

Preparation of Molybdate-Permanganate Conversion Coating for Corrosion Resistance

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Abstract— This work aims to prepare, chrome-free, molybdate-permanganate coatings to protect electrogalvanized steel (EGS) from corrosion in automotive and appliances industries. The coatings were prepared by immersion EGS in a mixture solution of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and potassium permanganate (KMnO_4) at a molar ratio of 1:0.2 and 1:1 for 1, 1.30, 2 and 5 minutes at temperature of 50°C. The pH used was 3 and 4. The results stated that the superior corrosion resistance molybdate-permanganate coating prepared from solution having Mo:Mn molar ratio of 1:0.2 at pH 4 had corrosion resistance similar to that of commercial chromium(III) conversion coating. Moreover, it delayed corrosion onset longer than commercial chromium(III) conversion coating because of its low anodic and cathodic reactivities together with a crack-free surface.

Keywords— Chrome-free coating, corrosion, molybdate conversion coating

I. INTRODUCTION

Chromium(VI) or chromate conversion coating is usually used to delay corrosion of zinc-coated steel, namely electrogalvanized steel (EGS), in automotive and appliances industries. Chromium(VI) conversion coating provides good corrosion resistance because it acts as barrier coating and self-healing coating. The self-healing property is the result from the existence of hexavalent chromium (Cr(VI)) within coating. Once the coating is damaged by scratching or attacked by aggressive ions such as chloride ions, Cr(VI) will transport to the damaged area and reduced to be chromium oxide (Cr_2O_3) film to heal the damage. Therefore, its corrosion resistance is restored. Nevertheless, chromium(VI) is a carcinogenic substance which is restricted follows the RoHS directive [1]. This limitation impacts Thailand in terms of manufacturing and exporting goods to European Union [2]. Despite the fact that low-toxic chromium(III) conversion coating is being used to replace chromium(VI) in industrial applications, the chrome-free conversion coatings such as molybdate-based, cerium-based, vanadate-based and tungstate-based conversion coatings are of interest. The previous work about non-chrome coatings, cerium- and molybdate-conversion coatings, conducted at KMUTT Bangkok Thailand [3] indicated that molybdate conversion coating not only delay corrosion onset of EGS longer than cerium conversion coating but cost of preparation was comparatively low as well. However, the

corrosion resistance of molybdate coating was not as good as chromium(VI) conversion coating. By these reasons, the corrosion resistance enhancement of molybdate coating is attempted in this work by doping with manganese to form molybdate-permanganate coating. The development will be benefit to industrial applications.

II. EXPERIMENT

The electrogalvanized steel (EGS) size of 50 mm x 50 mm x 1 mm was used as substrate for conversion coating. It was cleaned and activated by submerging into 0.6% v/v HNO_3 for 30 seconds. The molybdate-permanganate conversion coating (Mo-Mn-CC) was prepared by dipping the substrate into the mixture solution of 100 mM $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 20, 100 mM KMnO_4 for 1, 1.30, 2 and 5 minutes at 50°C. The pH of coating solution was adjusted to 3 and 4 with concentrated phosphoric acid (H_3PO_4). Afterwards, it was rinsed with deionized water then dried with air blower. The molybdate conversion coating (Mo-CC) and commercial chromium(III) conversion coating (Cr(III)-CC) were also prepared to be the control samples. The Cr(III)-CC was prepared followed the manufacturer instruction while Mo-CC was prepared by immersion in 100 mM $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solution for 5 minutes as explained in details elsewhere [3].

The Mo-Mn-CC and control samples were salt spray tested followed ASTM B117 for 24 hours. Duration time at white rust observed was recorded. After exposure to salt spray for 24 hours, the sample was immersed in 100g/L NH_4Cl at 70°C for 3 minutes to remove corrosion product according to ASTM G1-03. The attacked area was evaluated by image analysis method using image J software. The electrochemical corrosion behavior of coating and control samples were also studied by anodic and cathodic polarization measurements using Autolab Potentiostat/Galvanostat (PGSTAT30). The measurements were performed in 3.5% NaCl at a scan rate of 1 mVs^{-1} with test area of 1 cm^2 . The reference and counter electrodes used were Ag/AgCl and platinum rod respectively. To compare cathodic reactivities of control samples and Mo-Mn-CC coatings prepared from various conditions, their cathodic current densities at applied potential of -1.2 V were selected. The selected cathodic current densities were in between open circuit potential (OCP) and limiting current density which represented current densities from cathodic

reaction without those from side reaction of hydrogen evolution. To correlate between surface properties and corrosion resistance, coating morphology and chemical composition were examined by SEM-EDS.

