MONITORING OF HYDROGEN ASSISTED SCC ON MARTENSITIC STAINLESS STEEL BY ACOUSTIC EMISSION TECHNIQUE

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Abstract

Aim of the work is to investigate by using acoustic emission technique (AE) the hydrogen assisted Stress Corrosion Cracking (SCC) phenomena, in a martensitic stainless steel. In particular a study based on time domain approach was carried out in order to analyse the corrosion phenomena by using data variables evolution. An appropriate set of variables was presented, some of them directly related to the acoustic phenomena, such as Amplitude, Duration and other descriptors of the AE waveform, while others have been derived from them, such as b-value and Ib-value, that are descriptors about the time domain distribution of the AE event energy.

Tests were carried out on a X12Cr13 martensitic stainless steel, according to NACE TM 0177 standard, using a modified sour corrosive environment (5% NaCl, 2.5% Acetic Acid and 10⁻² M Na₂S₂O₃).

Keywords: acoustic emission, stress corrosion cracking, time domain series, b-value and ib-value

1. Introduction

In many areas of industrial production, first of all the transport of hydrocarbons and of other dangerous chemicals, it is of primary importance the definition of effective corrosion activation and propagation indices, in order to guarantee efficient corrosion monitoring. It is necessary for the purpose to prevent sudden failures, and to obtain a reduction of infrastructure maintenance costs [1] [2].

Among all the forms of corrosion, Stress Corrosion Cracking (SCC) results to be one of the most critical and dangerous. That is due to its random nature and the lack of a complete comprehension of mechanisms at the basis of the corrosion phenomena [3] [4] [5].

Oil & Gas industry, moreover, deals with more and more aggressive environment. So the use of new corrosion resistant alloys [6] or a better identification of the application limits of already used metal alloys [7] [1] is fundamental.

For this issue recently the attention is being focused on martensitic and super-martensitic stainless steel, due to their resistance in moderate aggressive corrosion environments (high CO₂, medium to high chlorides and low H₂S) and reduced costs. H₂S indeed is highly aggressive so an increasing attention is still given to the identification of materials with high corrosion resistance in this environmental condition. Due to the high H₂S dangerousness for health, is commonly accepted the use of thiosulphate solution to simulate the sour gas environment [8] [9].

Among all the monitoring methodologies aimed to evaluate the SCC damage phenomena, Acoustic Emission (AE) technique plays a key role. The technique allows to identify the growing faults during the monitoring conditions and is satisfactory used to detect pitting initiation and propagation [10], as well as short and long range crack propagation [11] [12].

The data obtained from the acquired transients can be analysed by different methodology based on uni- and multi-variate approach [13], as well as Principal Component Analysis.
(PCA) or Neural network [14]. But these approaches could lead to difficulty in the data interpretation, due to the hidden and complex interaction between the AE variables. AE data analysis could be therefore improved with the use of some additional analysis procedures. In this work the authors coupled to the multidimensional data analysis the so called $b$ and $Ib$ value approach already in use in the geophysics field.

The $b$ value analysis is based on the event cumulative frequency-magnitude distribution and was originally applied on seismic science. It was developed to characterize earthquake data populations [15], but it was successfully applied in many other field, such as civil engineering [16][17], geotechnics [18]. It took its theoretical basis on the Gutemberg and Richter empirical formula [19]:

$$\log N = a - b(A_{dB}/20)$$

(1)

where $A_{dB}$ is the event magnitude, $N$ is the number of events with an amplitude higher than $A_{dB}$, and $b$ is the so-called $b$-value.

In order to avoid the problem to define amplitude range and number of AE data, the improved $b$-value ($Ib$-value) was proposed [20]:

$$Ib = \frac{\log_{10} N(\omega_1) - \log_{10} N(\omega_2)}{((\alpha_1 + \alpha_2)/\sigma)}$$

(2)

where $N(\omega_1)$ is the cumulative number of AE events with amplitude higher than $\mu-\alpha_1\sigma$, and $N(\omega_2)$ is the accumulated number of AE events in which the amplitude is more than $\mu+\alpha_1\sigma$, $\sigma$ is the standard deviation of the magnitude distribution for each group of events, $\mu$ is the mean value of the magnitude distribution for the same group of events, $\alpha_1$ and $\alpha_2$ are constants.

