Effect of Micaceous Iron Oxide Epoxy Coating on the MIC Behavior of Low Alloy Steel

Wang Jun\textsuperscript{1, a}, Li Qing-fen\textsuperscript{1, 2, b}, Fu Yu-dong\textsuperscript{2, c}

\textsuperscript{1} College of Mechanical and Electrical Engineering, Harbin Engineering University, Harbin 150001, China
\textsuperscript{2} College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China
\textsuperscript{a}wangjun@hrbeu.edu.cn, \textsuperscript{b}qingfli@yahoo.com.cn, \textsuperscript{c}fuyudong@hrbeu.edu.cn

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Abstract. Effect of micaceous iron oxide epoxy coating on the microbiological influenced corrosion (MIC) behavior of the low alloy steel was studied. Samples uncoated or coated with micaceous iron oxide epoxy coating in sterile seawater and SRB solution was investigated by using electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and so on. A series of data was obtained. Results show that micaceous iron oxide epoxy coating protected the base material effectively due to its excellent physical barrier property.

Introduction

The microbiological influenced corrosion (MIC) failures exist in many industries and the cost of such damage may reach billions of dollars annually [1]. Among them, the sulfate-reducing bacteria (SRB) influenced corrosion is one of the most severe one in marine environment as it is rapid and complex [2, 3]. Some techniques to control such corrosion are used, such as biocides, UV irradiation, and coating. It is common practice to coat the steel with a highly insulating coating to increase the service life and the main purpose of the coating is to provide a barrier to the corrosion environment [4, 5]. Micaceous iron oxide epoxy coating has high anti-acid / alkali corrosion property and is known as a useful method to protect steel against corrosion. The anti-corrosion performance of micaceous iron oxide epoxy coating has been investigated. However, few corrosion data for the coating used in the marine microbiological environment is available.

In this paper, the effect of micaceous iron oxide epoxy coating on the MIC behavior of the low alloy steel was studied.

Experimental

The chemical composition of the low alloy steel used in the present investigation is shown in Table 1. The uncoated test sample size is $\Phi 11.3 \times 6$ mm with working area of 1 cm\textsuperscript{2}. A copper wire was soldered to the lower surface. Samples were polished up to 1000 grit and then cleaned with deionized water. Coated samples were successively polished up to 1000 grit, cleaned with deionized water, dried with air and finally coating with micaceous iron oxide epoxy. The size of coated sample is $30 \times 25 \times 6$ mm (with working area of 6 cm\textsuperscript{2}). A copper wire was soldered to the lower surface. The dry film thickness of micaceous iron oxide epoxy coating is about 30µm. All specimens were sterilized under UV for 3 hours before test.
Tests were carried out in two solutions: the sterilized medium and the SRB solution. The SRB strains were isolated from the sea-mud in Qingdao seashore. The composition of the SRB solution is given in table 2. And the sterilized medium was made by sterilizing the seawater in the high pressure steam sterilizer at 121°C for 20 minutes.

MIC behaviors in different solutions were investigated with EIS, EDS, ESEM of XL30, and a XRD-D8 Advance. Corrosion potential and impedance measurements were performed using the IM6 electrochemical workstation of ZAHNER. Tests were carried out at ambient temperature using a three-electrode system. The uncoated sample (an applied voltage amplitude of 5mV was used at frequencies between 0.005 Hz and 10^5 Hz), and the coated sample (an applied voltage amplitude of 20 mV was used at frequencies between 0.005 Hz and 10^5 Hz) are of the working electrodes.

Table 1 Chemical Composition of the Low Alloy Steel [ wt %]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.09~0.14</td>
<td>0.17~0.37</td>
<td>0.30~0.60</td>
<td>≤0.03</td>
<td>≤0.035</td>
<td>0.09~1.20</td>
<td>2.60~3.00</td>
<td>0.20~0.27</td>
<td>0.04~0.10</td>
</tr>
</tbody>
</table>

Table 2 Composition of the SRB Solutions [ g/L]

<table>
<thead>
<tr>
<th></th>
<th>PH</th>
<th>K_2HPO_4</th>
<th>H_2O</th>
<th>MgSO_4·7H_2O</th>
<th>CaCl_2</th>
<th>Na_2SO_4</th>
<th>NH_4Cl</th>
<th>Sodium lactate</th>
<th>Vc</th>
</tr>
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<tr>
<td>Seawater</td>
<td>1</td>
<td>7.00</td>
<td>0.50</td>
<td>2.00</td>
<td>0.10</td>
<td>0.50</td>
<td>1.00</td>
<td>3.50</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Results and Discussion

Variations of the corrosion potential over time of both bare and coated samples in the sterilized medium and SRB solution at room temperature are shown in Fig. 1 and 2 respectively. Results of EDS of coated samples original and after 30 days exposure in sterilized medium and SRB solution are given in Table 3. Fig. 3 gives the EDS spectrum of coated samples original and after 30 days immersion. The surface micrographs of samples are shown in Fig.4.

Generally, a rise of potential in the positive direction indicates the formation of film over metal surface, a drop of potential in the negative direction indicates the breakage or dissolution of a film.

