Effects of Colloidal Silica Addition on the Self-healing Function of Chromate Coatings

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The corrosion prevention mechanism of the chromated metal materials is considered to be attributable to the self-healing function of the chromate coatings. In this study, the corrosion behaviors of dry-in-place type chromate coated galvanized steel specimens have been studied using a scanning vibrating electrode technique. By this method, the effects of colloidal silica addition in the chromate coating on the self-healing function have been examined. The results confirmed that the chromate coatings prevent the corrosion of metal under coating or at coating defects by their self-healing function. The self-healing function of the chromate coatings is due largely to the formation of a Cr compound layer from the dissolved Cr(VII) ions in the electrolyte. The addition of colloidal silica greatly enhances the self-healing function and corrosion protection of the dry-in-place type chromate coating.

KEY WORDS: dry-in-place type chromate; self-healing function; silica; corrosion prevention, galvanized steel.

1. Introduction

Chromate treatment is applied widely to metal materials for improved appearance as well as for enhanced corrosion resistance.1–3) The corrosion prevention mechanism of the chromated metal materials is considered to be attributable to the self-healing function of the chromate coatings. The self-healing function prevents not only the corrosion of metal substrate under the chromate coatings but also the development of corrosion at the coating defects, implying the spontaneous recovery of damaged part of the chromate coatings. While this function has been recognized to take place on the basis of empirical knowledge, experimental verification for the self-healing function has been scarce.

In the previous investigations,4–6) the authors have studied the self-healing behaviors with regards to the dissociation component of the chromate coatings. It has been clarified that the addition of colloidal silica enhanced the self-healing function and thus the corrosion resistance of a dry-in-place type chromate coating.7–9) In this study, a scanning vibrating electrode technique (SVET)10–12) and X-ray photoelectron spectroscopy (XPS) analysis have been employed to investigate the corrosion behaviors of galvanized steel treated with a dry-in-place type chromate treatment. The addition effects of the colloidal silica in the chromate coating on the self-healing function have also been examined.

2. Experimental

2.1. Specimen Preparation

The chromate solution used was Cr(VI) : Cr(III) : PO₄ = 1 : 1 : 0.8 (wt.) in composition.13) The colloidal silica with an average particle size of 7–9 nm in diameter9) was added in the chromate solution with a ratio of silica/Cr = 0 or 4 (wt.). The total Cr weight of the chromate coating formed on each electrogalvanized steel specimen was 100 mg/m². The detailed coating procedure has been reported elsewhere.1,2) All the chromate coated specimens were dried at 200°C in air. In some cases, a hole of 600 µm in diameter and 700 µm in depth was made in the central part of a chromated steel specimen as an artificial defect.10,11) Figure 1 shows another type of the specimens employed in this investigation. In this case, a cold rolled steel sheet (SPCC) coated with silica-free chromate coating on part of the specimen surface was used. The total Cr weight was 300 mg/m² and the coated specimen was dried at 200°C in air. XPS analysis for this specimen was made on the bare surface in the vicinity of coated area (Fig. 1) after immersed in a NaCl electrolyte.

2.2. SVET Observation

The SVET measurement system used in this investigation is schematically shown in Fig. 2.5) The sensor elec-
trode was kept a distance of 65 μm from the specimen surface with an amplitude of 10 μm and a frequency of 370 Hz. Each SVET observation over an surface area of 2100×2100 μm was scanned at an interval of 70 μm. All the experiments were carried out in 1.0×10^{-3} % NaCl electrolyte at room temperature.

2.3. XPS Analysis ²)

The XPS spectrometer of Shimadzu ESCA-850M was employed in this work. X-ray source was MgKα, and measured binding energy was calibrated against C–H peak. After immersed in the NaCl electrolyte, all the specimens were rinsed with de-ionized water and dried at 60°C before subjected to XPS analysis. In order to analyze the soluble chromate species in the test electrolytes, samples of the test electrolyte (300 ml) was collected in a glass beaker and dried in air.²) The dried powder samples were then transferred to the XPS spectrometer chamber for analysis. The detailed analysis methods and conditions of XPS has been reported elsewhere.²)

3. Results and Discussions

3.1. Effects of the Colloidal Silica on the Self-healing Function

3.1.1. Effects of the Colloidal Silica on the Corrosion Behaviors

Figure 3 shows the SVET results of the corrosion behaviors of two chromate coated galvanized steel specimens during a 30-d period of immersion in 1.0×10^{-3} % NaCl electrolyte. These dry-in-place type chromate coatings had silica/Cr ratios of 0 (Fig. 3(a)) and 4 (Fig. 3(b)), respectively.

