The hydrogen permeation of low alloy high strength steel at splash zone and the mitigation effect of a wrapping protection technique

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Summary
The corrosion of steel at marine splash zone is the most severe. Due to the characteristics of this zone, the surface of the steel cannot be completely dry especially after the formation of corrosion products. Experiments show that a pH as low as below 3 can be obtained beneath corrosion products at constant wetting conditions and a fairly low potential is achieved. These conditions enable the H⁺ reduction as part of the cathodic reaction except O₂ reduction and then facilitate the hydrogen entry. It was found that under same cathodic polarization potentials, the hydrogen permeation current and the total hydrogen permeated through the corrosion products covered specimens at a fixed time period are higher than those without corrosion products. High strength steel has a high SCC and HE sensitivity. This must be considered for high strength steel. A wrapping protection technique was developed in our laboratory for the corrosion protection of marine splash zone corrosion. This technique has the advantage of easy implementation not only for new structures but also for structures that have already suffered some extent of corrosion. The technique has been proved to be effective in reducing the corrosion rate at splash zone, but the effect of mitigating the hydrogen entry particularly for the corroded structures is unclear. If the technique has not only the ability in reducing the corrosion rate but also the ability in reducing the hydrogen entry, it would be very promising. Wrapping protection layers were applied to new and corroded specimens and then experiments were conducted to record the hydrogen permeation current under simulated seawater splash conditions. The hydrogen permeation currents of both the new and corroded specimens were greatly reduced. Slow strain rate tensile tests showed that the elongation of wrapped specimens without corrosion products under seawater splash conditions was close to that in air. The elongation of corroded specimens after wrapping was also larger than that without wrapping. It is concluded that the wrapping technique has potential applications in mitigating the hydrogen entry except corrosion prevention at marine splash zone.

Key words hydrogen permeation, high strength steel, marine splash zone, corrosion, wrapping protection

1. Introduction

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It is known that the corrosion rate of splash zone is the highest among the marine corrosive zones as a result of sufficient oxygen, sufficient sunshine, salt spray and periodic wetting, etc. [1,2]. Therefore the research and field test on anti-corrosion technique of steel structure in splash zone is fairly active with the development of marine oil and gas exploration recently. For instance, B.R. Hou et al. [3] had studied the thermally sprayed zinc and aluminum coatings and found that they can offer high corrosion resistance in splash zone. G. Li et al. [4] developed a solvent-free heavy-duty coating technique which was used extensively in marine structures. Hoar et al. reported that Zn-Al alloys and composites around a 50:50 composition were the best coatings from the exposure test result of various alloys and composite coatings in marine and industrial environment for 10.5 years [5]. Studies show that thermally sprayed metal coatings could protect steel in the splash zone to some extent [6]. However, these protection technologies were not ideal in splash zone and maybe not adequate for the repair of corroded facilities. A wrapping technique was developed in our laboratory for the protection of marine splash zone corrosion. The technique mainly consists of a layer of petrolatum anti-corrosion grease, layers of petrolatum anti-corrosion tape and a protective cover. Experiment show that it is fairly effective in protecting steel corrosion in splash zone, and it was proved by field marine engineering utilizations [7,8].

Hydrogen entry into high strength steels must be considered before its using in marine environment, since the susceptibility of high strength steels to hydrogen embrittlement increases with increasing of strength, restricting the practical application of high strength steels in certain conditions. The corrosion of splash zone is the most severe in marine environment. The hydrogen entry might be also severe accompanying with the severe corrosion. So, it is essential to study the hydrogen permeation behavior under splash zone corrosion conditions and the mitigation effect of corrosion protection technique on hydrogen entry. If a protection technique can both protect splash zone corrosion and mitigate hydrogen entry, it will be more likely promising in promoting high strength steels applications in marine environment considering the factor of hydrogen embrittlement.

In this paper, firstly, the electrochemical impedance measurement was used to confirm the effectiveness of wrapping technique in the marine splash zone corrosion protection of AISI 4135 steel. Then, the electrochemical hydrogen permeation test was used to characterize the hydrogen entry into AISI 4135 steel with and without wrapping protection under simulated splash zone conditions, allowing continuous monitoring of hydrogen entry. The effect of wrapping on stress corrosion cracking (SCC) protection was evaluated by slow strain rate test (SSRT). In order to explain the hydrogen entry during corrosion processes, the pH beneath rust layer was also measured.

