

# The combined use of the acoustic emission technique and electrochemical noise for the study of corrosion mechanisms in simulated brine containing thiosulphate

E. Proverbio, L. Calabrese, G. Scionti

Aim of the work is to identify, on the basis of a combined monitoring procedure, by means of acoustic emission technique (AE) and the electrochemical noise technique (EN), the evolution of the different damage mechanisms that are triggered during the stress corrosion cracking process on 13% Cr martensitic stainless steel samples in a brine solution containing thiosulphate. The combined use of the techniques allows to distinguish the phenomena associated with a predominantly electrochemical damage mechanism (identified by the EN technique) with respect to those associated with a predominantly mechanical damage mechanisms (identified by the AE technique). The results demonstrate the suitability of the approach in the discrimination of the different damage mechanisms. Over time, a clear transition has been identified from the pitting initiation, through crack propagation and final failure.

**KEYWORDS:** STRESS CORROSION CRACKING, ACOUSTIC EMISSION, ELECTROCHEMICAL NOISE, THIOSULPHATE

## INTRODUCTION

Brine saturated with  $H_2S$  have been traditionally used to investigate the sour gas resistance of materials as recommended by NACE Standard TM-177. To avoid safety limitations due to  $H_2S$  toxicity the use of brine containing thiosulphate solution was recently evaluated in the scientific literature [1], [2].

Iron sulphide scale growth, pitting corrosion and stress corrosion cracking [3] are competitive corrosion mechanisms observed on stainless steel alloys in this environment. Thiosulphate concentration and pH play a fundamental role in promoting the different corrosion mechanisms.

The definition of an investigation procedure able to discriminate the different forms of corrosion competing in such a complex process, such as stainless steels in thiosulphate, is a request of particular relevance to increase the scientific soundness of this research topic.

In this concern, it was already observed that some phenomena (e.g. short and long range mechanic crack

E. Proverbio, L. Calabrese, G. Scionti

Università di Messina

propagation as well as pitting initiation) can be successfully identified by Acoustic Emission (AE) technique [4]. On the other hand, several studies have indicated that, on the basis of Electrochemical Noise (EN) measurements, it was possible to detect and distinguish different corrosion types (e.g. metastable and stable pitting, crevice corrosion, uniform corrosion, and stress-corrosion cracking) [5]. In a previous work [6] it was observed that, during corrosion tests in simulated sour environment (thiosulphate containing brine) on 13% Cr martensitic stainless steel, acoustic emission greatly reduced after a strong activity period of about 200 hours until an acoustical quiescent stage lasting about 50-100 hours. It can be supposed that during this "quiescence" stage, due to a change in the chloride to thiosulphate ratio, pit growth mechanisms changed merging from thiosulphate sustained growth into an almost pure chloride mode [7]. On the other hand,

during the quiescence stage an intense electrochemical activity evaluated by EN monitoring was observed. Aim of this work was to identify based on a combined AE and EN monitoring the transition from the different corrosion mechanisms, to better understand the influence of testing condition on the activation of a specific mechanism and to correlate AE patterns and EN statistical parameters to the mechanism itself.

## EXPERIMENTAL PART

### Materials

Dog bone specimens, obtained by machining a martensitic stainless steel alloy bar (X12Cr13 – UNS S41000 - chemical composition details are reported in Table 1), were used as samples for stress corrosion cracking.

**Tab.1** - Chemical composition of the used X12Cr13 alloy. / Composizione chimica della lega X12Cr13 utilizzata.

Composition [wt%]							
Fe	C	Mn	Si	P	S	Cr	Ni
Balance	0.13	0.43	0.29	0.020	0.001	12.18	0.21

The sample geometry was characterized by a gouge section with 15 mm length and 3.81 mm diameter. All specimens were obtained from a single forging disk. The forged alloy was quenched and double tempered to reach a hardness of 22 HRC, according to ISO 15156 standard. Furthermore, the tensile strength (UTS) of the heat treated martensitic stainless steel was 760 MPa, yield strength of 0.2% is 618 MPa and maximum elongation 24%.