These two parameters have a slightly different behaviour: $b$-value shows the material response to the applied load, i.e. the variation of load as for a stress redistribution [16], while $Ib$-value shows a better sensitivity to the corresponding fracture processes [2].

Aim of this work is to investigate the hydrogen assisted Stress Corrosion Crack phenomena, in a martensitic stainless steel, by using acoustic emission technique. The different phases of the corrosion phenomena have been investigated using an appropriate set of variables in a time domain approach, furthermore $b$ and $Ib$ values analysis was adopted to better identify critical transients.

### 2. Experimental part

#### 2.1 Materials

Tests have been conducted on a martensitic stainless steel X12Cr13. It is one of the most popular alloy in industrial field since is fairly good corrosion resistance and mechanical properties. Chemical composition of the alloy is reported in table 1.

**Table 1: Nominal chemical composition [wt%] of X12Cr13 alloy**

<table>
<thead>
<tr>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>0.13</td>
<td>0.43</td>
<td>0.29</td>
<td>0.020</td>
<td>0.001</td>
<td>12.18</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Specimens were machined with a surface roughness of 0.3 μm from a forging disk used to obtain compressor impellers used in oil & gas industry. To get the higher mechanical properties and toughness specimens were extracted along the circumferential direction at maximum diameter. After heat treatment the specimens were characterized by an ultimate
tensile strength (UTS) of 760MPa, a 0.2% yield strength of 618MPa and an elongation at break of 24%.
Specimens were machined in a dog-bone shape, with a reduced diameter of 3.81 mm in the central section (the gauge section with a length of 15 mm), and a diameter of 9 mm in the upper and lower sides having a length of 62.5mm each one (including the junction section).

2.2 SCC test set-up

Tests have been carried out in standardized conditions, according to NACE TM 0177. Corrosive environment was a modified sour solution (5% NaCl, 2.5% acetic acid and 10^{-2}M Na_2S_2O_3). Test solution preparation was carried out under nitrogen gas bubbling in order to obtain an oxygen free solution. Test cell was sealed to avoid air inlet for the whole test duration.
SCC set-up was composed by a vessel for tensile shape specimen (NACE TM 0177 method A) composed by a Pyrex ring and two Teflon flanges (with a central hole for accommodating the specimen). This SCC vessel was then mounted on a dead weight type machine, to guarantee a constant stress on specimen. Load was set to the 90% of the 0.2% yield strength of the material.

2.3 AE set-up

AE signals were recorded by a 8-channel Vallen AMSY-6. It was setted with an amplitude thresholds of 26.7dB, a risetime threshold of 2 µs, and a pre-amplification of 34dB (from 2.5kHz to 1MHz). Recording was active for the full period of the test.
Acquisition set-up was then completed by the use of three piezoelectric transducers VS150-M. These sensors have a high sensitivity and works in the 100-450kHz frequency range, with resonance frequency at 150kHz. Two sensors were placed at the two ends of the specimen, while the third one was used as a guard sensor (connecting it to an independent block), its role was to acquire all the external noise signals, useful for a subsequence filtering procedure.
Sensors were coupled to the specimen with a proper grease layer, without any significant acoustic attenuation or interference.

3. Results

Test were repeated 5 times, obtaining always a fracture in a time range from 300 to 400h. Similar results have been obtained by each test showing an appreciable homogeneity in acoustic emission trends. For simplicity and clarity of results each picture, graph and data reported in this paper are related to a single test used as reference.

3.1 Corrosion phenomena morphology

The fracture surface of a specimen after SCC test is reported in Figure 1. The specimen showed an irregular fracture surface, with a mix of brittle and ductile propagation modes.

