Acoustic Emission during Hydrogen Charging of a Pipeline Steel

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Acoustic emission (AE) during hydrogen-induced cracking (HIC) of low-carbon pipeline steel immersed into H2S containing media was investigated aiming at discriminating between damage mechanisms and getting a better insight on the kinetics of damage. Two kinds of steel samples - sensitive and resistant to hydrogen induced cracking - were tested. Three different kinds of acoustic emission signals were discriminated by a cluster analysis involving either spectral shape recognition or parametric c-means classifier. It is demonstrated that AE is associated with three primary mechanisms involving hydrogen bubbles evolution, sulfide film formation and fracture due to HIC. Hence, AE is shown to be very efficient for quantitative description of hydrogen induced damage accumulation in steels.

KEY WORDS: acoustic emission; hydrogen-induced cracking; hydrogen charging; pipeline steel.

1. Introduction

Nowadays, carbon steel pipes are widely used to transport gas and crude oil over long distances. During service these steels experience permanent contact with a very aggressive media containing hydrogen sulfide, H2S. Under immersion in such an aggressive soil environment, the steels corrode and become brittle. Hence, they could fail prematurely causing severe ecological catastrophes. The failure occurs in a localized manner in a form of blistering and cracking1) and become brittle. Hence, they could fail prematurely causing severe ecological catastrophes. The failure occurs in a localized manner in a form of blistering and cracking1) and is referred to as hydrogen induced damage. Several standard procedures have been proposed and put into practice in the last years to assess the materials susceptibility to hydrogen attack. The NACE TM0284 standard,2) which was developed last years to assess the materials susceptibility to hydrogen induced damage (HIC), assumes exposing a steel sample to the H2S environment followed by structural observations. The Crack Sensitivity Ratio (CSR), Crack Length Ratio (CLR) and Crack Thickness Ratio (CTR) are commonly calculated from the observed geometrical dimensions of damage markings or three equi-distant cross-sections of the sample. Apparently, the assessment of damage, which relies solely on calculation of these ratios, suffers from obvious drawbacks. The reliability issues often arise because of small number of cross-section involved in the analysis. Besides, metallographic observations show only the final state of damage accumulated during a whole test and does not disclose any information about kinetics of damage accumulation. Development of a non-destructive technique, which would be capable of early identification of environmentally assisted damage, is therefore challenging and demanding task, especially in view of anticipating practical applications.

An acoustic emission technique, which is sensitive to the rapid release of elastic energy within a material, has long been recognized as powerful tool capable of real-time monitoring of various kinds of structural re-arrangements and damage processes which may occur in solids under load, temperature and/or influence of aggressive environment. The AE capacity of delivering real-time information differs this method drastically from other non-destructive testing (NDT) techniques such as ultrasound and color magnetic powder diagnostics. Cracks are among the most powerful AE sources, which are of primary concern in assessment of environmentally assessed degradation of steels. AE is widely used in detection and monitoring of corrosion and stress corrosion cracking.3–7) Many attempts are also known to correlate the rate of corrosion and AE parameters.8) HIC was also in focus of many studies, e.g.9) Using bivariate correlation between the AE energy and signal duration Simano et al.9) successfully discriminated AE features corresponding to HIC from other relevant sources, such as hydrogen evolution and formation and/or cracking of the iron sulfide layer. Most early studies, however, perform only qualitative analysis of AE parameters and their distributions, which makes it difficult to propose any automatic non-supervised scheme for real-time damage evaluation in-situ. No attempts to quantify the damage mechanisms with respect to the AE spectral density are known to the author’s best knowledge.

The present work aims at clarifying the kinetics of embrittlement associated with the ingress of hydrogen and to identify the signatures of hydrogen-induced damage in a 09GSF pipeline steel (a close analogue of an API 5L X52 steel), which is widely used in oil and gas industry. This objective is reached by intelligent signal processing involving categorization of AE signals recorded during hydrogenation with respect to their origin.
2. Materials and Experimental Procedures

2.1. Sample Preparation and Microstructure

Two commercially available grades of a pipeline steel 09GSF (Russian designation) were chosen for the present study: # the cold resistant #S and HIC resistant #R. Chemical compositions of both grades are shown in Table 1. Both compositions are similar, falling within the standard requirements for the 09GSF steel. Two different schedules of thermo-mechanical treatment of were applied to the present steels to obtain the samples with different degree of susceptibility to hydrogen induced cracking as shown in Table 2.