The output potential of the lock-in amplifier in proportion to the current value was used as the Z-axis in the figure.¹⁰)

The corrosion current of the silica-free specimen exhibited a high distribution density of local anodic and cathodic sites (Fig. 3(a)). This corrosion behavior would be explained by the fact that the chromate coating was an ultra thin film of several tens of nanometers and it may not fully cover the metal surface as a homogeneous membrane. After 8 d of immersion, however, the intensity of the anodic and cathodic distribution decreased, an indication of the self-healing effect of the chromate coating, even though not significantly, on suppressing the local corrosion current. Therefore, 8 d of immersion in 1.0×10^{-3} % NaCl seemed to be required for the self-healing of the silica-free chromate coating. With the further immersion, a large anodic site appeared after 15 d. This anodic site became more intensified after 30 d of immersion and at the same time, visual inspection revealed white rust on the surface. Therefore, it appears that the self-healing and corrosion protection function of this type of coating lasts 22 d in the electrolyte.

On the other hand, the density of the anodic and cathodic sites and the intensity of corrosion current for the specimen treated with silica containing chromate coating was very small at the initial stage of immersion (Fig. 3(b)). After 10 h, most of these local corrosion sites disappeared completely as a result of the corrosion prevention effect provided by the self-healing function of the coating. After 8 d, sporadic local corrosion sites were detected. However, they were insignificant in terms of the corrosion site density and corrosion current intensity as compared with the situation of the silica-free coating. It is noticeable that corrosion prevention effect of the chromate coating continued for more than 30 d. No visible white rust spot was found during the entire test period. The smaller corrosion current at the initial stage would be due to the barrier effect of the fine silica particles in the coating.

The SVET measurement results in Fig. 3 are rearranged in Fig. 4 to demonstrate the maximum potential difference, which is related to the local corrosion current intensity, as a function of immersion time. It is clear that the specimen coated with silica-free chromate coating (silica/Cr=0) ex-
hibited a significantly large local corrosion current at the initial stage. Although the corrosion current was greatly suppressed by the self-healing function of the chromate coating after 8 d, the corrosion current increased again at 15 d and the corrosion continued to develop in a more localized form throughout the rest of the test period (Fig. 3). On the other hand, the local corrosion current for the silica containing chromate coating (silica/Cr$_4^+$) was negligible, as compared to that for the silica-free coating. A slight increase in local corrosion current was observed during the first 15-d period. The corrosion current started to decrease after 15 d and finally dropped to very low level at end of test, which is consistent with the fact that no visible corrosion spot was identified after the immersion test. These experimental results clearly demonstrated an effective and prolonged corrosion protection by the chromate coating that contained colloidal silica particles.

The surface XPS analysis result on the chromated specimen after 30 d of immersion test is shown in Fig. 5. Here the Cr$_{2p_3/2}$ spectra of the silica-free chromate coating (Fig. 5(a)) and the silica containing chromate coating (Fig. 5(b)) are compared. It can be seen that the Cr(VI) component in the silica-free chromate coating was about 4% in atomic percentage, much lower than the value of 22% for the silica containing chromate coating. Apparently, the chromate coating containing silica demonstrated a higher Cr(VI) retention ability. Since the total Cr weights in both coatings are similar, the higher Cr(VI) content in the silica containing coating would be explained by a process of Cr adsorption–desorption on the silica particles. The dissociated Cr(VI) ions from the coating would gradually diffuse into the aqueous solution, which eventually causes a depletion of Cr(VI) in the coating. In the case of silica containing chromate coating, the Cr(IV) depletion rate is much lower (Fig. 5(b)) because the adsorption–desorption effect at the silica particles retards the dissociation and diffusion of Cr(VI) ions. Therefore higher Cr(VI) ions retained in the coating provides more efficient, durable self-healing function and corrosion protection.

3.1.2. Effect of Colloidal Silica on the Duration of the Self-healing Function

In order to further clarify the effect of silica addition in the chromate coating on the duration of the self-healing function, SVET experiments were carried out on the chromated galvanized steel sheet specimens with artificial defects. The results shown in Fig. 6 depict the development of
corrosion at the artificial defect sites for both the silica-free and silica containing chromate coatings.