Figure 1. Specimen lateral surface (on the left) and fracture surface (on the right). SEM micrographies.
Several pits with wide eye shape were generated on lateral surface (with a major diameter of about 650 µm and minor diameter of about 420 µm), occasionally smaller rounded pits in proximity of them (diameter of about 150 µm) have been observed. Extended crevice corrosion was observed at the base of the specimen in correspondence to the lower o-ring position.

3.2 Signal De-noising

Preliminarily a signal de-noising procedure was applied on raw AE data [21]. In particular spurious events, identified by only one sensor or by the guard sensor, were accurately removed from the population of data. Furthermore, position identification for all AE events was carried out through an event localization procedure. All events located outside the gauge section were removed during data pre-processing. Thus treated signals were subsequently computed to calculate some derived variables, to get a complete and useful description of the system.

3.3 Multidimensional Data Analysis

By using the entirely acquired data-set, it is possible to give information concerning corrosion phenomena evolution occurring during time. In Figure 2 the cumulative plot of hits during SCC test is reported.

![Figure 2. Cumulative Hits trend](image)

According to cumulative hits plot five regions can be identified and related to specific corrosion damage stages. A first region was identified as the initiation region, in which acoustic events are very limited both in occurrence and in amplitude. A second region was identified as activation region, in which a growing increase in AE occurrence was observed. When the cumulative trend changed its slope a knee can be identified. This region was called pre-quiescence. This region was the prelude of a long time period (about one third of the total duration of the test) during which the amount of acoustic events was very limited and an event frequency was very low. This region event if acoustically silent was however characterized by a high electrochemical activity [22].
Then, last region was the re-activation region, in which the acoustic activities re-starts. The localized corrosion grow up with an increase of pit dimension and crack evolution. In this phase cracks propagate in large parts of the specimen, increasing progressively their dimension, until the failure of the sample took place.

From the uni-variate trends it is possible to obtain a physical interpretation for each temporal region. The first region was indeed characterized by a low event frequency (point 1 in Figure 3e), at the same time AE hits with low rise-time are not observed (point 1 in Figure 3b). It seems to be a low-significance region, in which the corrosion phenomena could be related to initial adsorption of thiosulphate ions and FeS scale formation.

Then, the activation region was characterized by higher waveform frequency (Average Frequency reach 150kHz value, point 2 in Figure 3d). A slight increase of amplitude magnitude can be also identified (point 2 in Figure 3a). This region, predominantly characterized by acoustic events with low and occasionally high intensity events, can be associated to activation of local surface defects such as pits (low intensity events) [23] and sulphide scale build up and cracking (high intensity events) [24]. Afterwards, a pre-quiescence stage can be clearly identified. This region was characterized by events with the absence of low-value rise-time (point 3 in Figure 3b) and with a reduction in magnitude of amplitude (about 40dB, point 3 in Figure 3a). That implies that events with low RA values, under 200 ms/V, disappeared (point 3, Figure 3c). The simultaneous moderate

![Figure 3. a) amplitude (A), b) rise-time (R), c) RA, d) average frequency (AVG) and e) event frequency trends](image-url)
lower average frequency values, suggest a progressive transition from a different AE source type.

The quiescence region shows a substantial absence of acoustic events. The duration of quiescence period in some tests lasted over one third of the full test duration. This phase was mechanically inactive, i.e. characterized by a very low AE activity (point 4, Figure 3e). This behaviour was associated with a change in pit growth mechanisms from thiosulphate promoted accretion to a load assisted anodic dissolution mechanism [13]. Furthermore hydrogen discharge at the pit tip promoted hydrogen diffusion and trapping in the martensitic matrix where high stress caused then microplasticity and transgranular cleavage fracture mechanisms anticipating intergranular brittle fracture. Final phase is the re-activation region, that is the prelude of the final specimen failure. During this phase we can note the re-activation of AE sources. AE hits are characterised mainly by high event frequency (point 5, Figure 3e), with a relative high mean amplitude (but lower maximum magnitude), (point 5, Figure 3a). In particular a significant amount of AE signals evidenced an amplitude with a magnitude in the range 40-60 dB. Average frequency and RA values decreased revealing that the cracking propagation phenomena are shifted firmly in the shear mode [25].