Typical processing, which is commonly used for this type steel, involved (i) slab reheating, (ii) controlled rolling finished at 790°C and 830°C, for the #S and #R grades, respectively, (iii) accelerated controlled cooling (ACC) followed by (iv) either accelerated tempering for the #S grade at 630–650°C or conventional tempering at 680°C for the #R grade. After treatment, the thickness of the plates for the #S and #R plates was 11 and 12 mm, respectively. The round samples of 10 mm diameter and 120 mm long were turned from the plates.

The microstructure of both type samples in the as-received state, i.e. after thermo-mechanical treatment, is shown in Fig. 1. The controlled rolling according to the above standard industrial regime #S was completed in the temperature interval AC1-AC3 which ensured a good cold resistance of this steel.10) As can be seen in Fig. 1(a), this regime results in formation of a ferrite-perlite structure with significantly elongated grains having average dimensions in rolling direction of 80 μm. The perlitic phase exhibiting a characteristic banded contrast is clearly seen together with a large fraction of ferritic grains with a well-developed polygonized dislocation substructure and coarse segregations of cementite at the boundaries, Fig. 1(b). The accelerated tempering did not give rise to substantial change in the cementite appearance.

The controlled rolling according to the regime #R was completed at higher temperatures in the austenitic region. This regime provides a higher resistance to HIC at just slightly compromised strength characteristics and higher ductility, Table 2. The susceptibility to HIC has been evaluated by CLR and CTR measurements in accord with NACE TM0284 recommendations. Several strength pertinent mechanical characteristics of the steels under investigation are gathered in Table 2. Increasing cooling rate after deformation promoted formation of a typical bainitic-martensitic structure. Subsequent tempering results in degradation of the bainitic-martensitic structure and in spheroidization of carbides. The microstructure of the #R samples is shown in Figs. 1(c) and 1(d). The samples which have been produced via regime #R are differed from #S by their significantly more uniform structure consisting of equiaxed ferrite and perlite grains. Polygonization has not been observed in #R samples.

Hence, the two type samples of the commercial grade steel with similar chemical compositions and mechanical properties but with different microstructures and different susceptibility to HIC have been received and labeled as #S and #R, cf. Tables 1 and 2.

According to the purpose of this work, by comparing AE histories in the steel with different susceptibility to environmental attack, the identification of AE signatures associated with hydrogen embrittlement and cracking is supposed to be feasible. The susceptibility to HIC was evaluated in accord with NACE TM0284 recommendations in terms of CLR and CTR.

2.2. Hydrogen Charging and Acoustic Emission Measurements

A schematic diagram of the experimental setup is shown in Fig. 2. For hydrogen charging, the sample was mounted in the corrosion cell lid. Its gauge part was immersed into a corrosive solution, leaving the sensor clamping area outside. The 20 mm diameter wideband AE sensor MSEA-L2 with the head-in 27dB preamplifier was mounted on a truncated cone shape coupler which was made of the same steel of 30 mm length and designed to adjust the diameter of the sensor and specimen. The coupler was soldered to the sample. Testing was performed in the NACE TM0284 standard soar solution containing 5% NaCl and 0.4% CH₃COONa in distilled water under 1 bar partial pressure of the H₂S gas.

| Specimens | C   | Si  | Mn  | S   | P   | Cr  | Ni  | Cu  | Al  | V   | Fe  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| #S        | 0.10| 0.57| 0.56| 0.003| 0.009| 0.07| 0.09| 0.16| 0.034| 0.05| balance |
| #R        | 0.10| 0.58| 0.56| 0.002| 0.010| 0.07| 0.25| 0.13| 0.038| 0.06| balance |

Table 1. Chemical composition of the 09GSF pipeline steel.

| Thermo-mechanical treatment | Mechanical Properties during Tensile Testing | Impact Toughness, MJ/m² | Ductile Component Fraction in Fracture Relief of Impact Specimens Tested at –50°C | Hardness, HRB | Susceptibility to Hydrogen Embrittlement* |
|-----------------------------|---------------------------------------------|--------------------------|---------------------------------------------------------------------------------|---------------|----------------------------------------|
|                            | Yield Stress (YS), σ₀₂, MPa | Ultimate Tensile Strength (UTS), σ₅₉₅, MPa | Elongation at Break, δ | Stress Ratio σ₀₂/σ₅₉₅ | KCV–40 | KCV–50 | CLR | CTR |
| #S                         | 437                          | 540                       | 25                      | 0.81                          | 245 | 269 | 28.0 | 4.2 |
| #R                         | 424                          | 525                       | 32                      | 0.82                          | 337 | 333 | 84   | 0.5 |

* According to NACE TM0284.
samples were exposed to the aggressive environment for 100 h. AE was recorded periodically every day (2–4 recording sessions daily). Every AE recording session lasted for 2 h. The signal from the sensor was transferred through a main low-noise filter-amplifier MSAE-FA010 to a PC-controlled AE system for data acquisition, storage and processing. The AE set-up is based on a 12 bits ADC with the 16 K buffer memory on-board which provides the agreement between the high-speed data acquisition at the 6.25 MHz sampling rate and the rather slow computer-to-board PCI interface.