For the silica-free chromate coating, initial corrosion developed at the defect site. Although inefficient, the self-healing function of this coating was observed, as indicated by a slight decrease in the corrosion current after 5 h (Fig. 6(a)). The corrosion at the defect site continued to develop and white rust appeared around 20 h. On the other hand, the corrosion initially developed at the defect in the silica containing chromate coating completely disappeared after 10 h (Fig. 6(b)). This self-healing effect continued functioning until after 70 h. To examine the corrosion protection effect of the chromate coatings, similar experiments were performed on an as-received galvanized steel specimen boring an artificial defect of the same size. It was observed that the white rust appeared approximately 7 h after immersion in the electrolyte. Therefore, the galvanized steel specimen only provided 7 h of corrosion protection for the artificial defect. The delayed occurrence of corrosion to 20 h for the silica-free chromate coating indicated the self-healing effect of the chromate coating, although this corrosion protection was not very effective. Significantly, the silica containing chromate coating completely suppressed the corrosion at the artificial defect for more than 135 h. Since the total Cr weight in both chromate coatings are similar, it is obvious that the colloidal silica addition prolonged the self-healing duration of the chromate coating for approximate 7 times with a more effective corrosion protection at the artificial defect.

3.2. XPS Analysis in Self-healed Surface Area

XPS analysis was also carried on the specimen partly coated with chromate coating (Fig. 1). The XPS results obtained from the bare surface area after 6 h of immersion in the test electrolyte are presented in Fig. 7. In this figure, the results from the dissolved Cr species are also given.\(^\text{54}\) It is interesting to note that a layer of Cr compounds was detected on the bare galvanized surface (Fig. 7(b)). Figure 7(a) shows that a major part of the dissolved Cr species in the electrolyte was in the form of Cr(VI). Hence, the formation of the Cr compound layer on the bare steel surface may be explained by the reaction of the dissolved Cr(VI) on the surface, resembling a chromate coating process. The self-healing and corrosion protection effects of the chromate coating would be attributed to the formation of such a Cr compound layer at the defect sites.

3.3. Corrosion Protection Mechanism by the Self-healing Function

The above results clarify that Cr(VI) dissolves from chromate coating and it re-forms a chromate coating of some type on the nearby bare metal surface. From these results, the self-healing function of the chromate coating can be regarded as a reformation process of a chromate film on the bare metal surface by the dissolved Cr ions. The reformation of a chromate film due to the self-healing function is estimated to be similar to the formation reaction of a conversion type chromate coating,\(^\text{33}\) which involves the following phases:

- First phase: Dissolution of metal (Me) by corrosion.
  \[
  \text{Me} + n\text{H}^+ \rightarrow \text{Me}^{n+} + n/2 \cdot \text{H}_2
  \]
  (Anodic reaction: \(\text{Me} \rightarrow \text{Me}^{n+} + ne^\text{–}\))
  (Cathodic reaction: \(ne^\text{–} + n\text{H}^+ \rightarrow n/2 \cdot \text{H}_2\))

- Second phase: Dissociation and reduction reaction of \(\text{HCr}_2\text{O}_7\) (=Cr(VI))
  Dissociation reaction: \(\text{HCr}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{CrO}_4^{2–} + 3\text{H}^+\)
  Reducing reaction: \(2\text{CrO}_4^{2–} + 7\text{H}^+ + 6e^\text{–} \rightarrow 2\text{Cr(OH)}_3 + \text{H}_2\text{O}\)

- Last phase: Due to the decrease in \(\text{H}^+\) ion through Eq. (2), the pH at Me/solution interface rises, and Cr(III) + Cr(VI) hydrate deposits as a chromate coating:
  \[
  2\text{Cr(OH)}_3 + \text{CrO}_4^{2–} + 2\text{H}^+ \rightarrow \text{Cr}^\text{III} + \text{Cr}^\text{VI} \text{Cr(OH)}_3 \text{Cr(OH)}\text{CrO}_4 + 2\text{H}_2\text{O}
  \]

Essentially, the dissolved Cr(VI) ions accept the electrons generated in the corrosion anodic region as an anode inhibitor,\(^\text{13}\) which are therefore reduced to Cr(III). The reduced Cr(III) ions fixate on the metal surface and a self-healed chromate coating is reformed. This re-formed chromate coating during corrosion causes the self-healing of the defects in the coating and it contributes to prevent further corrosion of the substrate metal. On the other hand, the recurrence of corrosion at the self-healed area after long term immersion is due to the limitation of Cr(VI) ions available.

4. Conclusions

The self-healing function of the Cr(VI)–Cr(III)–PO\(_4\) dry-in-place type chromate coatings has been studied with re-
pect to their corrosion prevention behaviors and the effect of colloidal silica addition. From the experimental results obtained, the following conclusions can be drawn:

1) The chromate coating is confirmed to protect the substrate metal from corrosion under the coating or at the coating defect sites through its self-healing function.

2) The self-healing function of the chromate coating can be attributed to the reformation of a Cr compound layer at the defect sites by dissolved Cr(VI) ions.

3) The silica addition in the dry-in-place type chromate coating enhances the self-healing function and the corrosion protection of the chromate coating, which may be due to the high Cr(VI) retention ability of the colloidal silica particles.

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