STUDY OF THE ENERGY FOR EMBRITTLEMENT DAMAGE INITIATION BY SPT MEANS. ESTIMATION OF K_{EAC} IN AGRESSIVE ENVIRONMENTS AND RATE CONSIDERATIONS.

B. Arroyo[1*], J.A. Álvarez[1], R. Lacalle[1]

[1]LADICIM, Depto. de Ing. del Terreno y los Materiales (Universidad de Cantabria)
Avda. de los Castros, 44, 39005 Santander (Cantabria)

[*] E-mail: arroybo@unican.es

ABSTRACT

There is large experience on the determination of crack propagation initiation parameters in SCC and HE scenarios by fracture mechanics tests. Although there are satisfying experiences, the estimation of a parameter in those situations by Small Punch means is in continuous research.

In this work a new approximation for the parameter K_{EAC} is presented. It is based on the energy for embrittlement damage initiation on notched Small Punch specimens in SCC and/or EH conditions. Likewise another key aspect is analyzed, as it is the punch rate for SPT in aggressive environments, aiming not to have an influence on propagation mechanisms. Finally, bases for future research in this field are established.

KEYWORDS: Small Punch Test, SCC y HE, Solicitation rate

1. INTRODUCTION

A critical aspect concerning high strength steels working in petroleum derivates installations is its resistance facing Stress Corrosion Cracking (SCC) and Hydrogen Embrittlement (HE) phenomena, that produces degradation in its mechanical properties [1].

This work is about evaluating the behavior facing HE of high strength steels by means of the Small Punch Test. For this purpose, new methodology based on the energy for embrittlement damage initiation on notched Small Punch specimens in SCC and/or EH conditions is presented.

This work is focused on two main objectives: to present a new approximation for the parameter K_{EAC}, and to analyze the punch rate for SPT in aggressive environments, setting the bases for future research.

2. TESTS IN EMBRITTLEMENT SCENARIOS

2.1. HE classic testing and its disadvantages

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 typical from H_2S presence (as in gas transport pipelines). Both phenomena, HE and SCC, are similar, resulting in brittle failures in the presence of an aggressive environment and maintained stress. Meanwhile cathodic polarization issues HE occurrence decreases SCC mechanisms. Both phenomena are dependent on the crack deformation rate, even disappearing for higher ones, but at very slow strain rates Hydrogen keeps an embrittling effect. Different methodologies for testing HE have been investigated since the publication of the "ASTOH Selected Technical Papers" in 1947 [2].

Tests based on fracture mechanics in order to determine the behavior facing SCC and HE have been employed for the last 40 years [3,4], the most used are the so-called slow rate tests [5,6]. Fracture mechanics tests based on HE are performed with the aim of determining K_{Iscc} and crack growth rate data. The specimens contain fatigue pre-crack, K_{Iscc} is determined by means of crack initiation tests under constant load, or from crack arrest test on constant deflected specimens. There are different standards that supply procedures to be followed in order to evaluate the behavior of steels facing HE, ASTM E-1681-95 [7], ISO 7395-6 [4]. Other type of tests are the Slow Strain Rate (SSRT) [8], based on the use of tensile un-notched specimens, so that its capacity to evaluate K_{Iscc} is quite comparative, resulting in the parameter threshold stress, σ_{scc}.

The condition of threshold of crack propagation initiation, as well as the propagation itself, occurs due to a series of local crack processes that take place in the plastic zone that encircles the crack tip [3,9]. There is a large variety of models that estimate the threshold of crack growing K_{Iscc} and its propagation rate da/dt based on a local plastic zone analysis.

It's well known the influence of the test rate on the previously indicated parameters. One of the aspects that pushed large labors and discussions was the choice of the suitable displacement rate to determine accurately KIscc and da/dt. The recommendations presented by various research groups during the last decades have been collected on the standard ISO 7539-9 [4]. It establishes requirements concerning specimen size and solicitation rate, but does not solve definitively the procedure to follow in numerous applications.

The application of the Linear Elastic Fracture Mechanics in SCC scenarios using K_I as the main parameter is based on the assumption of limited plasticity conditions, basically plane strain conditions are required on the crack propagation plane. In the case of high strength steels facing HE there is a great disagreement between the specimen size required for the tests and the thickness of the real component being studied, often ISO 7539 forces it to employ specimens of higher thickness than the component under study. In this condition an elastic-plastic fracture mechanics study should be done [3].

There are particular situations where standards such as [4,7] can't be followed to perform characterizations on in-service components, mostly due to the impossibility to mechanize specimens fitting the dimensions, or mainly the thickness required [4]. One of those situations is usually present in welded joints of any type of structure. In other cases it can be just a harsh task to test material due to the inherent operational difficulties and uncertainties of standard CBT and HE tests.