Post-experimental data processing included the power spectral density calculations as documented in.11) For every recorded realization the 4096 point Fourier power spectral density (PSD) $G(f)$ was calculated with a 20 kHz rectangular spectral smoothing window. Several parameters were calculated both in time and frequency domains for each realization. Two descriptive variables - the “AE energy per event” ($E$) and “median frequency” ($f_m$) – were selected among a variety of other measurable characteristics for AE characterization. The energy “per event” is calculated by integrating $G(f)$ over a whole frequency range from $f_{\text{min}}=50$ to $f_{\text{max}}=1250$ kHz: $E = \int_{f_{\text{min}}}^{f_{\text{max}}} G(f) \, df$. Then all spectral densities were normalized to the energy for comparison. The median frequency of the PSD function $G(f)$ is calculated from definition. Both parameters $E$ and $f_m$ are obtained after smoothing of $G(f)$ and subtraction of the power spectral density of the pre-recorded noise.

All signals were categorized with respect to the shape of their PSD functions, using a partitioning algorithm described in.12,13) The correlation coefficient (known also as the coefficient of discrimination) was used as a measure of similarity/dissimilarity between pairs of PSD functions. In other words, the origin of signals belonging to the same group is supposed to be the same, whereas it is different for the signals belonging to different groups. During each recording session, up to ten groups of signals were recognized with respect of the typical shapes of spectra. Then, the groups containing a small number of signals amounting to less than 1% of the total number of recorded signals were considered as outliers and were excluded from the analysis.

After spectral categorization, the quality of grouping was cross-verified by means of parametric clustering using a c-means fuzzy logic clustering procedure (see a seminal work by Bezdek14) for details) in the energy-median frequency coordinates. The c-means fuzzy logic clustering algorithm
was implemented in MATLAB™ environment.

3. Results and Discussion

Optical observations of the specimen surface after testing revealed hydrogen induced cracks only in the #S sample. The damage appears in a form of surface blistering typical of the hydrogen attack in this type carbon steel, Fig. 3. Requiz et al.1) have investigated the susceptibility to hydrogen damage on API 5L X52 steel, which is a close analogue of the steel used in the present work. The blistering observed in1) was associated with the presence of inclusions.

All recorded AE signals fall naturally into three primary categories denoted as I, II and III, respectively, differed substantially by their PSDs, Fig. 4. Besides, it is also possible to distinguish between modifications of these extreme cases: I-II, II-I and II-III. It seems evident, that the latter secondary groups have frequency features inherited from respective pairs of primary categories. As will be shown below, the AE histories for the above classes of signals differed substantially in the #S and #R specimens, Fig. 5.

It is worthy noticing that the signals belonging to only two primary classes I and II and their mixed modifications I-II and II-I were observed in the #R specimens, Fig. 5. From visual observations of the typical spectral shapes, it is plausible to suppose that the spectral modifications I-II and II-I arise from superposition of signals of type I and II emitted at the same time or within a short time interval not exceeding a duration of a single recorded AE realization. No substantial change in the AE behavior is noticed during the first 48 hours: the signals of type I constitute of 65% of the total number of recorded signals, while the signals of the type II correspond to about 22%. After about 50 h, the number of type I signals increases steadily, while the number of type II signals reduces and then completely vanishes. On the late stage of hydrogen charging the type I signals alone remain active, Fig. 5(a).

The picture is considerably more complicated for the samples #S. Similar to #R, signals of only types I and II are observed during the first 24 h. However, the majority of the signals can be regarded as being of mixed type I-II. Furthermore, after 24 h almost 40% of all signals belong to a new category III and mixed II-III, which has never been observed in #R specimens, Fig. 5(b). Then, after 48 h exposure to the aggressive environment the signals of virtually all major types are present in #S specimens. Finally, after 94 h the type I signals dominate again as it was seen in the case of #R specimens on the late stage of hydrogenation.