III. RESULTS AND DISCUSSION

A. Appearance of Mo-Mn coatings and control samples

Fig. 1 shows typical images of Mo-Mn-CCs prepared from pH 3- and pH 4- coating solution compared with EGS, Mo-CC and commercial Cr(III)-CC. The EGS substrate (Fig. 3(a)) was smooth and glossy gray. After applied Mo-CC (Fig. 3(b)), Cr(III)-CC (Fig. 3(c)) and Mo-Mn-CC from pH 4 solution (Fig. 3(e)) on EGS substrate, they became glossy blue. For Mo-Mn-CC prepared from pH 3-solution, the coating was a poor adhesion-white layer as shown in Fig. 3(d).

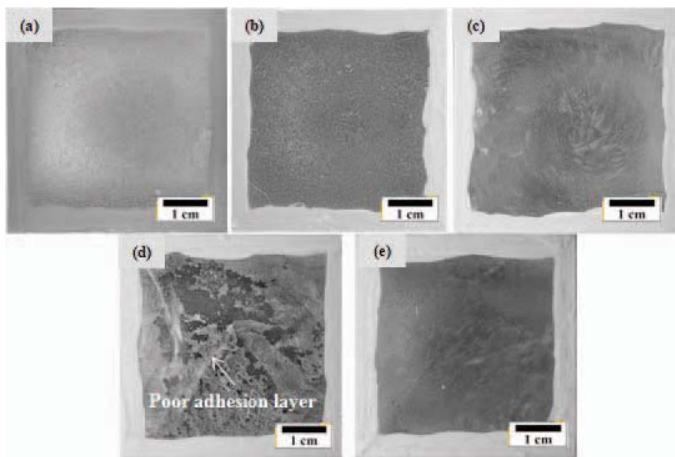


Fig. 1 Appearance of (a) EGS, (b) Mo-CC, (c) Cr(III)-CC, Mo-Mn-CC prepared from solution having Mo:Mn molar ratio of (d) 1:0.2 at pH 3 and (e) 1:0.2 at pH 4.

B. Corrosion resistance determined by salt spray test

Fig. 2 shows corrosion attacked area after salt spray test for 24 hours and duration at white rust observed on Mo-Mn-CCs prepared from solution having Mo to Mn mole ratio of 1:0.2. The white rust was observed on Mo-Mn-CCs after exposure to salt fog for 180-300 minutes while those of EGS, Cr(III)-CC and Mo-CC were observed at 30, 180 and 120 minutes respectively. It is indicated that Mo-Mn-CCs could delay corrosion onset longer than EGS and Mo-CC. In case of corrosion attacked area, that of EGS, Cr(III)-CC and Mo-CC were 48%, 1% and 26% correspondingly. Slight attacks on Cr(III)-CC possibly caused by oxidation of some trivalent chromium to hexavalent chromium; thereby, the self-healing property was established [4]. The attacked area on Mo-Mn-CC varied in the wide range of 3-31%. The coatings prepared from pH 4 solution at coating time of 2 and 5 minutes had attacked area percentage about 3% which was nearly to that of Cr(III)-CC ($\approx 1\%$).