2.2. HE alternative testing by Small Punch means

To find a solution to these types of scenarios the miniature tests family was developed, which uses specimen sizes much smaller than the required by standard tests. Among these alternative techniques the Small Punch Test (SPT) is the most notable, based on punching a reduced dimensions plane specimen, which allows to estimate parameters as the yield stress, ultimate tensile strength and even fracture toughness of metallic materials with high reliability [10]. During the last years many groups are developing creep behavior models too [11]. Although a reference standard that includes the tensile and fracture estimations by SPT is currently in preparation, a European Code of Practice was developed in 2006 [12].

The SPT allows to test in-service structures, since the extraction of a sample with such a small amount of material does not compromise the component's integrity. It has been applied to characterize embrittlement situation on steels, such as the evolution of materials properties with neutron irradiation [13], or environmental embrittlement [14]. Throughout the last years some authors have proved the validity of the SPT to be used in HE and SCC characterizations [14,15,16], having the advantage of being faster and easier to perform than standard tests.

3. MATERIAL AND LABORATORY EMBRITTLEMENT SIMULATION SYSTEMS

3.1. Material employed

The material used in this study is a Cr-Ni-Mn high-strength steel. It is obtained by quenching and tempering processes, which give the tempered martensite microstructure showed in Figure 1. This steel is received in the factory in bars, which are then forged to conform components by bending forces. Cylindrical tensile specimens and compact specimens were obtained in order to determine the mechanical behavior of the material as received [18,19,20]. The results are shown in Table 1.

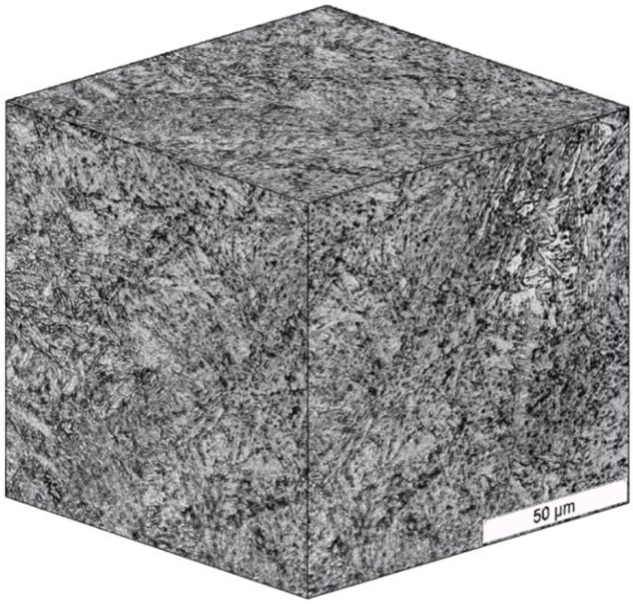

Figure 1. Microstructure of the steel employed.

Table 1. Mechanical properties of ths steel employed.

PARAMETER		VALUE
Yield Stress	(MPa)	920
Ultimate Stress	(MPa)	1015
Young's Modulus	(GPa)	205
Ramber-Osgood Parameters	n	14,5
	α	1,15
$J_{0,2}$	(KN/m)	821
$K_{J0,2}$	(MPa*m^1/2)	410

3.2. Simulating HE in lab tests

Two different environmental conditions have been analyzed in this work. The first one, 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 or predict that can seriously affect the structural integrity of the component exposed.

The technique of cathodic protection (CP) is used to avoid corrosion phenomena for marine water environments. It involves the use of a sacrificial anode of aluminum (more active than steel), which in the 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, therefore will maintain the stability of the process. In this study an aggressive environment of marine water was simulated, consisting in a 3.5% in weight dissolution of NaCl in distilled H_2O [5]. An aluminum anode was employed. The reference electrode employed contained an Ag/AgCl solution. The PH was controlled at the range 5,5 - 5,7 [5] during the hole of the tests extension and room temperature 20ºC - 25ºC. Two levels of cathodic protection (aggressiveness) were analyzed, -950mV and -1050mV of fix potential imposed.

The technique of cathodic charge (CC) 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]. Environmental conditions in accordance with [2] were simulated, consisting of an 1N H_2SO_4 solution in distilled water containing 10 drops of CS_2 and 10mg of As_2O_3 dissolved per liter of dissolution. The solution of As_2O_3 was prepared using Pressouyre's method [2]. A platinum grid was used as an anode. The reference electrode employed contained an Ag/AgCl solution. The PH was controlled at the range 0,65 - 0,80 during the hole of the tests extension and room temperature 20ºC - 25ºC. Two levels of charge (aggressiveness) were analyzed, $1mA/cm^2$ and $5mA/cm^2$.

4. EXPERIMENTAL METHODOLOGY

4.1. Fracture Mechanics tests

According to test plan shown in Table 2, the analysis was carried out evaluating the effects on the Cr-Mn-Ni steel of the environments previously explained (cathodic protection and cathodic charge). The study clearly delineated two conditions of aggressiveness for each environment, as well as paying attention to the loading rate in each case. Prior to the test, the specimens were subjected to hydrogen absorption by exposing them for 48 hours to the same environment and aggressiveness conditions as the test itself, that was performed subsequently by applying the corresponding loading rate using a slow strain rate machine according to the Standard ISO-7539 [4].