### SCC test set-up

Samples were tested under tensile stress by means of a dead weight type machine. The applied stress was equal to 80% of the 0.2% yield strength of the material. Corrosion tests were performed in a modified method B NACE TM0177 standard solution at room temperature. It consisted in a solution containing 5.0 wt% ( $85.4 \cdot 10^{-2}$  M) NaCl, 2.5 wt% glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) in distilled water (standard NACE TM0177 test solution B) with the addition of  $10^{-2}$  M sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) [6].

AE signals were recorded by a Vallen AMSY-6 measurement system for the whole period of the test, by using two

sensors placed at the two ends of the sample. A third sensor has been employed as a guard sensor, connected to an independent block. The thresholds of amplitude and rise time parameters were set at 26.7 dB and 0.4  $\mu\text{s}$ , respectively. An amplification set at 34 dB was furthermore used.

EN signals (sampling frequency 5 Hz) were acquired using a SP-300 potentiostat (Biologic, Seyssinet-Pariset, France) equipped with a ZRA configuration module implemented for simultaneous recording of current and potential fluctuations. For this purpose, a three-electrode set-up was provided. The aforementioned dog-bone specimen was used as working electrode, while two cylindrical electrodes of the same materials and identical surface roughness were used as reference electrode and counter electrode respectively. EN measurements were implemented with a high impedance (1 Tera Ohm) PAR VersaSTAT 4 potentiostat. The effective working surface of the stressed specimen (working electrode) in contact with the test solution was approximately 24.1  $\text{cm}^2$ . The AE and EN acquisition covered the full period of the test. Before processing AE raw data were denoised according with usual procedure reported in the

literature [8].

**RESULTS AND DISCUSSION**

Fig. 1 shows the comparison of the evolution of the electrochemical noise potential (EN-E) transient and of the cumulative hits versus time. Both parameters can be identified as potential indices for a preliminary assessment of the degradation phenomena that trigger and evolve during the SCC test [9].

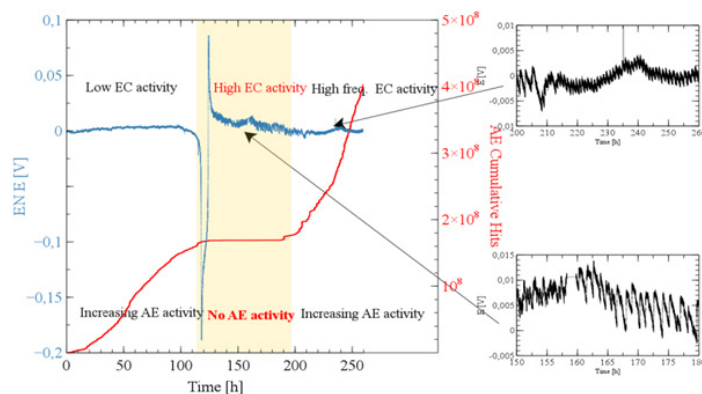
Three zones can be identified:

I. Stage I (0h-110h). At first, at low exposure time in thio-sulphate solution few AE events have been detected. The EN-E rapidly reaches an equilibrium. This stage can be defined as incubation period. After about 20h exposure time, the AE cumulative energy still remains low indicating low relevance of the occurred acoustic events. Afterwards, at increasing exposure time, in the range 20h-110h, an increase in the AE activity can be observed due to the increase of the energy magnitude and the amount of the recorded