Same trends are also clearly seen in Fig. 6 where bi-vari-ate distributions are shown in $E_{f_m}$ coordinates. C-means clustering applied to these distributions allows discriminating between three typical clusters with significantly distant centroids, which are shown by scatter ellipses at 95% confidence level in Fig. 6 (normal distribution of events within each cluster is assumed in construction of scatter ellipses). Cluster I comprises of signals with lowest median frequencies ranging between 60 and 70 kHz, which corresponds nicely to the characteristics of the group I in the spectral shape categorization, Fig. 4. Cluster II contains the signals with intermediate median frequencies ranging from 110 to 140 kHz. The clusters are denoted by the same symbols as

![Fig. 3.](image-url) Smooth and “defectless” surface of the #R specimen after immersion into a H$_2$S containing soar solution (a) and hydrogen-induced blistering on the surface of #S specimen (b) after the same exposure to aggressive environment.

![Fig. 4.](image-url) Typical shapes of AE spectra corresponding to different groups of signals distinguished by the spectral shape categorization technique. Spectral densities averaged over each group are shown for comparison.
those in Fig. 5. Cluster 3 is featured by signals with highest frequency $f_m=150–200$ kHz. The fine cross symbols in Fig. 6 denote the minority of signals (outliers), which have not been assigned to any of the major clusters I, II or III, as their quantity is not sufficient to form a definite cluster. Hence, the parametric cluster features appear to be in excellent agreement with the spectral shape categorization represented in Fig. 4. One should bear in mind that by using the parametric clustering scheme it is rather difficult to quantify the difference between realizations, which mix the features from different groups such as I-II. Nevertheless, in principle, both spectral shape categorization and parametric clustering yield similar results. This makes it possible to use automated procedures in order to discriminate between different active AE sources during hydrogenation of commercial pipeline steels with a high confidence. The discrimination procedure and its interpretation can be outlined as follows.

1. The majority of AE signals recorded during hydrogenation of the steel in the H$_2$S containing environment, belongs to the class of low-frequency type I signals in all tested specimens regardless of the exposure time. Hence, these signals are related to a certain process which commences shortly after immersion of the specimen into a soark solution and then it takes place quasi-continuously until the end of the test. It is therefore reasonable to associate these signals with hydrogen bubbles which are generated during hydrogen charging. The hydrogen bubbles have long been recognized as potential AE sources during corrosion processes.$^{3,4,15,16}$

2. Second type AE signals, II, are also observed in all specimens. However, the fraction of these signals reduces notably after a certain time interval (e.g. 48 h). Most likely this type signals is associated with formation of a sulfide film on the surface during corrosion process, (see, for example, Ref. 9) for details of FeS film formation and associated AE signatures). One can suppose that the sulfide film forms faster on the surface of samples #S which have been proven more susceptible to corrosion. Therefore, the activity of type II signals is reasonably high in #S samples. As a result, the

![Fig. 5.](image)

**Fig. 5.** Evolution of the fraction of different type AE signals recorded during hydrogenation of the 09G2F pipeline steel after special (a) and conventional (b) heat treatment.

![Fig. 6.](image)

**Fig. 6.** Scatter-plots showing distributions of AE parameters in Energy vs Median Frequency (E-fm) coordinates. Scatter ellipses show clusters of signals belonging to different types.
signals originated from two independent processes corresponding to hydrogen bubble (type I) and sulfide film formation (type II) can overlap giving rise to AE signals of a mixed type I-II, Figs. 4 and 6. A soon as a whole surface is covered by the sulfide film, the type II signals cease to emit, Fig. 5.

(3) Taking into account that the signals of types III and II-III are observed only in the specimens #S, which are particularly susceptible to hydrogen attack, the nature of AE type III signals is transparent: the signals of this kind are caused by hydrogen induced cracking. During blistering the fresh surface is exposed to an aggressive environment, Fig. 2. Hence the sulfide film will form again and, therefore, the activity of the type II signals in #S specimens remains considerably high during the test in contrast to #R specimens where the type II signals vanish after a certain period of time, Fig. 5.

4. Conclusion

The acoustic emission technique shows a high potential for monitoring of hydrogen embrittlement in pipeline steels. It is demonstrated that quantitative discrimination between different types of AE sources such as bubbles formation, sulfide film formation and hydrogen-induced cracking, which are active during hydrogen induced damage, is feasible by means of cluster analysis. Although further detailed clarification of underlying AE source mechanisms is still needed and is a scope of the further work, the proposed signal classification techniques can be potentially adapted for unsupervised workflow aiming at real-time damage evaluation in laboratories and in the field.

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