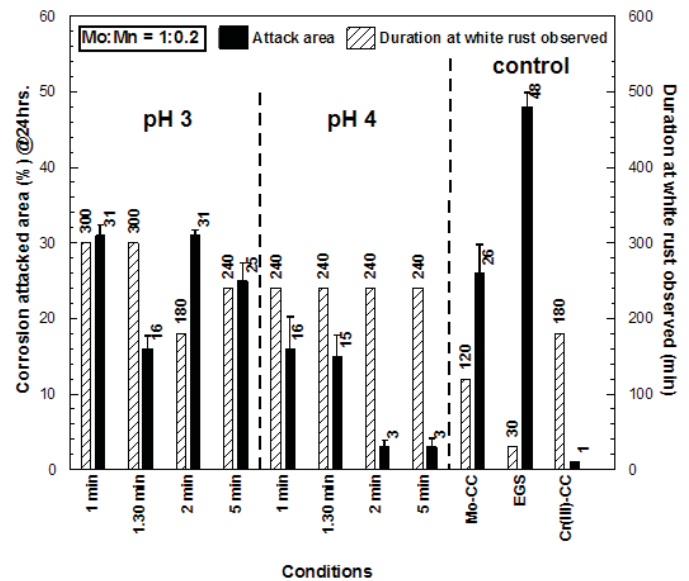


Fig. 2 Corrosion attacked area percentages after exposure to salt fog for 24 hours and duration at white rust observed on Mo-Mn-CCs prepared from solution having molar ratio of 1:0.2 compared with Mo-CC, EGS and Cr(III)-CC.

Corrosion attacked area and duration time at white rust observed on Mo-Mn-CCs prepared from solution having Mo to Mn molar ratio of 1:1 compared with the control samples are shown in Fig. 3. The coatings prepared from pH 3 solution had attacked area in the range of 27-41% whereas those from pH 4 solution were 6-7%. Additionally, most of the Mo-Mn-CCs prepared from Mo:Mn molar ratio of 1:1 (Fig. 3) could delay corrosion onset longer than those from molar ratio of 1:0.2 (Fig. 2) which was illustrated by extending the period at white rust observed to 300-420 minutes. This phenomenon was probably due to high manganese content in the coatings. Contrary to white rust delaying, the attacked area on Mo-Mn-CCs having Mo:Mn ratio of 1:0.2 was smaller than those from 1:1 especially the coatings prepared from pH 3 solution.

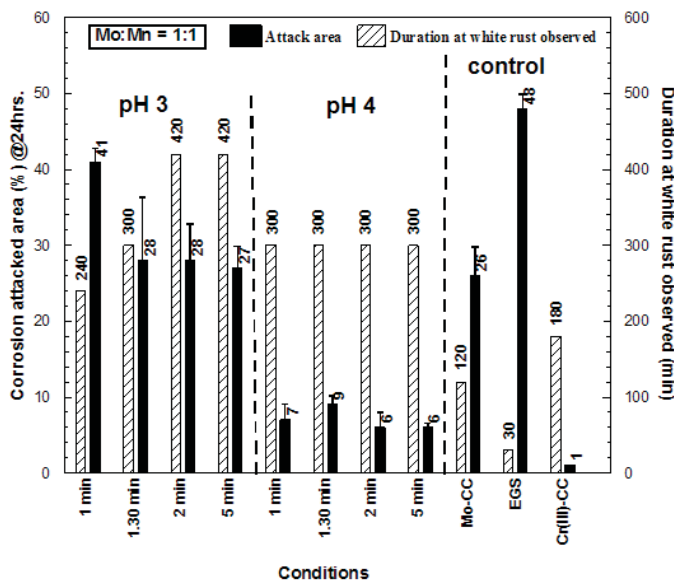


Fig. 3 Corrosion attacked area percentages after exposure to salt fog for 24 hours and duration at white rust observed on Mo-Mn-CCs prepared from solution having molar ratio of 1:1 compared with Mo-CC, EGS and Cr(III)-CC.

For both of the Mo to Mn molar ratio, coatings prepared from pH 4-solution were attacked lesser than those from pH 3 and control samples. The typical images of coatings prepared from pH 3- and pH 4-solution compared with control samples after exposure to salt fog for 24 hours are shown in Fig 4. It is evident that the Mo-Mn-CCs prepared from pH 4 had small amounts of attacked area (white area) than those from pH 3, control samples and nearly to that of Cr(III)-CC. Large attacked area on Mo-Mn-CC prepared from pH 3 solution probably caused by poor adhesion of coating as mentioned in the previous section.