2. Experimental
2.1 Materials and specimen
The material used was an AISI 4135 high strength steel. The chemical composition is shown in Table 1 and the heat treatment processes are shown in Table 2. The specimens for electrochemical impedance measurements were prepared with numerically controlled electric spark wire cutting machine to the size of $\Phi$ 10mm × 10mm. Each specimen was embedded into epoxy resin
leaving one end of 0.785 cm² as working surface. Then specimens were abraded with grit 240,400,600 SiC paper followed by rinsing with distilled water, degreasing with alcohol and then drying in a cool air flow. For the hydrogen permeation tests, circular plate specimens of 40 mm in diameter and 0.5 mm in thickness were used. Both surfaces of the specimens were polished with emery paper up to # 1000. One side of specimens was plated with Ni in Watt’s bath (NiSO₄·6H₂O 250 g L⁻¹, NiCl₂·6H₂O 45 g L⁻¹, H₃BO₃ 40 g L⁻¹) at room temperature with a current of 3 mA cm⁻² for 3 min [16]. The estimated thickness of the Ni plating was about 180 nm. Rod tensile specimens with the working part 25mm long and 4mm in diameter were used for the SCC evaluation.

Table 1 Chemical compositions of AISI 4135 steel

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.399</td>
<td>0.293</td>
<td>0.509</td>
<td>0.015</td>
<td>0.014</td>
<td>0.903</td>
<td>0.204</td>
<td>0.08</td>
<td>balance</td>
</tr>
</tbody>
</table>

Table 2 Heat treatment condition of AISI 4135 steel specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Heat treatment condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI4135</td>
<td>860 °C thermal insulation 50 min, 370 °C isothermal quenching 30 min, air cooling</td>
</tr>
</tbody>
</table>

2.2 Simulation of splash zone conditions

The schematic diagram of the apparatus for the simulation of splash zone conditions is shown in Figure 1. The electrolytic cell and spray chamber were made by organic glass. The wetting conditions of specimens were simulated by spraying seawater on the surface. The tidal changes and the severity of splash were simulated by adjusting the period of spraying and spraying frequency.

Figure 1: Schematic of the splash zone simulating device (C: counter electrode, R: reference electrode, W: working electrode)

2.3 Wrapping protection procedures

Petrolatum anti-corrosion grease and petrolatum anti-corrosion tape are the core parts of wrapping protection technique. Three different protection procedures are as follows:

(1) P1: coating petrolatum anti-corrosion grease on the specimen surface
(2) P2: coating petrolatum anti-corrosion grease and covering single petrolatum anti-corrosion tape on the specimen surface
(3) P3: coating petrolatum anti-corrosion grease and covering double...
petrolatum anti-corrosion tape on the specimen surface

The P1, P2 and P3 are then used to indicate the protection procedures throughout the manuscript.

2.4 Electrochemical impedance spectroscopy

The experiment was done by using three-electrode system. A SCE and a Pt electrode were used as reference and counter electrodes. Electrochemical impedance spectroscopy (EIS) tests were measured with specimens under seawater film at room temperature. The EIS was performed in a frequency range from $10^5$ to $10^{-1}$ Hz.

2.5 Hydrogen permeation tests

Hydrogen permeation tests were performed under simulated splash zone conditions as shown in Figure 1 at room temperature. The double cell similar to the Devanathan-Stachurski’s cell was used [17]. Three spraying intervals of 1 min, 10 min and 30 min were employed to simulate 3 different severities of seawater splash in this study. As illustrated in Figure 1, an Hg/HgO electrode was used as reference electrode and a Pt wire was used as counter electrode for the hydrogen detection cell. The cell was filled with 0.2 M NaOH solution and the Ni-plated side of specimen was polarized by using a potentiostat at 0.0 mV vs. Hg/HgO electrode for more than 24 h until the residual current lower than 100 nA cm$^{-2}$ was reached. Then the hydrogen permeation current was recorded as the specimen subjected to simulated splash zone corrosion conditions.