![Localization of AE events along specimen length](image)

Figure 4. Localization of AE events along specimen length (position is referred from upper specimen side). Blue lines delimit gauge section, green lines delimit fracture region.

Further information can be obtained analysing the AE source colour plot reported in Figure 5. This plot is a bidimensional representation of three variables: amplitude, position and time. It shows the localization during time of each acoustic event. Event marker dimension and colour is proportional to amplitude value of the event. Vertical lines represent the temporal segmentation as identified in Figure 2, while horizontal lines indicate different specimen regions. Failure region is evidenced between green lines. Blue lines identify gauge length. This graph is very useful to visually highlight cluster of events with a higher acoustic significance, identifying their spatial and temporal localization. By carrying out a comparative study of data-set values of events in these clusters [13] it was possible to identify them as hydrogen bubbling, FeS build up and cracking, pit initiation and growth, crack opening and final fracture (Figure 4).
3.4 $b$-value and $I_b$-value analysis

Data analysis based on $b$-value and $I_b$-value could help us to identify the transition from a mechanism to another in a more simple and immediate way. The representation, based on amplitude values and their magnitude distribution, could give more information that is not possible to evidence by the conventional amplitude scatter plot. In Figure 5 $b$ and $I_b$ value trends, calculated separately on the different event populations localised on sample length, are shown.

Figure 5. $b$-value and $I_b$-value trends for different specimen spatial regions

Black circles identify all $b$ and $I_b$ values that have been computed on small data population (less than 50 events), that corresponded to a not optimal statistical population of data. That leads to consider these points statically not reliable. Plots are related to the different specimen regions: specimen upper side, gauge section above the fracture, fracture area, gauge section below the fracture area, specimen lower side, crevice area.

Each location had its own temporal segmentation in order to evidence the $b$ and $I_b$ value trend during corrosion evolution phenomena on the specific specimen regions. Black vertical lines indicate temporal segmentation related to each local segment.

A variation in $b$-value and in $I_b$-value trends indicates that a change in the corrosion phenomena on the specimen was occurring. Instead, a constant trend indicates that no significant variation on corrosion mechanism took place.

Observing the fracture area plot, it is possible to note in particular that quiescence region was longer that in other sample sections. The re-activation started in a subsequent step respect the other regions. Such evidence could indicate that the evolution of plastic zone at crack tips was more intense compared with the other regions. During the reactivation stage the $b$ and $I_b$ trend evidenced a significant variation. Furthermore, the $I_b$ value was always significantly higher than the $b$. Being the $I_b$-value more sensitive to the fracture mechanisms [16], it could be considered a valid precursor for the imminent failure. Afterwards, in correspondence of
failure events, a significant drop of $b$ and $I_b$ values occurred as a consequence of the presence of high amplitude value related to failure crack. Furthermore, a significant increase in $b$ and $I_b$ value trends, can be also observed in the zone e and f (lower side regions) during the activation phase. This trend could be attribute to H$_2$ bubble evolution generated in the crevice area (see also Figure 4). These $b$ and $I_b$ peaks can be discriminated from failure crack propagation considering that these trends are not anticipated by a quiescence stage. Consequently, the quiescence region plays an important role to support event discrimination in evolving corrosion phenomena.

4. Conclusions

The different corrosion mechanisms developing on martensitic stainless steel (X12Cr13) sample during SCC tests in a modified NACE TM0177 solution were evaluated by using acoustic emission technique. Acoustic emission data analysis allowed to reveal the different stages of the corrosion phenomena. The compared analysis between the acoustic waveform parameters and the source localization allowed to differentiate AE sources. The use of $b$ and $I_b$ values trends lead to an immediate and simple recognition of the damage transition on specimen surface. A sudden variation in trend corresponded to a change in corrosion mechanism. A more clear increase in $I_b$-value than in $b$-value, anticipated by a quiescent period, indicated the occurrence of a cracking mechanism that lead to the final failure. These outcomes, as confirmed by further investigation on different kind of stainless steel and different test typology, could be of great interest in developing preventative procedure for failure prediction.

References