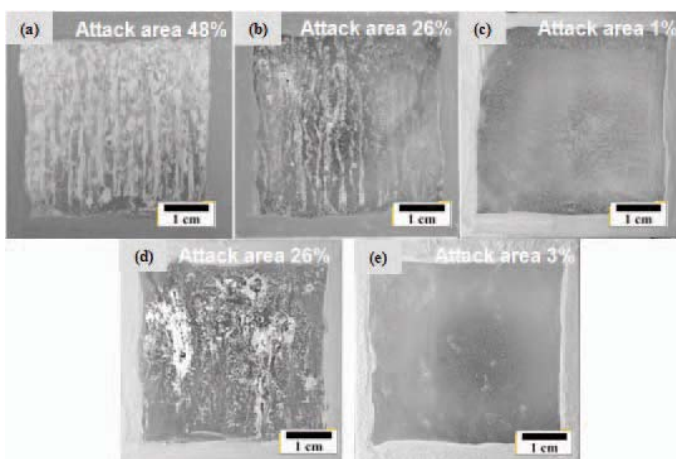


Fig. 4 The appearance of (a).EGS, (b).Mo-CC, (c) Cr(III)-CC, (d) Mo-Mn-CC prepared from solution having Mo:Mn molar ratio of 1:0.2, pH 3.0 and (e) 1:0.2, pH 4.0 after exposed to salt spray for 24hours.

Surface morphology of Mo-Mn-CCs examined by SEM are shown in Fig. 5. It is seen that the surface of Mo-Mn-CCs prepared from pH 3 solution (Fig. 5(a) and (b)) had micro-cracks while those from pH 4 solution (Fig. 5(c) and (d)) none of micro-cracks were observed. Due to crack-free and dense surface of Mo-Mn-CCs prepared from pH 4 solution, their corrosion resistance was better than those from pH 3 solution.

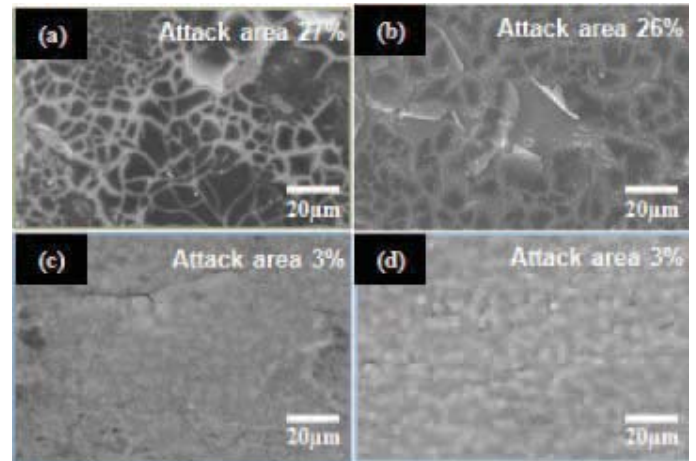


Fig. 5 SEM images of Mo-Mn-CCs prepared from solution having Mo:Mn molar ratio of (a) 1:1 (b) 1:0.2, pH 3 for 5 min (c) 1:0.2 and (d) 1:0.2, pH 4 for 5 min.

The chemical compositions of Mo-Mn-CCs analyzed by EDS were displayed in Table 1. Molybdenum (Mo), manganese (Mn) and phosphorus (P), from phosphoric acid, were found in the coatings. Great amount of zinc caused from the detection of EGS substrate. The molybdenum content depended only on pH of coating solution while manganese content related to Mo to Mn molar ratio, coating time and pH. Increasing in pH of coating solution reduced both of molybdenum and manganese content probably because of reduction in deposition rate. The Mo-Mn-CC prepared from pH 3-solution having Mo to Mn molar ratio of 1:1 at coating time of 5 minutes could delay corrosion effectively because of high manganese content but it was attacked severely because of poor adhesion.

From the results, it could be stated that superior corrosion resistance caused by various factors such as chemical compositions, surface morphology and electrochemical behavior which will be studied in the next section.