Table 2. Fracture Mechanics test plan.

ENVIRONMENT		RATE(m/s)	SAMPLES	RESULT
CC	$5mA/cm^2$	6.10-8	1 C.T.	KEAC
		6.10-9	1 C.T.	KEAC
	$1mA/cm^2$	6.10-8	1 C.T.	KEAC
		6.10-9	1 C.T.	KEAC
CP	-1050mV	6.10-8	1 C.T.	KEAC
		6.10-9	1 C.T.	KEAC
	-950mV	6.10-8	1 C.T.	KEAC
		6.10-9	1 C.T.	KEAC

From the straight zone of a Ø120mm chain link, 8 compact (CT) specimens 25mm thick in accordance to [4,17] were obtained. The specimens were machined in such an orientation that the crack propagation was transversal to the longitudinal axis of the chain link, as shown below.

An analysis was carried out obtaining the stress intensity factor, K_{EAC}, from each test, employing for this purpose the methodology based on the GE-EPRI procedure [3]. This method allows the crack size values to be obtained throughout the whole test from the experimental P-COD curve using the concept of iso-a curves [7], thereby it is also possible to determine the value of the J integral in their elastic and plastic components, and the equivalent stress intensity factor at which crack growth starts.

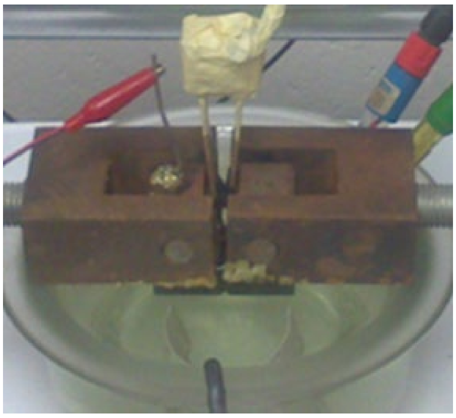

Figure 2. Fracture Mechanics test being carried out.

4.2. Small Punch Tests

Some works have been carried out proving the validity of the SPT to be used in HE and SCC characterizations [14,15,16]. In this work the material embrittlement by Small Punch means is studied using a new approach. The purpose is to obtain a correlation between the energy employed by the SPT for embrittlement damage initiation on a notched sample, E_{ini}, and the conventional stress intensity factor, K_{EAC}.

From the straight zone of a Ø120mm chain link, 32 SPT specimens were obtained in accordance to [10,12], having a lateral notch machined by electrowire cutting of 0.3mm of diameter and 4.8mm long (Figure 3). The specimens were machined in such an orientation that the crack propagation was transversal to the longitudinal axis of the chain link [10].

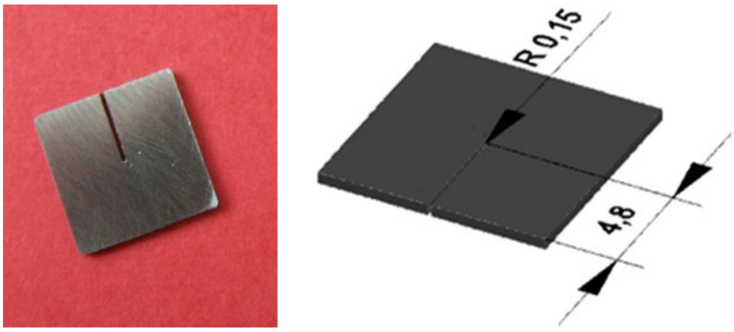

Figure 3. SPT notched specimen.

Prior to the test, the specimens were subjected to hydrogen absorption by exposing them during 2 hours to the corresponding environment and aggressiveness conditions, a period of time considered enough for a proper and complete diffusion of the Hydrogen inside the material [2] (Figure 4). Subsequently the samples were extracted from the solution, dried and tested. In parallel to each test, the hydrogen content was determined in an identical specimen.

Figure 4. SPT specimens during its Hydrogen charge.

As shown in Figure 5 (see experimental results in paragraph 5.2) when overlaying two SPT curves obtained from notched specimens, one testing the material in air and another embrittling it, both load-punch displacement recordings are coincident up to a point, showing the embrittled one a decrease in its load and displacement after it. This fact justifies the environmental effect on the crack initiation when a certain level of energy is reached, E_{ini}, which is dependent on the material and the embrittlement grade. It means that the embrittlement damage initiates due to the environmental effect in that point, that makes the embrittled specimen to have a different behavior than the non-embrittled one.