2.6 The measurement of potential and pH beneath rust layer

The change in pH beneath rust layer during wetting and drying was measured using the cells presented in Figure 2 and the pH value was recorded by a pH meter. Holes were bored on the outer rust to fit the capillary of salt

![Figure 2: Schematic for the measurement of potential and pH beneath rust layer during the alternation of wetting and drying. (Salt bridge and pH glass electrode are in contact with inner rust which is always wet as electrolyte is rich in the inner rust with high RH in marine splash zone.) bridge and the pH glass electrode beneath rust layer. The depth of holes satisfied the capillary of salt bridge and the pH glass electrode’s contact with the inner rust layer where the electrolyte was rich in the marine splash zone. Cross sectional cutting after measurements confirmed that the salt bridges and pH glass electrode were in contact with the inner rust layer.](image)

2.7 SCC test of specimens with and without wrapping protection
The SCC test was conducted on a slow strain rate test machine at a strain rate of $5 \times 10^{-6}$ s$^{-1}$. Seawater was sprayed onto specimen during the test at room temperature.

3. Results and discussion

3.1 Electrochemical Impedance Spectroscopy

As shown in Figure 3, for bare steel, at the initial stage, Nyquist plot is a semi-circle. The Nyquist plots of electrochemical impedance showed an oblique line with the increase of cycles. Moreover, the charge transfer resistance decreased. It is indicated that the corrosion of specimen was accelerated as wet/dry cycles increase and the corrosion products couldn’t block the occurring of corrosion.

![Figure 3](image)

Figure 3 The EIS results of specimen under seawater film without wrapping protection and those with P1, P2 and P3 protection under different wet-dry cycles

Under P1, P2 and P3 protection, the plots represent similar patterns after different wet-dry cycles. But under P1 protection, the resistance was lower than that under P2 and P3. The Nyquist plots showed a capacitive loop in high frequency range and an oblique line in the low frequency range, which may indicated that seawater had diffused to the coating/metal interface. Under P2 and P3 protection, the Nyquist plots of electrochemical impedance showed a single semi-circle with high impedance. It is indicated that some seawater penetrated into the coating but the anti-corrosion agent is very effective at the coating/metal interface [22]. As a whole, the wrapping protection played good anti-corrosion properties after different wet-dry cycles.

3.2 Hydrogen permeation of bare specimen under simulated splash zone conditions

The hydrogen permeation currents recorded under spraying interval of 1
min, 10min and 30 min are shown in Figure 4. Generally, the hydrogen permeation current increased with the increase of spray times. Some minor decrease at the beginning of spray was also observed. As the tide lowered that was during the dry process, the hydrogen permeation current decreased as time passed after a peak value was reached. The decrease of hydrogen permeation current at the beginning of spray is mainly because of the pH and potential increase after the spray, since the pH of fresh seawater is around 8. When the specimen surface was wetted by seawater continuously after it was covered by rust layer, the increased concentration of H\(^+\) and high chloride ion would enhance the hydrogen entry as a result of the pH lowering beneath the corrosion product layer [18]. The following hydrolysis reactions of ferrous ions lead to the lowering of pH values [19]. This was verified by the potential and pH measurements after seawater spray as shown in Figure 5.

\[
\begin{align*}
\text{FeCl}^- + \text{H}_2\text{O} &= \text{FeOH}^+ + \text{H}^+ + \text{Cl}^- \\
\text{FeCl}_2 \cdot \text{aq} + \text{H}_2\text{O} &= \text{FeOH}^+ + \text{H}^+ + 2\text{Cl}^- \\
\text{Fe}^{2+} + 6\text{H}_2\text{O} &= \text{Fe(OH)}_2 + 2\text{H}^+ 
\end{align*}
\]

Figure 4 Hydrogen permeation currents of unprotected specimen under different spraying interval

If we integrate the area below each curve shown in Figure 4, the amount of hydrogen permeated through specimens can be obtained. The calculated values are shown in Table 3. The effect of seawater spray frequency has little effect on the total amount of permeated hydrogen. This is presumably because of the high humidity at the splash zone. The drying process of seawater film formed on the metal surface is slow. The concentration of dissolved oxygen in the seawater film can be high irrespective of the seawater spraying frequency. The ferrous ions can be further oxidized as shown in equation (4). In addition, the chloride concentration can also be high after cycles of enrichment. These factors can further lower the pH value and increase the hydrogen entry by facilitating H\(^+\) reduction.

\[
4\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} = 4\text{FeOOH} + 8\text{H}^+ 
\]

Table 3 The amount of hydrogen permeated under different spraying interval within 48h

<table>
<thead>
<tr>
<th>Specimen</th>
<th>1min (H/mol)</th>
<th>10min (H/mol)</th>
<th>30min (H/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI4135</td>
<td>3.280×10(^{-7})</td>
<td>3.265×10(^{-7})</td>
<td>3.240×10(^{-7})</td>
</tr>
</tbody>
</table>
3.3 Hydrogen permeation currents of wrapping protected specimens under simulated splash zone conditions

