracture appearance, with a unique circumferential crack, was observed in all steels tested in air, and it is characteristic of ductile steels. Figure 8b shows the microvoids observed on the broken surface. When testing in hydrogen, the behavior changed totally in all steels, and brittle fracture was always observed, indicated by the presence of radial cracks. In the case of CrMoV-1, certain ductility was observed, and a circumferential crack was accompanied by several radial cracks, as shown in Figure 8c. Cleavage surfaces were observed on these cracks (Figure 8d). Similar observations were made in CrMoV-3. In the case of CrMoV-2, the most hydrogen-affected steel, only radial cracks were developed, as shown in Figure 9a. As can be seen in Figures 8d and 9b, transgranular fractures were always observed in the specimens tested in hydrogen.

4.2. Fracture mechanics

Figure 10 and the upper part of Table 4 show the results of the fracture mechanics tests performed on CT specimens. In the less aggressive cathodic protection cases (-950mV), the maximum load of the test machine was reached before showing any noticeable crack propagation, so it was impossible to predict the K_{EAC} value, giving as results the lower bound corresponding to the K_I values at that maximum load. From previous results, as attested in the bibliography [11,15], it could be observed that the more aggressive the test conditions are lower is the value of K_{EAC}. As a consequence of this, it can be observed that if a cathodic protection or cathodic charge scenario is fixed (a dissolution and a solicitation rate are fixed), if the applied intensity (or potential) is increased the value of K_{EAC} will decrease. On the other hand, for a fixed dissolution and intensity (or potential), if the solicitation rate is decreased the value of K_{EAC} will decrease.

Figure 11 presents the curves registered from the SPT tests carried out on notched specimens in order to determine the fracture properties of the material after hydrogen absorption testing them in air. Tests were carried out at two different loading rates, the regular one of 0.01mm/s recommended by [5] and another one 5 times slower of 0.002mm/s. In the lower part of Table 4 the numerical results of the previous tests are summarized, obtaining the fracture parameter K_{Jth25} (in order to be compared to the 25mm think C.T. specimens results).Regarding the experimental curves there can be found typologies from ductile, such as those from -950mV cathodic protection environments, to brittle ones, such as those from 5mA/cm^2 cathodic charge environments. It is easy to distinguish how the curve's shape becomes more typical from a brittle material as the environment becomes more aggressive, this fact means that as the hydrogen content must be higher (as it will be checked later by H_2 contents measurement tests). It is also observed that the more aggressive the environment is the lower the values of the load (P) and punch displacement (d) of the maximums of the curve are. This fact is also an evident marker of a higher Hydrogen content (checked by H_2 contents measurement tests) and a lower value of the fracture parameter, which is in accordance with experimental standard tests results [8,15].

Figure 12 shows fracture SEM images of the notched specimens pre-embrittled and subsequently tested in air. Two samples are shown; one belongs to a specimen tested in the most adverse environment (acid solution at 5mA/Cm^2 at 0.002mm/s), the other becomes from a test in the less aggressive environment (saline solution at -950mV at 0.01mm/s). It can be observed how the sample corresponding to the most adverse environment, whose curves have a typical brittle shape, also have a brittle fracture showing short crack tip opening (indicating short CTOD and toughness). On the other hand, the sample belonging to the least aggressive environment, whose curves have a typical ductile shape, show a ductile fracture with an important crack tip opening (indicating higher CTOD values and toughness).

Figure 13 presents the curves registered from the SPT tests carried out on notched specimens in order to determine the fracture properties of the material after hydrogen absorption testing them in the same environment. Tests were carried out at the loading rate of $5 \cdot 10^{-5}$mm/s recommended by [7]. In the lower part of Table 4 the numerical results of the previous tests are summarized, obtaining the fracture parameter K_{Jth25}.Regarding the experimental curves all typologies presented have a brittle aspect, but those from the most aggressive environment of 5mA/cm^2 cathodic charge have a more brittle shape than those others from the less aggressive one of -950mV cathodic protection. Also in this case, the more aggressive the environment is the lower the values of the load (P) and punch displacement (d) of the maximums of the curve are, meaning a higher Hydrogen content and a lower value of the fracture parameter [8,15]. In both cases, comparing to its homologous in Figure 11, curves shapes are more brittle, due to the lower rate and the continuous H_2 diffusion to the crack tip that permits the Hydrogen damage capacity to produce its complete effect.

Figure 14 shows fracture SEM images of the notched specimens embrittled and tested in the aggressive environment at a very low rate of $5 \cdot 10^{-5}$mm/s [7]. Two brittle samples are shown; one belongs to a specimen tested in the most adverse environment (acid solution at 5mA/Cm2), the other becomes from a test in the less aggressive environment (saline solution at -950mV). It can be observed how the sample corresponding to the most adverse environment, whose have the most brittle shape, also have an extremely brittle fracture showing a very slightly crack tip opening. On the other hand, the sample belonging to the less aggressive environment, shows also brittle fracture with a higher crack tip opening than the previous ones. In both cases, comparing to its homologous in Figure 12, fractures are more brittle, due to the lower rate and the continuous H_2 diffusion to the crack tip that permits the Hydrogen damage capacity to produce its complete effect.

