HYDROGEN-ENHANCED STRESS CORROSION CRACKING OF LOW ALLOY STEELS IN SEAWATER

ABSTRACT

The susceptibility to stress corrosion cracking of carbon and two low alloy steels of different strength was determined in seawater at corrosion and cathodic potentials with the Slow Strain Rate Tensile Test. The slight decrease in time-to-failure, fracture energy and reduction-in-area at corrosion potential and substantial decrease in those parameters at application of cathodic polarisation in comparison with the values measured in air, were observed. The significant linear relationships between the degree of degradation and the content of diffusive hydrogen were obtained for investigated steels. Within the potential range existing on the ship hull at its cathodic protection, no important difference in the loss in mechanical properties was stated between tested steels, despite their different strength.

INTRODUCTION

The hydrogen degradation is a common term used to describe the hydrogen-enhanced localised plasticity, formation and decomposition of brittle hydrides, formation of blisters and hydrogen microbubbles, which cause the loss in plasticity and propagation of slow cracks, observed in a variety of steels [1] and over a hundred of non-ferrous metals and alloys [2]. The phenomenon observed during slow strain rate tests made in presence of substantial amounts of hydrogen, e.g. during cathodic polarisation, has been recently described as hydrogen-enhanced stress corrosion cracking.

The best resistance to hydrogen embrittlement of low strength carbon steels is well-known and steels of tensile strength below 800 MPa are relatively immune to hydrogen cracking. For those materials, their blistering and failure along the lines of non-metallic inclusions rather than the hydrogen-induced delayed cracking should occur [3, 4]. Microstructure plays a secondary role as compared with that of strength level [3], and pearlite – ferrite microstructure is susceptible to hydrogen degradation to similar extent as that of tempered martensite [5]. The inclusions of sulphides and oxides may trap a substantial quantity of hydrogen and initiate cracks [5, 6].

High strength low alloy steels are the structural materials of wide and increasing application. According to the rules of the Classification Societies [7], the three groups of hull ship steels are allowed: carbon steels of normal strength ($R_{e\min} = 235$ MPa and $R_m = 400$-$502$ MPa) of four grades A, B, D, E (of different temperature of Charpy test), high strength low alloy steels of three different yield stress ($R_{e\min} = 315$ MPa, $355$ MPa or $390$ MPa) and different temperature of Charpy notch test (grades A, D, E, F), and extra high strength low alloy quenched and tempered steels of six different yield stress value ($420$, $460$, $500$, $550$, $620$ and $690$ MPa) and four grades
A, D, E, F. The difficult welding of low alloy steels and their uncertain resistance to general and localised corrosion, stress corrosion cracking, hydrogen degradation and corrosion fatigue limit wide application of the last group of materials in shipbuilding industry.

The low alloy steels of increased strength have been suggested to corrode at similar rate as ordinary steels. The thinning of steel walls corresponds to increase in stress forced on the ship hull construction. On the other hand, application of cathodic protection and danger of overprotection, especially in presence of sulfate-reducing bacteria, may result in the appearance of huge amounts of hydrogen, its penetration and finally hydrogen degradation or hydrogen-induced stress corrosion cracking of both carbon and alloy steels [8-11].

The possibility of hydrogen-enhanced stress corrosion cracking is one of reasons considered at making decisions of an application of high strength and extra high strength low alloy steels in shipbuilding industry to construct the ship hulls and superstructures. The present work has been aimed to study this task and, especially, to quantitatively determine the relationships between the degree of hydrogen degradation and the hydrogen diffusivity, total hydrogen content and diffusive (mobile) hydrogen concentration.

**EXPERIMENTAL**

**Materials**

Three steels were tested: carbon steel St41 (grade A), high strength low-alloy steel 15G2ANb (grade AH36), and extra high strength low alloy, quenched and tempered, 17HNMBVA steel (grade E690). The characteristics of steels are given in Table 1.

As the test solution, the artificial seawater of chemical composition and preparation according to the Polish Standard was used.