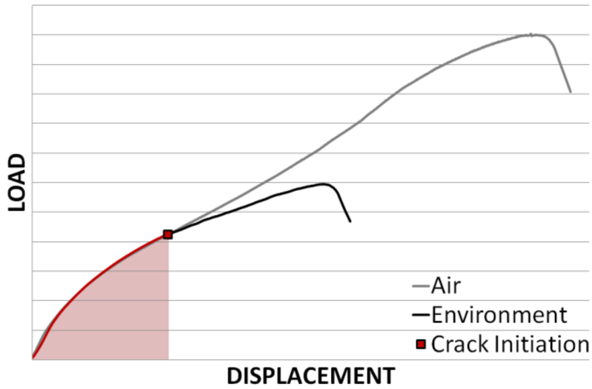

Figure 5. Energy for embrittlement damage initiation, EIni, determination.

The environments and aggressiveness levels studied where the same used in fracture mechanics tests, also the punch loading rate effect was evaluated performing tests at two different rates, the regular one of 0.01mm/s recommended by [12] and another 5 times slower, of 0.002mm/s, with the aim of analyzing the effect of the displacement rate on the value of the fracture parameter. The result of all this was the small punch test plan shown in Table 3.

Table 3. Small Punch Test plan.

ENVIRONMENT		RATE (mm/s)	SAMPLES	RESULT
CC	$5mA/cm^2$	0,010	4 SPT	Eini
		0,002	4 SPT	Eini
	$1mA/cm^2$	0,010	4 SPT	Eini
		0,002	4 SPT	Eini
CP	-1050mV	0,010	4 SPT	Eini
		0,002	4 SPT	Eini
	-950mV	0,010	4 SPT	Eini
		0,002	4 SPT	Eini

For each test condition (environment + aggressiveness level + loading rate) it was obtained the value of the Energy under the load-punch displacement recording from its origin up to the embrittlement damage initiation point, as shown in Figure 4. The representative value of the energy of initiation, E_{ini}, was obtained as the average of 4 results got from the notched specimens tested.

5. EXPERIMENTAL RESULTS

5.1. Fracture Mechanics tests

Figures 6, 7 and 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 getting any noticeable crack propagation, so it was impossible to predict any K_{EAC} value.

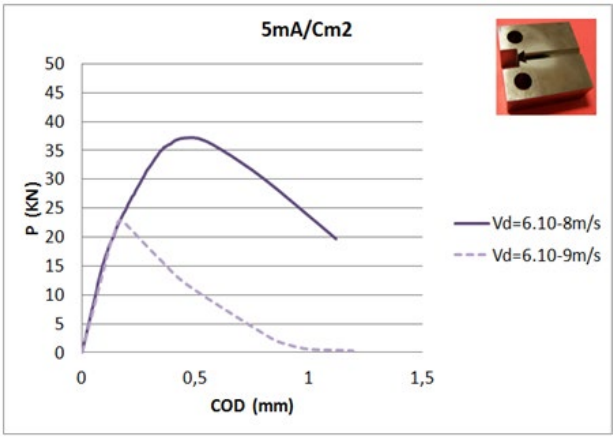

Figure 6-a. Experimental curves from Fracture Mechanics tests at 5mA/cm².

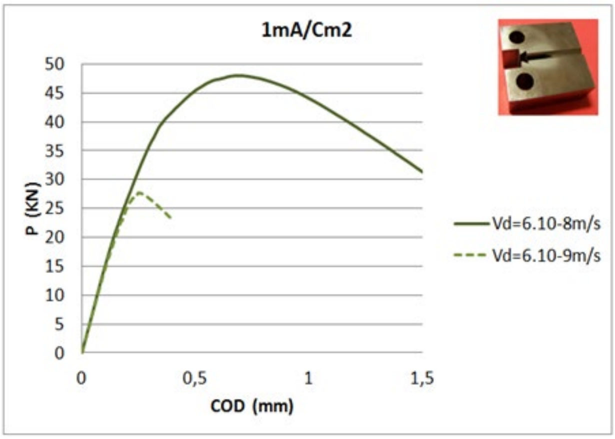

Figure 6-b. Experimental curves from Fracture Mechanics tests at 1mA/cm².

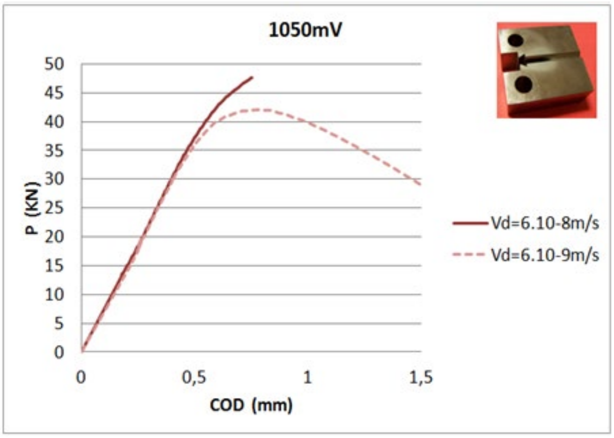

Figure 6-c. Experimental curves from Fracture Mechanics tests at 1050mV.

