Biofouling of Cr-Nickel Spray Coated Films on Steel Surfaces

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Abstract. Nowadays, corrosion of metals brings us serious economic loss and it often reaches several percentage of GNP. Particularly the marine corrosion was serious and the counter measure was very hard to be established, since the number of factors is huge and complicated. One of the complicated factors in marine corrosion is biofouling. Biofouling was classified into two main categories, microfouling and macrofouling. The former is composed of biofilm formation mainly. Marine bacteria are attached to material surfaces, seeking for nutrition in oligotrophic environment and they excrete polysaccharide to form biofilm on metal surfaces. Then larger living matters are attached on the biofilms to develop biofouling on metal surfaces, which often lead loss and failures of metals in marine environments. From the viewpoint of corrosion protection and maintenance of marine structures, biofouling should be mitigated as much as possible. In this study, we applied spray coating to steels and investigated if chromium-nickel spray coating could mitigate the biofouling, being compared with the conventional aluminium-zinc spray coating in marine environments. The specimens used for this investigation are aluminium, zinc, aluminium-zinc, stacked chromium/nickel and those films were formed on carbon steel (JIS SS400). And the pores formed by spray coating were sealed by a commercial reagent for some specimens. All of those specimens were immersed into sea water located at Marina Kawage (854-3, Chisato, Tsu, Mie Prefecture) in Ise Bay for two weeks. The depth of the specimen was two meter from sea water surface and the distance was always kept constant, since they were suspended from the floating pier. The temperature in sea water changed from 10 to 15 degrees Celsius during the immersion test. The biofouling behavior was investigated by low vacuum SEM (Hitachi Miniscope TM1000) and X-ray fluorescent analysis. When the spray coated specimens with and without sealing agents were compared, the former showed higher antifouling properties generally. Aluminium-zinc alloy spray coated films had higher antifouling property. And the anti-property decreased in this order: Al-Zn alloy spray coating > Zinc spray coating > Aluminium spray coating > Stacked chromium/nickel spray coating. Aluminium and zinc spray coating has been evaluated high conventionally for anti-biofouling in marine environment. However, the Cr/Ni spray coating showed pretty high anti-fouling property.

1. Introduction
Corrosion of metallic materials brings us a lot of economic failures in our modern society. One of the estimation about them suggests that the failure reached several percentages of GDP in advanced countries usually¹. Particularly, the corrosion in marine environment is the most remarkable to affect on economical failures, since it is very usual one. When biofilms form on material surfaces, oxygen concentration cells are established around biofilms, which leads to serious corrosion failures. With and without biofilm formation, the corrosion rate is generally very different. However, the precise evaluation and differentiation between usual corrosion and microbiially influenced corrosion (MIC)²⁶ has been very hard, since the involvement of microorganism would be always very delicate and difficult to be fixed.
In this study, the effect of spray coating on the biofilm formation and MIC were investigated. Concretely speaking, various spray coated steel were immersed in marine environment and the biofouling behaviors were measured, evaluated and discussed.

2. Experimental

2.1. Specimens

| Table 1 Spray coating conditions for various specimens. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| coating materials               | aluminum        | zinc            | aluminum-zinc   | chromium        | nickel          |
| spray coating process           | arc spray coating | arc spray coating | arc spray coating | plasma spray coating | plasma spray coating |
| voltage (V)                     | 30              | 20              | 20              | 20              | 62              |
| current (A)                     | 125             | 50              | 50              | 50              | 500             |
| gas pressure (kg/cm²)           | 5-6             | 5-6             | 5-6             | Ar 75Psi, H₂ 50Psi | Ar 75Psi, H₂ 50Psi |
| spray coating distance          | 150mm           | 150mm           | 150mm           | 120mm           | 100mm           |

A general carbon steel (JIS SS400) was used as substrate. Aluminium, zinc, aluminium-zinc, chromium/nickel (Nickel layer was spray coated and then chromium layer was formed on it.) were spray coated on the substrate, respectively. The conditions for those spray coating processes were shown in the following table (Table 1). The figures below the table were schematic illustration of the spray coating process. The readers should note that chromium/nickel spray coating process was composed of two steps (nickel and chromium spray coating processes.)

After the spray coating process, the pores of spray-coated films were sealed by a commercial sealant, Permeate (D & D Co., 78 Sakura, Yokkaichi, Mie, 512-1211, Japan)[6][7]. And those sealed specimens were compared to those without sealer.
2.2. Marine immersion tests

All of spray coated specimens were fixed to a jig for the immersion test and the jig with those specimens were immersed in sea water at Marina Kawage (854-3, Chisato, Tsu, Mie Prefecture, Japan) in Ise Bay. The jig with the specimens was hung from a floating dock and kept at the depth of 2m from the sea surface. The temperature of sea water was changed between 10 degrees Celsius and 15 degrees Celsius. The appearance of the jig and immersion site were shown in Fig.1.

2.3. Surface Observation

After immersion, specimens were taken out of the sea, washed by water and served to observations by low pressure Scanning Electron Microscopy (TM 1000, Miniscope, Hitachi). The acceleration voltage of 15kV was applied to the specimens and the reflection image was observed. In addition to that, fluorescent X-ray analysis (MESA 500W, Horiba Co.) was carried out to identify elements on specimens’ surfaces before and after immersion.

3. Results and discussion

3.1. Low Pressure SEM Observation

The specimens were immersed in the sea for two weeks and observed by the low pressure SEM after the immersion. Some of the SEM photos were shown in Fig. 2 and Fig.3.