<table>
<thead>
<tr>
<th>Mechanical property/composition</th>
<th>Unit</th>
<th>Grade of steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>St41</td>
</tr>
<tr>
<td>Yield stress</td>
<td>MPa</td>
<td>339</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>425</td>
</tr>
<tr>
<td>RA</td>
<td>pct.</td>
<td>30.2</td>
</tr>
<tr>
<td>Impact toughness</td>
<td>J</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>wt%</td>
<td>0.134</td>
</tr>
<tr>
<td>Mn</td>
<td>wt%</td>
<td>0.479</td>
</tr>
<tr>
<td>Si</td>
<td>wt%</td>
<td>0.242</td>
</tr>
<tr>
<td>Cr</td>
<td>wt%</td>
<td>0.0682</td>
</tr>
<tr>
<td>Ni</td>
<td>wt%</td>
<td>0.0591</td>
</tr>
<tr>
<td>P</td>
<td>wt%</td>
<td>0.00150</td>
</tr>
<tr>
<td>S</td>
<td>wt%</td>
<td>0.0229</td>
</tr>
<tr>
<td>V</td>
<td>wt%</td>
<td>&lt;0.00050</td>
</tr>
<tr>
<td>B</td>
<td>wt%</td>
<td>0.00100</td>
</tr>
<tr>
<td>Content and shape of oxides*</td>
<td></td>
<td>TP-a3</td>
</tr>
<tr>
<td>Content and shape of sulfides*</td>
<td></td>
<td>S-b4</td>
</tr>
</tbody>
</table>

*According to the Polish Standard PN-64/H-04510
Experimental procedure

The potential range was set up upon the basis of theoretical distribution of electrochemical potential over the ship hull. The distribution of electric field over the area of ship hull in sea water was calculated with the boundary elements method for flat area of the 173 m long ship hull, on which four 0.3 m long polarisation anodes surrounded by anode screens 7 m long were placed. The boundary was divided into 686 elements. The approximation was made with the isoparametric boundary elements assuming that the solution of the Laplace equation is constant over the length of element.

The susceptibility to stress corrosion cracking was determined with the Slow Strain Rate Testing. The round smooth specimens, 5 mm in gauge diameter, were immersed in artificial seawater and simultaneously strained at a rate of \(10^{-6} \text{s}^{-1}\). The undeaerated test solution was slowly flowing through the chamber. The fracture energy, reduction-in-area (RA) and time-to-failure were measured during or after the test. The reference specimens were strained at the same strain rate in dry air (humidity below 15%). The tests were carried out with fully computerised, especially designed and constructed equipment, following the requirements shown in [12]. The tests were made at different cathodic potential and repeated at least three times for every steel and cathodic potential, and the mean values were taken into account.

The hydrogen permeation through the membranes (0.1 cm thick) made of studied steels was measured electrochemically by the Devanathan-Stachurski [13] method. The ingress side of membrane was exposed to the test solution and polarised at cathodic potential within the range calculated for the cathodic protection. The egress side of membrane was coated with palladium and exposed to 0.1N NaOH solution. The anodic polarisation +150 mV was applied to the egress side, and the anodic current, being the measure of hydrogen permeation rate, was recorded in the egress cell. At application of cathodic polarisation to the ingress side, the build up hydrogen permeation transient was recorded until the steady state value of permeation current \((J_{\infty,n})\) was attained. After that, higher cathodic potential was applied to the ingress side, and the next transient was recorded. At the end, polarisation of ingress side was cut-off and the decay permeation transient was recorded in the egress cell. The content of permeable (mobile) hydrogen at the ingress side of a membrane \((C_S)\) at applied potential and the hydrogen diffusivity \((D)\) were established from the build-up and decay transients, respectively, according to equations:

\[
D = 0.05* L^2 / \tau_{th}
\]

\[
C_S = 29.46*10^{-7} \{J_{\infty,n}^*L/D\}
\]

where: \(L\) – the thickness of the membrane, \(\tau_{th}\) – the breakthrough time as measured from the decay permeation transients, \(J_{\infty,n}\) – the steady state values of hydrogen permeation current at build up transients at given \((n)\) cathodic potential.

The total hydrogen content \((C_t)\) was measured by the vacuum extraction technique at 673 K for specimens subjected to cathodic polarisation at constant potential for 120 h. The hydrogen content extracted from the as-received specimen was subtracted from the hydrogen content established for hydrogen charged specimens in order to estimate the amount of absorbed hydrogen. The scattering of vacuum extraction measurements was as high as 15%. The mean results for three measurements were taken into account.