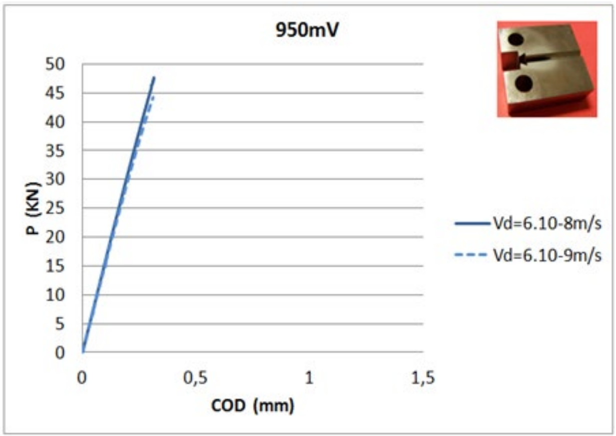

Figure 6-d. Experimental curves from Fracture Mechanics tests at -950mV.

Table 4. Fracture Mechanics tests results.

ENVIRONENT		RATE (mm/s)	K_{EAC} (MPa*$m^{1/2}$)
CC	5mA/cm^2	0,010	32,80
		0,002	30,92
	1mA/cm^2	0,010	46,04
		0,002	36,69
CP	-1050mV	0,010	139,26
		0,002	117,28
	-950mV	0,010	#
		0,002	#

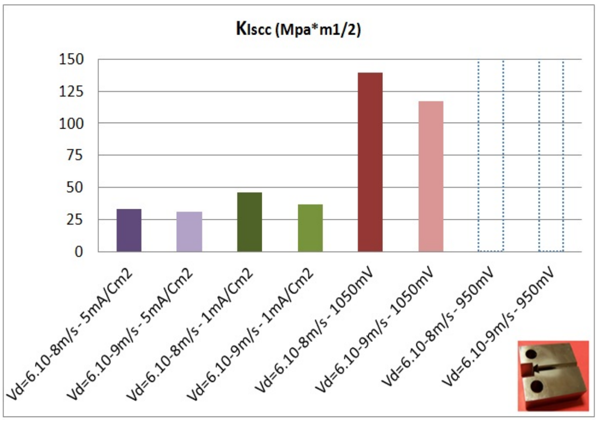

Figure 7. Comparison of the K_{EAC} results.

From previous results, as attested in the bibliography [18], the more aggressive the test conditions, the lower the value of K_{EAC}. It also can be observed that if a cathodic protection or cathodic charge scenario is fixed (a dissolution and a solicitation rate are fixed), then K_{EAC} will decrease if the applied intensity (or potential) is increased.

5.2. Small Punch Tests

Presented in Figure 8 are the curves obtained from the SPT tests carried out, overlaid to another from a sample tested in air. The value of E_{ini} is calculated form them as the mean in each condition, shown in Table 5 and Figure 9.

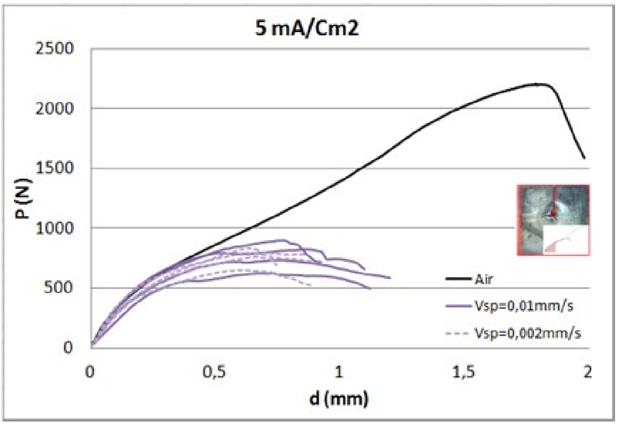

Figure 8-a. SPT tests performed on notched specimens at 5mA/cm^2, overlaid to SPT test in air.

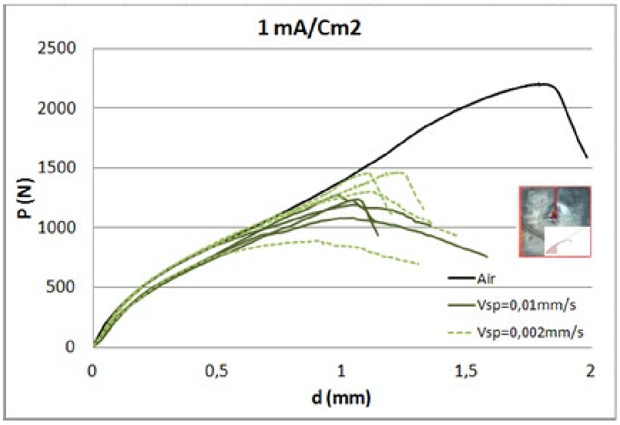

Figure 8-b. SPT tests performed on notched specimens at 1mA/cm^2, overlaid to SPT test in air.