The hydrogen permeation currents of corroded and un-corroded specimens under wrapping protections are shown in Figure 6 and Figure 7. Compared Figure 6 and Figure 7 with Figure 4, the hydrogen permeation current density decreased dramatically under wrapping protections. Under P1 protection, the composite petrolatum anti-corrosion grease contains organic compounds with polar group and long hydrocarbon chain. Before the rust formed on the metal surface, the protective film can be formed on the specimen interface and blocked the corrosion medium such as seawater, oxygen and so on by the polar group adsorbing on the metal surface [7]. This protective film reduced the rate of corrosion dramatically. Therefore, the hydrogen permeation current was small. The grease can play double function of de-rusting and antirust. When the metal surface was covered with rust, the rust transformation agent can react with rust and form ferrum complex. The protective seal layer can be

Figure 5 The pH value and corrosion potential variation of specimen A

Figure 6 Hydrogen permeation currents of corroded specimen under wrapping protections (1 min, 10 min and 30 min are different spraying intervals)
Figure 7 Hydrogen permeation currents of none corroded specimen under wrapping protections (1min, 10min and 30min are different spraying intervals) formed on the interface of rust- anticorrosion grease and blocked the further corrosion. The rust transformation agent is constituted of tannin and phosphoric acid. Tannin can react with FeOOH of rust layer to form ferric tannates film which is relatively stable on the steel surface [20]. Phosphoric acid can react with rust to form stable phosphate passive film which has protective effect. Moreover, the petrolatum can block the rust pore with composite antirust and make the adsorbed film more complete [8]. Consequently, the diffusivity of hydrogen became lower, dramatically reducing the hydrogen permeation current density compared with that without P1 protection. But the rust transformation agent could not prevent the corrosion of base metal [21], so the remnant of corrosive species may still present. Therefore, the hydrogen permeation current density of rusty specimen is higher than that of none corroded specimen under P1 protection.

As shown in Figure 6 and Figure 7, the hydrogen permeation current has no significant change under P2 and P3 protection. The petrolatum anti-corrosion tapes contain not only the similar anti-corrosion composition to petrolatum anti-corrosion grease but also enhance the sealing property and intensity. In addition, the filler of petrolatum anti-corrosion tape has good chemical stability and mechanical strength. It can provide further protection for the metal by preventing the dripping off of petrolatum anti-corrosion grease, blocking the corrosion medium such as seawater and oxygen’s entering into the tape-specimen interface. Therefore, the corrosion process became difficult, reducing the possibility of H⁺ reduction.

The amount of hydrogen permeated through specimens obtained from
Figure 6 and Figure 7 are shown in Table 4. The wrapping technique can provide better protective role for none corroded specimens. Protection at the beginning is recommended.

Table 4 The amount of hydrogen permeated under wrapping protection within 48 h

<table>
<thead>
<tr>
<th>Specimen</th>
<th>With rust (H⁺/mol)</th>
<th>Without rust (H⁺/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1min</td>
<td>10min</td>
</tr>
<tr>
<td>P1</td>
<td>7.453×10⁻⁸</td>
<td>6.233×10⁻⁸</td>
</tr>
<tr>
<td>P2</td>
<td>2.133×10⁻⁸</td>
<td>1.866×10⁻⁸</td>
</tr>
<tr>
<td>P3</td>
<td>1.588×10⁻⁸</td>
<td>1.536×10⁻⁸</td>
</tr>
</tbody>
</table>

3.4 The effect of wrapping on SCC sensitivity

Figure 8 shows the effect of wrapping protection on SSRT stress-strain curves. The results show that the elongation of wrapped specimen without corrosion products under seawater splash conditions was close to that in air. The elongation of corroded specimens after wrapping was also larger than that without wrapping. The wrapping protection on SCC is very effective.

![Figure 8](image)

**Figure 8** SSRT stress-strain curves of AISI 4135 steel bare specimen, wrapping protected specimens with and without rust under seawater splash conditions compared with that in air.

5. Conclusion

(1) The hydrogen entry into high strength steel occurs during splash zone corrosion conditions, and the effect of seawater spray frequency has little effect on the total amount of permeated hydrogen.

(2) The wrapping protection can not only effectively mitigate the corrosion of high strength steel but also the hydrogen entry under splash zone conditions, reducing the sensitivity of SCC.

Acknowledgements

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References