The microstructure of steels was examined with the light microscope. The fracture examinations were made with the XL-50 Philips scanning electron microscope.
RESULTS

Microstructure

The microstructure of studied steels is shown in Figure 1. The ferrite-pearlitic structure of the St41 steel contained about 30% pearlite volume fraction, traces of rolling texture, and various grain size. The 15G2ANb steel exhibited ferrite-pearlitic structure, of about 40% volume fraction of pearlite, traces of rolling texture, uniform and very small grains. The 17HMBVA steel exhibited sorbitic structure of tempered martensite with relatively coarse needles. The high number of inclusions of oxides and sulphide was observed in the St41 and 15G2ANb steels.

![Microstructure of studied steels](image1.png)

Fig. 1. Microstructure of studied steels

Calculation of distribution of electrochemical potential

The obtained distribution of electric field over the ship hull contour is shown in Figure 2. The very high increase in potential is observed around the polarisation anodes. Assuming that anode screens protect sufficiently that area, the lowest value of potential at the boundary of anode screens may be estimated at $-1250 \text{ mV}_{\text{SCE}}$. However, taking into account the possibility of overprotection or underprotection occurred in some places of hull during the service, all the tests were done within the range from the corrosion potential up to $-1700 \text{ mV}_{\text{SCE}}$.

![Distribution of electrochemical potential](image2.png)

Fig. 2. Distribution of the electrochemical potential along the ship hull
Mechanical tests

The fracture energy, time-to-failure and RA expressed as relative values (ratio of each value measured in corrosion solution to that measured in air) are demonstrated in Figures 3-5 for tested steels as a function of electrochemical potential. For all steels the measured parameters gradually decreased with cathodic polarisation: the loss of fracture energy and decrease in time-to-failure were apparently lower than loss in RA. The degree of hydrogen degradation was similar for all materials.

Fig. 3. Effect of cathodic potential on the relative values of: fracture energy (RFE), time to failure (RTTF) and reduction in area (RRA) measured in SSRT tests in seawater for the St41 steel

Fig. 4. Effect of cathodic potential on the relative values of: fracture energy (RFE), time to failure (RTTF) and reduction in area (RRA) measured in SSRT tests in seawater for the 15G2ANb steel
Fractography

The selected results of fractographic examinations are shown in Figures 6-8. The ductile fracture faces were observed for all steels tensed in air. The lamination and inclusions of manganese sulfide appeared for steels ST41 and 15G2ANb (Figures 6a and 7a). In hydrogen charged steels mixed ductile–brittle fracture occurred.

Fig. 6. Fracture surface of steel ST41: (right) tested in air: plastic fracture, lamination in area of the manganese sulphide and (left) tested in seawater at -1640 mV: mixed plastic-brittle fracture
Hydrogen permeation and extraction measurements

Table 2 shows the values of hydrogen diffusivity (D) for studied steels, estimated from the hydrogen permeation measurements. The highest diffusivity exhibited the St41 steel, the lowest one – 17HMBVA steel.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Diffusivity (D), m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>St41</td>
<td>$1.92 \times 10^{-9}$</td>
</tr>
<tr>
<td>15G2ANb</td>
<td>$9.65 \times 10^{-10}$</td>
</tr>
<tr>
<td>17HMBVA</td>
<td>$1.9 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Figure 9 shows the content of mobile hydrogen at the ingress side of the studied steels membranes (Cₘ) at their cathodic polarisation. The highest mobile hydrogen content exhibited the 17HMBVA steel. At polarisation more cathodic than about –1400 mV, no further increase, or even slight decrease in hydrogen content was observed. The effect was probably due to the alkalisation of near electrode electrolyte due to the hydrogen evolution at cathodic polarisation, which may cause the decrease in hydrogen evolution.

The mean values of total hydrogen content (Cₜ) absorbed by studied steels at cathodic polarisation are shown in Figure 10.

**Fig. 9.** Effect of electrochemical potential on the content of mobile hydrogen established in hydrogen permeation tests for studied steels

**Fig. 10.** Effect of electrochemical potential on the content of total hydrogen established in hydrogen extraction measurements for studied steels
DISCUSSION

The relationships between the estimated hydrogen-related parameters (concentration of mobile hydrogen and total hydrogen content) and any of three material-related parameters, including the time-to-failure, fracture energy and RRA value in the slow strain rate tests, expressed as relative values, were analysed. There was no good correlation found between either of material-related parameters and the total hydrogen content. However, significant linear correlation was observed between almost relative values of all considered mechanical parameters and the content of the mobile hydrogen. The Pearson product-moment correlation coefficients between both mobile and total hydrogen contents, and fracture energy, time to failure and RA value are shown in Table 3. It is worthy to note that the relative RA value appeared to be the most reliable parameter in mechanical tests, in accordance with previous results [14-16]. Such relationships between mobile hydrogen content and RA value are demonstrated in Figure 11.