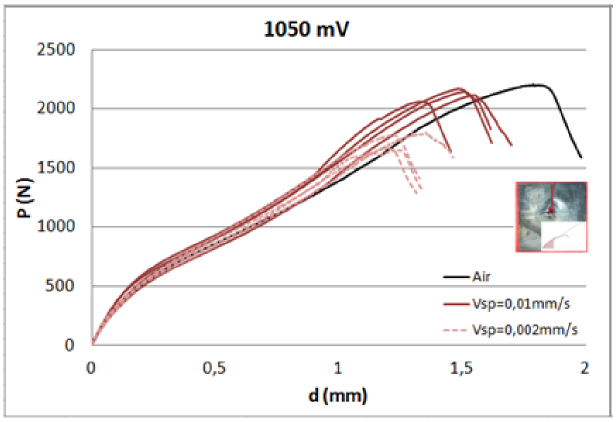

Figure 8-c. SPT tests performed on notched specimens at -1050mV, overlaid to SPT test in air.

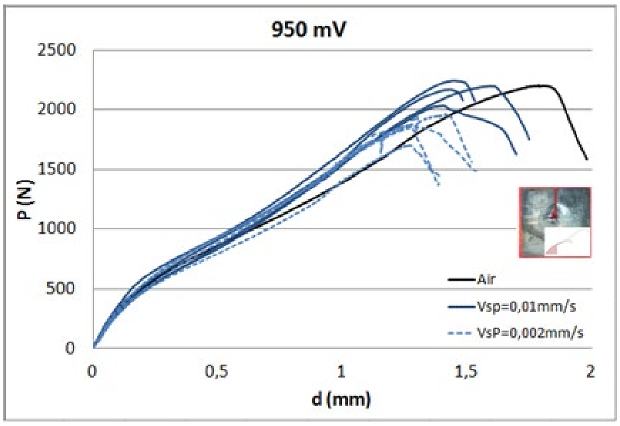

Figure 8-d. SPT tests performed on notched specimens at -950mV, overlaid to SPT test in air.

Table 5. Small Punch Tests results.

ENVIRONMENT		RATE (mm/s)	E_{ini} (J)
CC	$5mA/cm^2$	0,010	0,14
		0,002	0,06
	$1mA/cm^2$	0,010	0,52
		0,002	0,49
CP	-1050mV	0,010	1,75
		0,002	1,19
	-950mV	0,010	1,77
		0,002	1,30

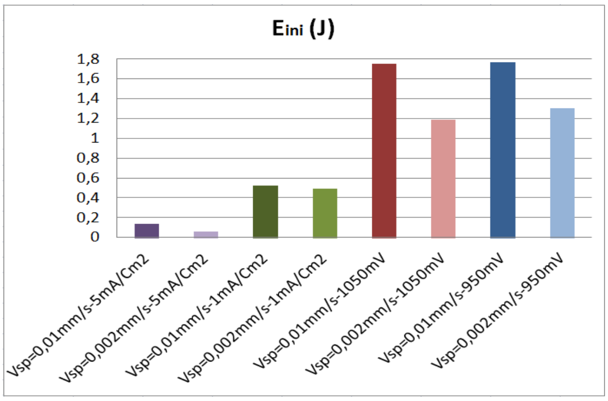

Figure 9. Comparison of the E_{ini} results.

From previous results, the more aggressive the test conditions, the lower the value of E_{ini} It also can be observed that if a cathodic protection or cathodic charge scenario is fixed (a dissolution and a solicitation rate are fixed), then E_{ini} will decrease if the applied intensity (or potential) is increased.

In Figure 10 are presented fractographies of SPT specimens after being tested in air, and in just after H_2 charge in the most aggressive condition ($-5mA/cm^2$ and 0,002mm/s). It can be observed how hydrogen produces an embrittlement in the material, developing paths among grain boundaries. This is related to the fact that the energy for crack initiation decreases when the aggressiveness level increases, since grains joints are affected, the typical brittle shape of the SPT curves (mainly those at $5mA/m^2$ and $1mA/m^2$) matches also with these facts.