In Figure 15 is shown a comparison between the values of K_{EAC} obtained by fracture mechanics tests and the two approaches of the fracture parameter by SPT test previously exposed. Regarding the comparison of two different loading rates for the same environment lower values of K_{Jth25} are obtained for lower punch displacements rates, and also fixing a punch rate lower values of K_{Jth25} are obtained for more aggressive environments. These facts, added to the different shapes of the curves, mean that the Small Punch test performed in adverse conditions can show the effect of the punch loading rate on the specimen.

It can be observed in Figure 16 that both techniques can predict embrittlement using SPT, giving correct trends when compared to fracture mechanics tests . In the trends presented in Figure 16, the values corresponding to the tests at -950mV of cathodic protection have been dashed for a better accuracy, due to the fact that the results of KI_{EAC} from standard fracture mechanic tests (see Figure 10) could just be calculated as a lower bound at the point that the machine reached its maximum load capacity. The previous results show that the SPT tests performed in an adverse shows qualitatively correct results in aggressive environment characterizations.

Hydrogen determination tests were also performed on the CrNiMn steel. The obtained results are presented in Figure 17. Hydrogen concentrations were measured just after the embrittlement, after 5 minutes exposition and after 10 minutes exposition (times necessary to perform tests under punch displacement rates of 0.01mm/s and 0.002mm/s). As a comparison tool, the intrinsic hydrogen content of CrNiMn R5 grade steel is also represented by a horizontal line in the same graph. It can be observed that the more aggressive the environmental conditions are, the higher is the Hydrogen concentration. It is also noticeable that the highest hydrogen concentration rate of decrease takes place during the first minutes of the sample being exposed to air. The previous H_2 content results are in agreement with the experimental SPT curves, when the curve's shape becomes more typical of a brittle material the hydrogen content gets increased.

The curves in this work have been from ductile curves, such as those from -950mV cathodic protection environments holding hydrogen contents of approximately 1ppm to 2ppm, to fragile curves as those from 5mA/Cm2 cathodic charge environments showing hydrogen contents of approximately 4ppm to 5,5ppm. It is also observed that once the hydrogen content of the material reaches a high value between 3ppm and 5ppm (as occurs in 5mA/Cm2 and 1mA/Cm2 cathodic charge environments), the hydrogen trapped in the microstructure is sufficient to produce cleavages at the crack tip without the need for these to be exposed to a continuous source of hydrogen, thus leading to crack propagation under hydrogen embrittlement.

5. SUMMARY AND CONCLUSIONS

In this paper, the small punch test has been validated as a method for characterizing materials under stress corrosion cracking and hydrogen embrittlement scenarios, and some basic guidelines have also been established to perform this characterization.

First, it was demonstrated that SPT can be a very useful tool to estimate the deterioration of structural steels due to hydrogen embrittlement, in terms of tensile properties. Nevertheless, the aggressiveness of the test environment has to be properly selected, a more profound study of this issue is still necessary in order to obtain universal relationships between results obtained in SPT and in standard tensile tests.

Moreover, regarding fracture mechanics, by comparing the SPT in different environments and different loading rates, it was proved that the test is able to show the effect of the environment on the material, as well as the effect of punch displacement rate variations. By comparing the SPT with standard crack propagation tests, it was proved that the SPT gives qualitatively correct results in aggressive environment characterizations, although tests performed in air after being hydrogen pre-charged are not able to give accurate results. This fact might be explained by differences at the crack tip in terms of strain rate and hydrogen diffusion and accumulation.

The issue to be solved in a future work concerns the displacement rate that should be employed in SPT tests in order to accurately reproduce the environmental conditions taking place during a conventional standard test. Important attention should be played to the circumstances involving what is taking place at the crack tip in terms of deformation rate and hydrogen diffusion. It seems that the whole test must be performed in similar conditions to those present in conventional crack propagation tests in order to obtain the good results. A quasi-static displacement rate should be used, while the specimen remains submerged into the hydrogen environment, which will definitely reproduce the same micromechanisms that take place at the crack tip during conventional tests.

Another type of approach, such as an energetic one, could also be studied in order to find more accurate estimations [16]. In [16] it is analyzed how load-punch displacement recordings from embrittled and non-embrittled SPT notched specimens are coincident up to a point, where a certain level of energy is reached, showing the embrittled one a decrease after it. This fact justifies the environmental effect on the crack initiation when that certain level of energy is reached, meaning that the embrittlement damage initiates due to the environmental effect in that point.

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