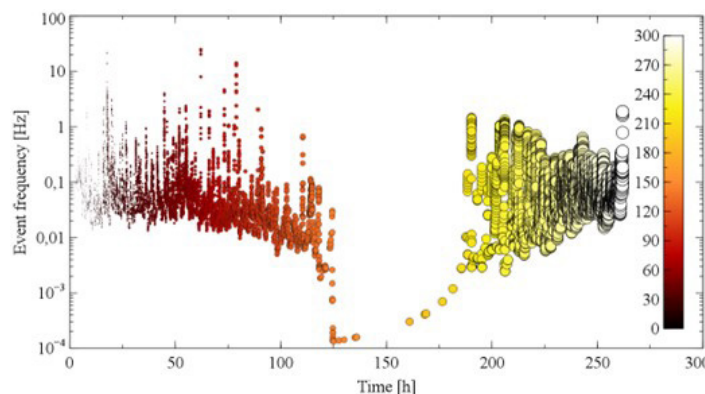
AE hits. At the same time, no evidence of modification of EC activity can be identified. During stage I mixed electrochemical (due to depassivation and repassivation) and mechanical (due to FeS scale build up/break and crevice phenomena and responsible of the acoustic emission) mechanisms could be suggested [6].

II. Stage II (110h-200h). At about 110h a significant modification of the signal trend can be identified. The electrochemical noise activity increases significantly coupled to a low AE activity. This was defined quiescence stage, where the cumulative hits is quite constant. This stage extends up to about 200h, evidencing a quite homogeneous trend of acoustic and electrochemical noise contributes. During this quiescent phase only AE events with very low amplitude and high duration parameters were recorded (Fig. 2).

III. Stage III (200h-failure). Finally, at long exposure time a slight reduction of EN activity can be observed. At the same time, the AE activity rises again significantly until specimen failure occurs.



**Fig.1** - Evolution of the electrochemical noise potential (EN-E) and cumulative AE energy versus time (red curve) / Andamento del potenziale di rumore elettrochimico e cumulativo degli eventi di emissione acustica nel tempo (curva rossa).



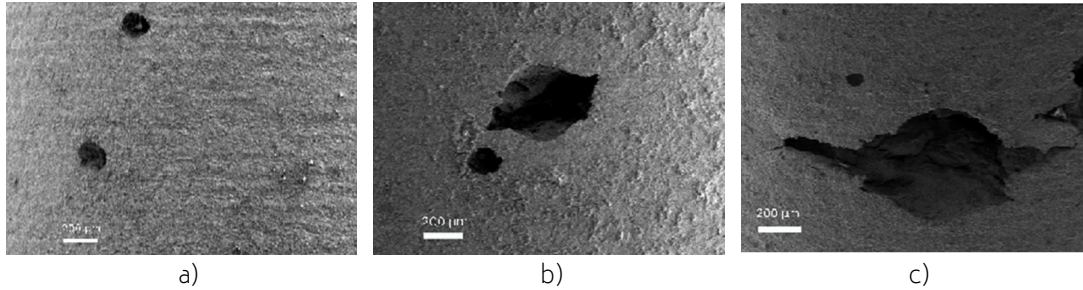
**Fig.2** - Frequency of acoustic emission events vs time. The acoustic quiescence (stage II) is clearly evident. / Frequenza degli eventi di EA nel tempo. La quiescenza acustica (stadio II) è ben evidente.

In order to better correlate the different stages of damage at increasing time, SCC tests, intentionally interrupted befo-

re fracture, were carried out at well-defined time intervals. Fig. 3 shows the morphology of the surface defects, identi-

fied by SEM micrographic images, at varying test time. Fig. 3a, shows the damage morphology after 150h, during phase II coded as quiescence stage. In this time interval, electrochemical activity is significantly more relevant than acoustic one. As highlighted in the figure, there is the for-

mation and propagation of some small pits in the surface. The pits are regular, circular-shaped with diameter size about 100-150  $\mu\text{m}$ .