Table 3. Pearson product-moment correlation coefficients for relationships between mechanical parameters determined with the Slow Strain Rate Test and hydrogen-related parameters for studied steels

<table>
<thead>
<tr>
<th>Mechanical parameter</th>
<th>Mobile hydrogen concentration</th>
<th>Total hydrogen concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>St41</td>
<td>15G2ANb</td>
</tr>
<tr>
<td>Relative fracture energy</td>
<td>–0.38</td>
<td>0.72*</td>
</tr>
<tr>
<td>Relative time-to-failure</td>
<td>–0.73</td>
<td>–0.75*</td>
</tr>
<tr>
<td>Relative RA value</td>
<td>–0.91*</td>
<td>–0.79*</td>
</tr>
</tbody>
</table>

*correlation significant at p = 0.05

Fig. 11. Relationship between relative RA values and content of mobile hydrogen for studied steels
The susceptibility to hydrogen induced degradation is related to the microstructure features governing the hydrogen mobility and trapping in the metal structure. Hydrogen traps may be irreversible or reversible [17], the former contributing to the quantity of total hydrogen and could only slightly affect the hydrogen mobility. On the other hand, the established values of mobile hydrogen \( (C_S) \) reflect the diffusive hydrogen and hydrogen associated with the reversible traps. If the mean hydrogen content established in vacuum extraction measurements \( (C_t) \) were associated only with the mobile hydrogen, the rough relationship \( C_t = 0.5*C_S \) should have been expected. The measured much higher amounts of total hydrogen content (cf. Figures 9 and 10) should be accounted for the presence of hydrogen within the traps in the metal structure.

Hydrogen, irreversibly trapped within the structure of medium and high strength steels, does not affect the metal susceptibility to hydrogen cracking of steels, whereas, the reversible trapped hydrogen may decide on the degree of the steel degradation.

The reversible trapping results in initiation of cracks followed by their propagation provided the hydrogen transport is fast enough. Because there is an equilibrium between lattice hydrogen and hydrogen trapped by reversible traps, the change in degree of hydrogen cracking should follow the change in quantities of both forms of hydrogen. As a result, the relationship between the concentration of mobile hydrogen and the loss in plasticity has been observed for studied steels.

The obtained results show (Figure 9) that the amount of mobile hydrogen is much higher in the martensitic extra high strength steel than in the other steels. Therefore, the critical hydrogen concentration causing the critical degradation of metal should be relatively high in 17HNMBVA steel. This may be related to the different microstructures of investigated steels: the low number of non-metallic inclusions in the martensitic steel in comparison to the high number of inclusions, especially the long sulphides in pearlite – ferrite steels. Inclusions trapped hydrogen and caused the local stress concentration; both phenomena impact the initiation of cracks [18, 19]. Therefore, the required amount of mobile hydrogen may be lower in the case of high number of crack initiation sites. The higher hydrogen content required to cause the degradation of 17HNMBVA steel might be also associated with lower hydrogen diffusivity in this steel (Table 2). In such a case, the delay in crack propagation may be expected due to the hampering of hydrogen transport to the crack tips.

**CONCLUSIONS**

1. The tested St41 carbon steel, 15G2ANb high strength low alloy steel and 17HMBVA extra high strength low alloy steel revealed the moderate degree of susceptibility to hydrogen degradation. Within the potential range corresponding to the cathodic protection, no distinct difference in susceptibility to hydrogen damage was observed for studied steels, despite the difference in strength and microstructure.

2. For each tested steel, the good linear correlation between degree of hydrogen degradation (decrease in time-to-failure, reduction in area or fracture energy) and the content of permeable (mobile) hydrogen was established. Reduction-in-area, the parameter related to plastic properties of metals, was the most sensitive index in determining the hydrogen degradation.

3. The obtained results suggest that susceptibility of tested steels to hydrogen degradation might be related to the quantity of hydrogen trapped by reversible traps.
REFERENCES

12. ASTM G 129-95: Slow strain rate testing to evaluate the susceptibility of metallic materials to environmentally assisted cracking.