Table 1
Chemical compositions of Mo-Mn-CCs prepared from pH 3- and pH 4- solution

Sample	Element (Wt.%)				
	Mo	Mn	P	Fe	Zn
Mo:Mn(1:1), pH 3.0, 5 min	0.61	0.79	1.58	1.02	Bal.
Mo:Mn(1:0.2), pH 3.0, 5 min	0.57	0.55	1.31	1.13	Bal.
Mo:Mn(1:0.2), pH 4.0, 5 min	0.27	0.36	0.63	1.49	Bal.
Mo:Mn(1:0.2), pH 4.0, 2 min	0.28	0.28	0.64	1.39	Bal.

C. Electrochemical polarization measurements

Corrosion behavior of Mo-Mn-CCs was evaluated by potentiodynamic method in 3.5% NaCl. The anodic polarization curve represented kinetic of corrosion process in positive direction or oxidation reaction while the cathodic polarization curve related to reduction reaction [5].

Anodic polarization curves of Mo-Mn-CCs compared with control samples—EGS, Cr(III)-CC, and Mo-CC are shown in Fig. 6. Control samples and most of the Mo-Mn-CCs exhibited normal behavior of anodic polarization curve which their current densities increased when applied potential increased. The anodic polarization curve of Mo-Mn-CC prepared from pH 4 solution having Mo to Mn mole ratio of 1:0.2 at coating time of 2 minutes behaved in different way by revealing low current density plateau, well-known as passive region, similar to that found in Cr(VI)-CC [6]. The passive region represented the lowering of oxidation reaction which leads to the reduction of corrosion rate [7]. The results corresponded to salt spray test that the Mo-Mn-CC prepared from this condition was gently attacked ($\approx 3\%$).

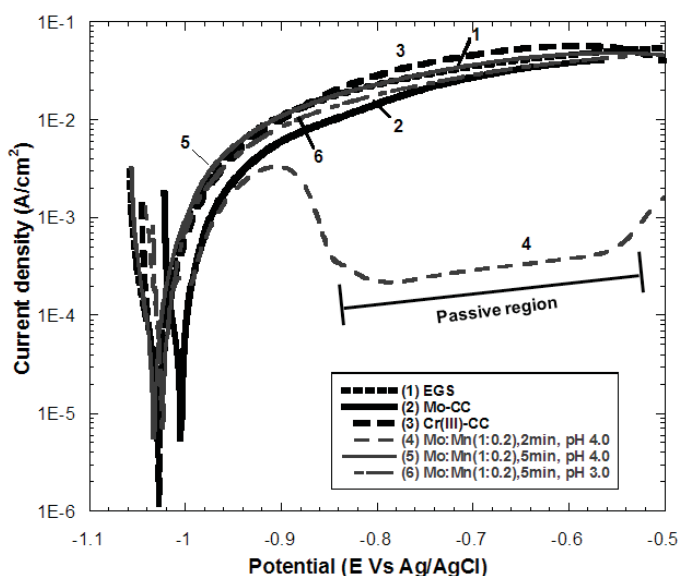


Fig. 6 Typical anodic polarization curves of EGS, Mo-CC, Mo-Mn-CCs and Cr(III)-CC in 3.5% NaCl at a scan rate of 1 mVs^{-1} .

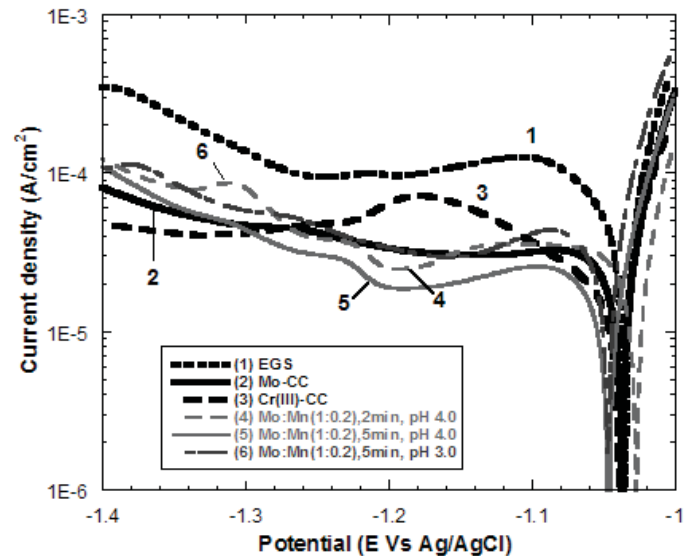


Fig. 7 Typical cathodic polarization curves of EGS, Mo-CC, Mo-Mn-CCs and Cr(III)-CC in 3.5% NaCl at a scan rate of 1 mVs^{-1} .