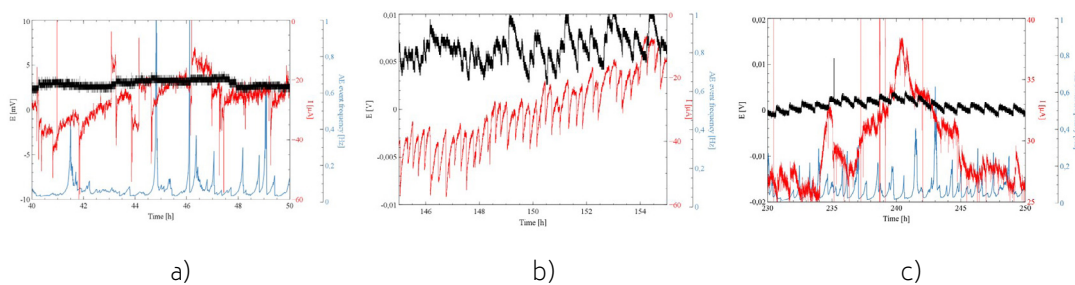
**Fig.3** - Micrographs of sample surface after a) 150h b) 240h c) at failure during stress corrosion test / Micrografie dei campioni dopo a) 150 h, b) 240 h, c) alla frattura, durante i test di tensocorrosione.

After 240 hours, (Fig. 3b), there is a synergistic interaction of electrochemical and mechanistic phenomena. The pits generated during phase II, further grows. In Figure 3b, the size of the defect is about 600  $\mu\text{m}$ , about four time larger than the observed ones in Figure 3a. Furthermore, it is noted that because of the stresses there is a principle of opening of the pit which superficially acquires an elongated shape.

Finally, at failure (Fig. 3c), the surface defect has assumed an eyelet morphology. Cracks triggered and propagated from the pit edge. The propagation line takes place orthogonally to the direction of loading. At this stage, the mechanistic contribution, identifiable by AE signals, becomes increasingly relevant. The electrochemical contribution, identifiable by the EN signals; becomes progressively less intense.

To better assess the main key features of AE and EN parameters during the different stages of the SSC damage evolution, Fig. 4 shows the evolution of E and I EN transients coupled to AE event frequency in the three SCC stages. In particular:

- Time interval 40-50h (Fig.4a). Low voltage fluctuations and high current spikes weakly correlated with acoustic emission are identifiable. This AE and EN coupling can be related, according to [10] to mixed surface degradation mechanisms (electrochemical: depassivation and repassivation and mechanical: FeS scale build up and break);
- Time interval 145-155h (Fig.4b). At intermediate testing time, a strong electrochemical activity without any acoustic emission can be observed. This stage was ascribed to a quiescence mechanistic stage where chloride assisted pit propagation takes place;
- Time interval 230-255h (Fig.4c) At this stage, acoustic emission events increase in amount and magnitude. They are significantly related to anodic current pulses. The current characteristic is based on an abrupt increase and progressive decay, indicating a crack propagation phenomenon where slip dissolution/repassivation at crack tip is occurring [11]. During this stage, large cracks are originated anticipating the future failure of the sample.



**Fig.4** - Evolution of E and I EN transients coupled to AE event frequency (blue line) during the three SCC stages - Evoluzione dei transienti di potenziale e corrente di noise associati alla frequenza di EA (linea blu) durante le tre fasi del processo di SCC.

## CONCLUSIONS

In the present paper it was assessed the complementary capabilities of AE and EN technique in evaluation corrosion mechanism transition during SCC test on 13% Cr martensitic stainless steel in simulated thiosulphate containing brine under constant tensile load. In particular:

- During the pitting activation low EN voltage fluctuations, high current EN spikes weakly correlated with acoustic emission have been observed. During this stage mixed electrochemical (due to depassivation and repassivation) and mechanical (due to FeS scale build up/break) mechanisms were suggested.
- Strong electrochemical activity without any acoustic

emission have been observed during the so called quiescence phase. During this stage a chloride assisted pit propagation mechanism has been suggested as the main factor of AC activity.