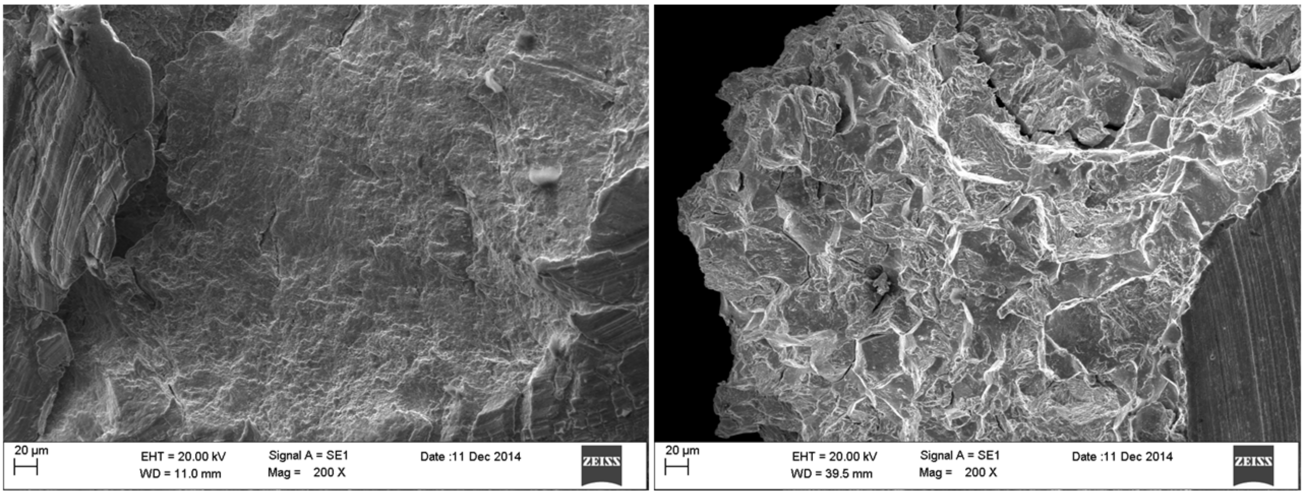

Figure 10. Fractography of SPT notched specimens tested in air (left) and at 5mA/cm² (right).

6. CONCLUSIONS AND FUTURE WORK

6.1. Conclusions

As proved, the numerical values of K_{EAC} and E_{ini} are qualitatively related, being E_{ini} and K_{EAC} lower for more aggressive conditions and higher for milder ones. In Figure 11 a correlation is made between pairs of results of tests performed in equivalent environments, at lower rates in each case (6.10-9 m/s for CT and 0,002 mm/s for SPT) or higher ones (6.10-8 m/s for CT and 0,01 mm/s for SPT).

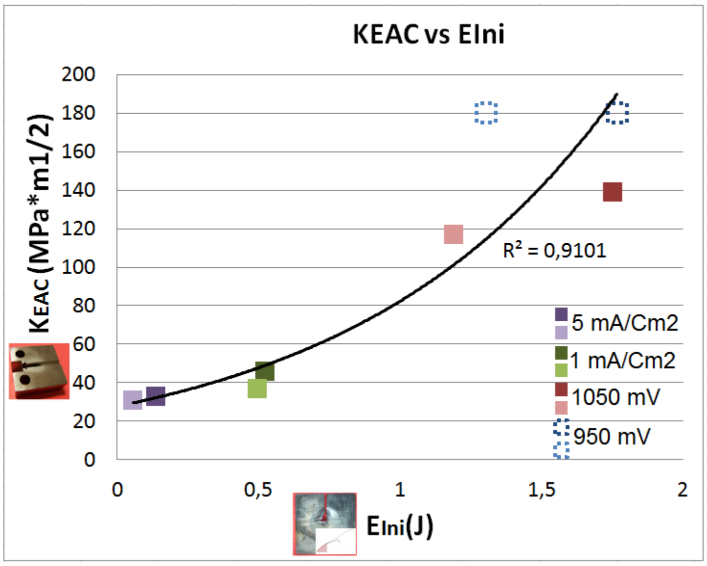

Figure 11. Trend between pairs of results of tests performed in the same environment at the lower or higher solicitation rates.

In this paper, the Small Punch Test has been re-validated as a method for characterizing materials in HE scenarios. A high strength steel Cr-Ni-Mn had been studied, characterizing it in 4 different aggressive environments by both conventional and Small Punch Tests, taking into account the effect of 2 different loading rates in each case.

SPT shows embrittlement effects (Figures 8 and 9) when pre-embrittling specimens and testing them subsequently in air at conventional rates (0,01mm/s and 0,002mm/s). The Small Punch Test is able to show the effect of the environment on the material, as well as the effect of punch loading rate variations.

A new approach to study embrittlement in steels using the Small Punch Test was presented. From it, a correlation could be established between both conventional and alternative SPT using notched specimens, in order to estimate the stress intensity factor in environment, K_{EAC}, from the energy employed by the SPT for embrittlement damage initiation, E_{ini}.

6.2. Future work

The issue to be solved is relative to the solicitation rate that should be employed in SPT tests in order to reproduce accurately the environmental conditions taking place during conventional standard test.

Some experiences using un-notched specimens to estimate σ_{scc} [19] use the basis of Small Punch Creep Tests looking for similar breaking times in standard and SPT tests, stating that the most suitable will be performing static tests in environment (which gives punch rates arround 1E-5 or 1E-6 mm/s). Others propose to calculate a theorical equivalence between the solicitation rate in standard fracture mechanics tests and the punch rate in SPT [20], in order to have a same magnitude order CTOD variation in both cases, but there are not evident conclusions in this field yet.

There is not a definitive conclusion about the most suitable punch rate to be used. It seems that rates around 100 to 1000 times slower than recommended by [12] will be suitable. In this situation pre-embrittling the specimens and testing them in air is not an option, because the embrittlement effect will disappear after the first minutes (and the test will take hours or days). Finally, future work seems to be on the line of performing very low punch rate SPT's, mainly using the static load method.