Fig. 7 shows cathodic polarization curves of Mo-Mn-CCs compared with control samples. In comparison to anodic polarization curves, the cathodic current densities were lower ($\approx 10^{-5} \text{ A/cm}^2$) than the anodic current densities ($\approx 10^{-2} \text{ A/cm}^2$) significantly. It is indicated that the cathodic current densities or reduction reaction was inhibited by coatings predominantly. For un-coated EGS, its cathodic current density was lower than its anodic current density as well. It is probably due to the formation of zinc oxide film which acted as barrier film hindering cathodic reaction.

Due to cathodic polarization curve of all samples were similar, their cathodic current densities at applied potential of -1.2 V were compared as displayed in Fig. 8. The cathodic current density of EGS substrate (un-coated) was relatively high ($\approx 1 \times 10^{-4} \text{ A/cm}^2$) because none of coating was applied to hinder the cathodic reaction. Among of the coated samples, cathodic current densities of Mo-Mn-CCs were lower ($\approx 2 \times 10^{-5} \text{ A/cm}^2$) than those of Mo-CC ($\approx 3 \times 10^{-5} \text{ A/cm}^2$) and Cr(III)-CC ($\approx 6 \times 10^{-5} \text{ A/cm}^2$). It is notable that the Mo-Mn-CC prepared from pH 4 solution showed minimum cathodic current density. The significant reduction in cathodic and anodic current densities of Mo-Mn-CC prepared from this condition led to corrosion reduction denoted by slightly attacked after salt spray test for 24 hours.

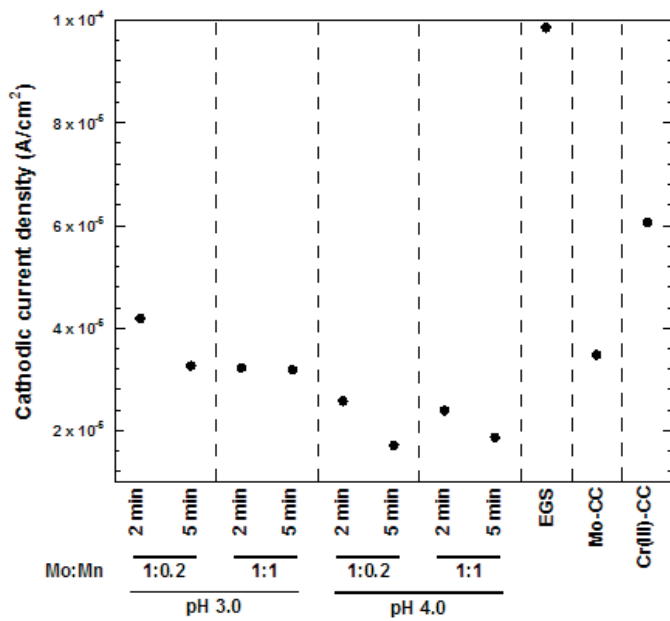


Fig. 8 Magnitude of cathodic current densities of EGS, Mo-CC, Mo-Mn-CCs and Cr(III)-CC at applied potential value of -1.2 V vs. Ag/AgCl

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From the results, the important factor influencing corrosion resistance of Mo-Mn film on electrogalvanized steel was the pH of coating solution. The coatings obtained from pH 4 solution produced crack-free surface and proper manganese content. It was also possible that the coating formed from this condition produced appropriated chemical compounds which will be studied further. These synergy factors were able to produce high corrosion resistance coating.

IV. CONCLUSIONS

- Corrosion resistance of molybdate conversion coating could be enhanced by doping with manganese.
- Superior corrosion resistance of Mo-Mn-CC prepared from solution having Mo:Mn molar ratio of 1:0.2, pH 4 at 50°C caused from its low anodic and cathodic reactivities together with crack-free surface.

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