- After the quiescence phase the cracks triggering and propagation occurred. Acoustic emission activity are significantly synchronized to anodic current pulses. This behaviour can be related to the pit transition to cracks. Furthermore crack propagation mechanisms associated to transgranular fracture has been suggested.
- Eventually, a Brittle Intergranular Fracture (BIF) was the dominant mechanisms during the final failure

## REFERENCES

- [1] Zanotto F, Grassi V, Balbo A, Monticelli C, Zucchi F. Stress corrosion cracking of LDX 2101® duplex stainless steel in chloride solutions in the presence of thiosulphate. *Corros Sci* 2014;80:205–12. doi:10.1016/j.corsci.2013.11.028.
- [2] Kappes MA. Evaluation of thiosulfate as a substitute for hydrogen sulfide in sour corrosion fatigue studies. Ohio State University, 2011.
- [3] Newman RC, Wong WP, Ezuber H, Garner A. Pitting of Stainless Steels by Thiosulfate Ions. *Corrosion* 1989;45:282–7. doi:10.5006/1.3577855.
- [4] Delaunois F, Tshimombo A, Stanciu V, Vitry V. Monitoring of chloride stress corrosion cracking of austenitic stainless steel: identification of the phases of the corrosion process and use of a modified accelerated test. *Corros Sci* 2016. doi:10.1016/j.corsci.2016.04.038.
- [5] Xia D, Song S, Wang J, Shi J, Bi H, Gao Z. Determination of corrosion types from electrochemical noise by phase space reconstruction theory. *Electrochem Commun* 2012;15:88–92. doi:10.1016/j.elecom.2011.11.032.
- [6] Calabrese L, Galeano M, Proverbio E, Pietro D Di, Cappuccini F, Donato A. Monitoring of 13% Cr martensitic stainless steel corrosion in chloride solution in presence of thiosulphate by acoustic emission technique. *Corros Sci* 2016;111:151–61. doi:10.1016/j.corsci.2016.05.010.
- [7] Laitinen T. Localized corrosion of stainless steel in chloride, sulfate and thiosulfate containing environments. *Corros Sci* 2000;42:421–41. doi:10.1016/S0010-938X(99)00072-4.
- [8] Proverbio E, Calabrese L. Artificial neural network analysis of acoustic emission data during longtime corrosion monitoring of post-tensioned concrete structures. 2015. doi:10.1016/B978-1-78242-327-0.00012-X.
- [9] Kietov V, Mandel M, Krüger L. Combination of Electrochemical Noise and Acoustic Emission for Analysis of the Pitting Corrosion Behavior of an Austenitic Stainless Cast Steel. *Adv Eng Mater* 2019;21:1800682. doi:10.1002/ADEM.201800682.
- [10] Klapper HS, Goellner J, Heyn A. The influence of the cathodic process on the interpretation of electrochemical noise signals arising from pitting corrosion of stainless steels. *Corros Sci* 2010;52:1362–72. doi:10.1016/j.corsci.2009.12.021.
- [11] Saito K, Kuniya J. Mechanochemical model to predict stress corrosion crack growth of stainless steel in high temperature water. *Corros Sci* 2001;43:1751–66. doi:10.1016/S0010-938X(00)00173-6.

# L'uso combinato della tecnica di emissione acustica e del rumore elettrochimico per lo studio dei meccanismi di corrosione in soluzioni saline contenenti tiosolfato

Lo scopo di questo lavoro è di identificare sulla base di un monitoraggio combinato attraverso la tecnica di emissioni acustica (AE) e quella del rumore elettrochimico (EN) l'evoluzione dei diversi meccanismi di danno che si innescano durante il processo di tensocorrosione su provini in acciaio inossidabile martensitico 13% Cr in una soluzione salina contenente tiosolfati. L'uso combinato delle tecniche permette di distinguere i fenomeni associati a meccanismi di danno prevalentemente elettrochimici (individuati dalla tecnica di EN) rispetto a quelli associati a meccanismi prevalentemente meccanici (individuati dalla tecnica di AE). I risultati dimostrano l'idoneità dell'approccio nella discriminazione dei diversi processi di danno. Nel corso delle prove, è stata identificata una chiara transizione dal fenomeno di innesco del pitting, alla propagazione della cricca fino alla rottura finale.

**PAROLE CHIAVE:** TENSOCORROSIONE, EMISSIONE ACUSTICA, RUMORE ELETTROCHIMICO, TIOSOLFATI

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