ACKNOWLEDGMENTS

The authors of this paper would like to thank the Spanish Ministry of Economy and Competitivity for the support received for the development of the research project MAT2011-28796-C03: "Metodologías para la caracterización de materiales metálicos en condiciones ambientales adversas mediante ensayos Small Punch".

REFERENCES

[1] HAMILTON, J.M., "*The challenges of Deep-Water Artic Development*", International Journal of Offshore and Polar Engineering, Vol. 21 (4), pp. 241-247, 2011.

[2] STEVENS, M.F., "Effect of microstructure and trapping on the hydrogen embrittlement susceptibility of a Titanium bearing HSLA steel", Doctoral Thesis, Carniege Mellon University, 1984.

[3] V. KYMAR, M. GERMAN, C.F. SHIH, "*An engineering Approach to Elastic-Plastic Solids*", Research project EPRI NP-1931, General Electric Company, NY, 1981.

[4] ISO 7539; "*Corrosion of metals and alloys*" -- Stress corrosion testing.

[5] GONZÁLEZ, J.J., "Influencia de la microestructura en el comportamiento de aceros de alta resistencia frente a fenómenos de corrosión bajo tensión", Doctoral Thesis, University of Cantabria, 1987.

[6] ÁLVAREZ J.A., "Fisuración inducida por hidrógeno de aceros soldables microaleados. Caracterización y modelo de comportamiento.", Doctoral Thesis, University of Cantabria, 1998.

[7] ÁLVAREZ J.A., GUTIÉRREZ-SOLANA F., *"An elastic-plastic fracture mechanics based methodology to characterize cracking behaviour and its application to environmental assisted processes"*, Nuclear Engineering and Design 188 (1999), pp. 185-202.

[8] ISO 7539-4:1989 ; "*Corrosion of metals and alloys*" - Stress corrosion testing - Part 4:Preparation and use of uniaxially loaded tension specimens.

[9] GUTIÉRREZ-SOLANA F., "*Fragilización por hidrógeno en tuberías de acero*", PhD Thesis, Universidad Politécnica de Madrid, 1981.

[10] LACALLE, R., "Determinación de las propiedades en tracción y fractura de materiales metálicos mediante ensayos Small Punch". Doctoral Thesis, University of Cantabria, 2012.

[11] ANDRÉS D., LACALLE R., ÁLVAREZ J.A., "Creep property evaluation of light alloys by means of the small punch test: creep master curves", Materials and Design, 2016.

[12] CWA 15627:2008. "*Small Punch Test for Metallic Materials*". European Comittee for Standarization (CEN).

[13] D. FINARELLY, M. ROEDIG, F. CARSUGHI, “Small Punch Tests on Austenitic and Martensitic Steels Irradiated in a Spallation Environment with 530 MeV Protons”, Journal of Nuclear Materials 328, 2004, pp.146-150.

[14] TAO BAI, PENG CHEN, KAISHU GUAN, "Evaluation of stress corrossion cracking susceptibility of sainless steel 304L with surface nanocrystalization by small punch test", Material Science & Engineering A, 561 (2013) 498-506.

[15] ARROYO B., ÁLVAREZ J.A., LACALLE R., GUTIÉRREZ-SOLANA F., GARCÍA T.E., "*Environmental effects on R5 steel under cathodic protection and cathodic charge. characterization using the Small Punch Test*", Proceedings of the 2nd SSTT, Austria, 2014.

[16] GARCÍA T.E., RODRÍGUEZ C., BELZUNCE F.J., PEÑUELAS I., ARROYO B., "*Development of a methodology to study the hydrogen embrittlement of steels by means of the small punch test*", Materials Science & Engineering A, 626 (2015), 342-351.

[17] ASTM E-1820-01, "*Standard Test Method for Measurement of Fracture Toughness*", Annual Book of ASTM Standards, 2001.

[18] CAYÓN, A., ÁLVAREZ, J.A., GUTIÉRREZ-SOLANA, F., DE CARLOS, A., "*Application of new fracture mechanics concepts to hydrogen damage evolution*", Final Report ECSC Contract. No 7210-PE-110, University of Cantabria, 2001.

[19] B. ARROYO, J.A. ÁLVAREZ, R. LACALLE, "*Analysis of the Small Punch Test Capability to Evaluate the Response of High Strength Steels Facing HIC or SCC*", Proceedings of ASME 2016 Pressure Vessels and Piping Conference, Hyatt Regency Vancouver - Vancouver, BC, Canada, 2016.

[20] B. ARROYO, J.A. ÁLVAREZ, R. LACALLE, T.E. GARCÍA y F.GUTIÉRREZ-SOLANA, "*Capacidad del Ensayo Small Punch para la determinación del parámetro de iniciación en condiciones de fisuración inducida por hidrógeno*", XXXII Encuentro del Grupo español de Fractura, Zamora, 2015.