ANALYSIS OF THE HYDROGEN DEGRADATION OF LOW-ALLOY STEEL BY ACOUSTIC EMISSION

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Abstract

The hydrogen effect of low-alloy steels applied to the petrochemical, chemical and energy industry is the phenomenon, which significantly influences the integrity and safety of industrial installations. Hydrogen degradation with other operating conditions, the elevated temperature, pressure and stress, produced many material defects in micro- and macro-scale. It is critical to determine the influence of degradation factors on mechanical properties of structural materials to assure safe operation. For the precise assessment by the AE, it is necessary to perform AE study in laboratory conditions and collect experimental data, which will provide information for analysis of AE measurements in the service conditions.

The study was performed on a 13CrMo4-5 steel with or without hydrogen charging. The AE signals were measured during loading applied by a testing machine. The AE study was compared to the investigation carried out by scanning electron microscopy, which showed many changes in the microstructure of material after hydrogen charging. The hydrogen charging was realized by cathode polarization. This presentation shows the results of laboratory study on the application of the AE testing during modified mechanical tests to evaluate the material degradation under the hydrogen influence and operating conditions.

Keywords: Low-alloy steel, degradation, hydrogen

Hydrogen Degradation

Systematic rise of interest in the use of hydrogen in different branches of the industry may be seen in recent years. Hydrogen is used for energetic purposes (as fuel, in synthetic fuel production processes involving coal liquefaction method, in refinery hydrogen processes) and non-energetic (as a raw material in chemical industry, as reducing gas in metallurgy). In the case of the oil refining industry, the desire of stepping up production of engine fuels is related to the inevitability of intensification of crude oil processing. It calls for starting new hydro-cracking or hydro-desulfurizing installations, and for launching new hydrogen generating plant. The material applied must show high resistance to the destructive influence of hydrogen. The degree of hydrogen degradation varies and depends on many factors (e.g., structural, mechanical). In the case of steel, hydrogen damage may reveal itself as delayed hydrogen cracking, degradation of mechanical properties, especially ductility, and can change microstructures and create bubbles filled with molecular hydrogen, methane or hydrogen sulfide. Intensity of the material degradation caused by hydrogen saturation, depends considerably on the speed of diffusion of hydrogen in the given type of steel, as well as on the metal’s ability to dissolve hydrogen. Hydrogen penetration through the low-alloy steels is very high because of high coefficient of hydrogen diffusion through the crystal lattice of iron. Hydrogen can also be transported through the core of dislocation or grain boundaries, which greatly increases its penetration [1, 2]. The
process of hydrogen destruction of metals and its alloys is complex and therefore it is not possible to determine one form of hydrogen degradation. Predicting the form of hydrogen destruction or the degree of its intensity, and suggesting universal parameters allowing for prediction of deterioration of any material, without detailed experiments that match each case, is not possible. Aggressive thermo-mechanical conditions, to which materials are subjected under real operating conditions and the presence of hydrogen, create real danger of hydrogen degradation taking place. Those materials may undergo high temperature hydrogen attack, but their hydrogenation may take place at ambient temperature as well, e.g., in petrochemical installations where in real corrosive conditions, we also deal with hydrogen penetration.

Experimental Procedures and Results

The study was performed on a low-alloy steel 13CrMo4-5 (1Cr-1/2Mo). Results of experiments performed on the steel in the initial state, after cathodic hydrogen charging and after exposure to operating conditions were compared in this study. The hydrogen charging was by cathode polarization in a 0.5M-H2SO4 solution with the addition of 5 mg/dm³ As2O3, to promote hydrogen penetration at ambient temperature. The current density used was 20 mA/cm² for an exposure time of 3 hrs. The samples in the exposed state were taken from cut-outs of an industrial pipe, used for 10 years. This pipe was selected by performing non-destructive testing (NDT) that detected the reasonable hydrogen degradation. The substance transported through the pipe contained hydrocarbons, hydrogen, water and sulfur-containing fuel and had higher concentrations of H2S. The maximum operating temperature of the pipe reached 60°C.

In order to show the effect of hydrogen on the microstructure, microscopic observations were carried out by using a scanning electron microscope (SEM). Samples selected for examination were chemically etched with 4% Nital. In order to determine the degree of material degradation, hardness tests, tensile tests and fracture toughness tests were performed. Hardness tests were conducted with Rockwell (A scale) and Vickers (HV5) methods. Tensile tests were performed at ambient temperature, with a strain rate of 4.17 x 10⁻⁴ [s⁻¹]. Fracture toughness tests were performed at ambient temperature with compact-type samples.