![SEM photos](image)

(1) Al-Zn spray coating  
(2) Zn spray coating  
(3) Al spray coating  
(4) Cr/Ni spray coating

Fig.2 Low Pressure SEM Observation for spray coated specimens without sealer

In Fig.2, the results for the specimens with sealer were shown, while those without sealer in Fig.3. When biofouling occurred on the surface of specimen to some extent, the surface color usually changes and the fouling matters could be observed by naked eyes in most cases. As for both of sealed and non-sealed specimens, Al-Zn specimens were the hardest to have biofouling. The fouling was observed on the specimen’s surface to some extent. However, there were few fouling places by naked eyes. Therefore, it could be judged to be the hardest for biofouling. The zinc coated specimen and aluminum coated specimens followed in this order. The Cr/Ni coated specimen was the easiest one
for biofilms to form on the surfaces. For the Cr/Ni coated specimens, red rusts were often observed. Since they were obviously iron oxides (mainly Fe₂O₃) formed on the specimens’ surfaces.

Fig.3 Low Pressure SEM Observation for spray coated specimens with sealer

Table 2 Fluorescent X-ray analyses for spray coated specimens without sealer

| Element | Mass Concentration (%) | Before Immersion | After Immersion |
|---------|------------------------|------------------|-----------------|
| Zn      | 58.66                  | 85.03            |
| Al      | 37.61                  | 11.95            |
| Si      | 0                      | 1.46             |
| Cl      | 0                      | 1.19             |
| Mg      | 1.92                   |                  |

(1) Al-Zn

| Element | Mass Concentration (%) | Before Immersion | After Immersion |
|---------|------------------------|------------------|-----------------|
| Zn      |                        | 99.38            | 95.14           |
| Si      | 0                      | 2.78             |
| Cl      | 0                      | 1.32             |

(2) Zn

| Element | Mass Concentration (%) | Before Immersion | After Immersion |
|---------|------------------------|------------------|-----------------|
| Al      | 98.35                  | 77.86            |
| Cl      | 0                      | 13.52            |
| Si      | 0                      | 6.61             |
| Fe      | 0                      | 1.68             |
| Mg      | 1.36                   |                  |

(3) Al

| Element | Mass Concentration (%) | Before Immersion | After Immersion |
|---------|------------------------|------------------|-----------------|
| Cr      | 99.53                  | 93.73            |
| Ni      | 0                      | 1.32             |
| Fe      | 0                      | 2.16             |
| Si      | 0                      | 2.06             |

(4) Cr/Ni
by the reaction between iron and oxygen or hydroxyl ion. For all of specimens, sealed coatings showed higher anti-corrosion resistance than non-sealed ones did. It indicates clearly that the sealer had a certain inhibition effect of biofilm formation and improved corrosion resistance to much extent.

3.2. Fluorescent X-ray analyses

Table 3 Fluorescent X-ray analyses for spray coated specimens with sealer

| Element | Mass Concentration (%) |
|---------|------------------------|
|         | Before Immersion | After Immersion |
| Zn      | 59.34            | 90.35           |
| Al      | 43.12            | 7.06            |
| Si      | 0                | 1.51            |

(1) Al-Zn

| Element | Mass Concentration (%) |
|---------|------------------------|
|         | Before Immersion | After Immersion |
| Zn      | 97.09            | 98.51           |
| Al      | 0                | 1.07            |
| Si      | 1.11             | —               |

(2) Zn

| Element | Mass Concentration (%) |
|---------|------------------------|
|         | Before Immersion | After Immersion |
| Al      | 99.81            | 93.27           |
| Si      | 0               | 5.8             |

(3) Al

| Element | Mass Concentration (%) |
|---------|------------------------|
|         | Before Immersion | After Immersion |
| Cr      | 96                | 94.67           |
| Ni      | 1.45              | 1.12            |
| Cl      | 0                 | 1.26            |
| Fe      | 0                 | 1.13            |
| Si      | 1.03              | 1.00            |

(4) Cr/Ni

All of the specimens were analyzed by a fluorescent X-ray apparatus. Table 2 and 3 show those results. The former corresponds to the results for the spray coated specimens without sealer, while the latter for those with sealer. According to the results, silicon was remarkable for all of the specimens. The change of the silicon contents was caused mainly by the incorporation of silicon from the sea water. Silicon compounds were incorporated into biofilm, dried in it after immersion and reflected in the results[8],[9]. Therefore, it could be an evaluation tool for the extent of biofilm formation. From the viewpoint, all specimens immersed into the sea showed the biofilm formation to some extent. On the other hand, chloride concentrations were pretty high for some specimens. It suggests that those specimens corroded remarkably. In this study, the strict and correct gravimetry was not carried out. However, the tendency was measured. According to the results, the weights for aluminum coated, zinc coated and chromium coated specimens decreased remarkably. Those metals are less noble than iron. Therefore, they dissolved significantly due to the galvanic cells between the metals and iron and the total weights decreased correspondingly. For Cr/Ni coated specimens, the red rust corresponding to iron oxide were observed on the specimens’ surfaces. It suggests that the
local galvanic cells established between the surface films and substrate also induced the corrosion and produced iron oxides on the surfaces of these layers.

From the viewpoint of gravimetry, silicon concentrations and observation by naked eyes, we concluded the fouling order among specimens for this experiment. The results were summarized in Table 4.

4. Conclusions

Various spray coated specimens with and without sealer (aluminum, zinc, aluminum-zinc and chromium/nickel coated specimens) were immersed into sea water and the biofouling behaviors were measured. The low pressure SEM observation and fluorescent X-ray analysis were used for the evaluation of biofilm formation. All of these results were investigated, discussed and summarized in Table 4. The order of inhibition effects against biofilm formation increased in the order shown in Table 4. The highest inhibition effect was shown by aluminum zinc spray coated film with sealer, while the worst one by chromium nickel spray coated specimen without sealer.

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