Table 3 EDS results of coated specimens original and after 30 d immersion in sterile seawater and SRB solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>66.71</td>
<td>18.07</td>
<td>01.80</td>
<td>01.00</td>
<td>00.97</td>
<td>02.60</td>
<td>00.21</td>
<td>00.00</td>
<td>00.38</td>
<td>01.04</td>
<td>06.30</td>
</tr>
<tr>
<td>In SS</td>
<td>64.07</td>
<td>21.65</td>
<td>00.96</td>
<td>00.52</td>
<td>00.56</td>
<td>00.93</td>
<td>00.20</td>
<td>00.18</td>
<td>00.46</td>
<td>04.96</td>
<td>24.91</td>
</tr>
<tr>
<td>In SRB</td>
<td>26.96</td>
<td>40.29</td>
<td>01.64</td>
<td>01.01</td>
<td>00.84</td>
<td>02.63</td>
<td>02.06</td>
<td>02.12</td>
<td>04.67</td>
<td>05.99</td>
<td></td>
</tr>
</tbody>
</table>
From Fig. 1, we see that the potential of the uncoated samples in the sterile medium decreased quickly at first and then moved slowly toward the positive direction and then dropped slightly. It indicates that the specimen surface of steel without protective biofilm was initially corroded quickly because of the anodic dissolution or cathodic depolarization effect of Cl$^-$, H$_2$O and so on. Then the deposition of organic culture medium and corrosion products in the solution over the surface of specimen increased the corrosion resistance and decreased the corrosion rate. Comparing with the uncoated one in the same solution, the E$_{corr}$ of the coated sample increased quickly at first and decreased quickly in the next four days, and then kept decreasing slowly in the following days. And that the E$_{corr}$ of the coated sample was always higher than the uncoated one. It suggests that the barrier protection of micaceous iron oxide epoxy coating is perfect and the corrosion products increased the corrosion resistance obviously at first. Then the high degree percolation of H$_2$O and Cl$^-$ decreased the barrier protection effect of the coating, and the E$_{corr}$ decreased. However, corrosion products over the surface of specimen increased the corrosion resistance and decreased the corrosion rate finally. The corrosion resistance of the coated sample was always higher than the uncoated one.

Fig. 2 show that the corrosion potential of the uncoated samples in the SRB solution increased quickly at the first 7 days and decreased slowly in the next 7 days, then moved slowly toward the positive direction in the following 16 days. It suggests that with the increasing of SRB, the accumulated biofilm on the specimen surface prevented the contact between the test steel and solution and increased the corrosion resistance at first. But then the corrosive products resulting from the metabolism of SRB, such as H$_2$S, accelerated the corrosion of steel and the biofilm was no
longer protective. After that the increasing corrosion product precipitates on the surface of specimen restrained the corrosion process in the following 16 days. Comparing with the uncoated one in the same solution, the $E_{\text{corr}}$ of the coated sample increased quickly at first and then decreased quickly at the next 7 days. After that it moved toward the positive direction and the $E_{\text{corr}}$ of the coated sample was higher than the uncoated one in the following days. It indicates that the inert material of coating offered effective barrier protection to the base steel originally. Although the corrosive products resulting from the metabolism of SRB accelerated the corrosion at several days, the corrosion rate was reduced finally with the accumulation of corrosion products over the coating surface in the following days. The corrosion resistance of the coated sample was higher than the uncoated one finally.

Results of energy dispersive spectroscopy (EDS) gave the same conclusion. From Table 3 and Fig.3, we can see that, comparing with the original sample, the content of element Fe and C of the sample after 30 days immersion in the two solutions decreased obviously, and a small content of element S appeared after 30 days immersion in the sterile medium and a high content of S about 1.12 in SRB solution. It suggests that the percolation of $H_2O$ and $Cl^-$ in the solutions and the metabolism product of SRB, such as $H_2S$, accelerated the corrosion of iron-based alloy. However, we can also see that the content of element Ca and O increased obviously. It indicates that the calcium-sediment appeared on the surface of the sample and the corrosion products over the surface of specimen may increase the corrosion resistance and decrease the corrosion rate finally.

The surface micrographs of samples (Fig. 4) show that slight corrosion uniformly appeared on the uncoated specimen in sterile seawater, and severe pitting corrosion appeared on the uncoated specimen in SRB solution after 30 days immersion. It indicates that the sulfate-reducing bacteria accelerated the corrosion behavior of low alloy steel. Comparing with the uncoated specimen, it can be seen that the micaceous iron oxide pieces lay ring upon ring over the original coated specimen. After 30 days immersion, it is clearly seen that the coated specimen covered with compact corrosion products which are thicker and more compact in SRB solution than in sterile seawater. No corrosion can be seen on the coated specimen surface. It is obvious that the basic low alloy steel was effectively protected by the micaceous iron oxide epoxy coating and also by the corrosion product depositions on the coating.

We may conclude that the barrier protection of micaceous iron oxide epoxy coating is perfect and the corrosion products increased the corrosion resistance.

Summary

Experiment investigation show that the MIC behavior of low alloy steel was improved obviously with the micaceous iron oxide epoxy coating. The micaceous iron oxide epoxy coating and the corrosion products depositions protected the low alloy steel effectively in the microbial environment with the physical barrier protection.

References