Acoustic emission (AE) examinations were performed during two different, modified mechanical tests, which were carried out with the help of the static loading machine of 5 kN maximum force. The first of them consisted in loading of the tested surface of the material with 5–mm diameter ball indenter. In order to perform this test specially designed test set-up was employed, which allowed for attaching AE sensor on the ball indenter. The maximum force during test was 0.6 kN. The second test was performed on compact-type samples for plane strain fracture toughness test with pre-cracks made before tests. Pre-cracks were made with the varying load method at 20-Hz frequency. The lowering of the force amplitude below 3 kN was the criterion for the pre-crack test end. The length of the pre-crack in the samples for AE tests was about 5 mm. During AE measurements, two AE sensors (150-kHz resonant frequency) were employed, mounted opposite on the sample surfaces parallel to the pre-crack plane. The maximum force during tests equaled 5 kN. Schematics of the AE tests together with the results are given later. Analysis of the registered AE signals is given as the diagrams of amplitude [dB] vs. time, which were correlated with the force graph. Those results were related to force vs. cumulative number of events (AE hits) graph, in order to show Kaiser and Felicity effect.
**Mechanical Tests**

Hardness tests did not reveal differences between materials in the initial state and after cathodic hydrogen charging and after exposure to operating conditions. Tensile test results demonstrated slight decrease of plasticity of material after exposure to the operating conditions of 5~10% in relation to the starting material. Yet all determined strength parameters of tested materials fulfilled all standard guidelines for steel types tested. In the case of fracture toughness tests, the sample size did not meet the criterion of plane strain state [3, 4]. For all cases, the plastic zone size at the crack tip was greater than 5% of the specimen thickness and crack surface morphologies indicated significant ductility. Additionally, the material subjected to operating conditions developed macroscopic structural defects, making further test impossible (Fig. 1). Microstructural defects under the cyclic loads increased to the critical size and stopped the crack propagation. Microstructure examination performed revealed numerous micro-structural changes in the degraded materials. The microphotograph showing changes in hydrogen charged material is displayed in Fig. 2.

![Sample after fracture toughness test, material taken from a pipe.](image1)

![Microstructural changes in hydrogen charged material.](image2)

In connection with problems described above, it was stated that quantitative determination of the degree of degradation of studied materials with the help of the mechanical tests performed is not possible.

![AE measurement results of hydrogen charged material during indenter loading.](image3)
Acoustic Emission Study

AE study, using indenter, was performed during cyclic material loading in two measurement sequences shown in Figs. 3 and 4. In the case of the hydrogen charged material (under laboratory conditions), the number of accumulated AE hits was 123 (Fig. 3). The cumulative AE hits vs. force curve (Fig. 3) shows the presence of the Felicity effect during repeated loading of the material between 320 s and 370 s of the test with Felicity ratio of 0.87. In the case of the material after exposure, a higher acoustic activity was registered with clear Felicity effect (Fig. 4) during second measurement sequence. Cumulative AE hits reached 758, and Felicity ratio equaled 0.35. Material after exploitation characterized itself with higher acoustic activity during loading. In the case of the material, in the initial state, the number of cumulative AE hits was 101 and the Felicity effect was not detected.

In order to compare the results obtained for all three materials, relationship between severity and historic index is shown in Fig. 5. This clearly reveals the difference between AE recorded for degraded materials and material in the initial state.

Though comparable number of signals recorded in the case of the hydrogen charged material and material in the initial state, severity values show, that these signals are of higher energy than those registered in the material in the initial state. SEM inspections performed on the material cross section under indentation surface revealed the presence of the cracks in the degraded
materials (Fig. 6). Cracks recorded may be the potential reason of increased AE activity during indentation tests.

AE tests of the compact samples with pre-cracks were performed during loading of the material according to the schematic shown in Figs. 7 and 8. One should note that the samples were subjected to hydrogen charging after pre-cracks were made. It could intensified the hydrogen-induced degradation at the pre-crack tip as comparing to specimens cut from the material after operating conditions. The atomic hydrogen during cathodic charging derived from metal-environment surface reaction diffuses to microstructural heterogeneities at the crack-tip such as voids and microcracks, recombines to the molecular form, and builds up a very high internal pressure [5]. Felicity ratio of the hydrogen charged samples prepared for fracture toughness test equaled 0.27.

![Fig. 7. AE measurement results of the hydrogen charged samples for fracture toughness test.](image)

![Fig. 8. AE measurement, during loading, results of the samples for fracture toughness test from the material after exposure to operating conditions.](image)

Characteristic of the material after exposure to operating conditions, as compared to other materials is the presence of AE during load decreases in the first and last cycles. Felicity ratio of the material after exposure amounted to 0.43. In the case of the material in the initial state number of AE hits recorded amounted to 83, and Kaiser effect was observed. Material after hydrogen charging produced more AE signals in the first part of the test, than the material after exposure. The different extent of the material degradation at the crack-tip could influence AE activity during the first loading to the maximum. Higher number of cumulated AE hits 1412
Comparison of the test results performed on the compact samples is shown in Fig. 9, which illustrates meaningful rise of severity value for material in the degraded state. In Fig. 10, one can see fracture of the sample made of the material after exposure, with visible micro-cracks characteristic of degraded material. Microscopic examination revealed change of the fracture character from ductile for samples in the initial state, to locally brittle and mixed brittle – ductile (partly brittle for samples exposed to degradation).

**Summary**

Standard mechanical tests do not always allow the estimation of the degradation of the material exposed to operating conditions with hydrogen environment. The use of acoustic emission in connection with modified mechanical examinations showed significant differences in AE signals recorded. Suggested method of examination was devised on the basis of numerous tests conducted on the material charged with hydrogen under laboratory conditions. On this basis a series of tests were performed on the material taken from cut-out of the pipe operated under real life conditions. This clearly revealed the differences in AE signals recorded in relation to material in the initial state.

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**References**