

Effects of Al addition to Molybdate Conversion Coating

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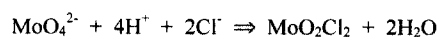
The effects of Al addition to molybdate conversion coatings to improve anticorrosive property were studied. Cathodic reactions on the surface of conversion coatings as well as the film itself and structure of conversion coatings were carried out by electrochemical method and Raman spectroscopy, respectively. It is found that the addition of Al to molybdate conversion coatings hinders more effectively cathodic reactions of dissolved oxygen and hydrogen evolution reactions than those of molybdate conversion coatings, from which could explain the enhanced anticorrosive property. Raman spectra revealed that molybdate conversion coatings are mainly composed of amorphous MoO₂ and trapped polymerized molybdate ion.

Keywords : Al addition, molybdate conversion coatings, anticorrosive property, Raman spectroscopy

1. Introduction

Many investigations have been carried out to replace chromate conversion coatings into more environmentally friendly one because of the toxic nature of hexavalent chromium to the environment.¹⁻⁸⁾ Among the alternatives such as molybdates, tungstates, permanganates and vanadates coatings, studies were concentrated on molybdates conversion coatings because of relatively low toxicity and good anticorrosive performance.

Devasenapathi and Raja⁹⁾ suggested that during stress corrosion cracking in stainless steel, further corrosion is inhibited by molybdate ions due to its ability to react with chloride according to the following reaction, and reduces the susceptibility of stainless steel to corrosion due to a low concentration of chloride at crack sites.



Although the anticorrosion performance is still very poor to compare with chromate conversion coatings,^{1-3),10)} some investigators attempted to add another coating agent such as phosphoric acid or permanganates to the treatment solutions for synergetic effects.^{2),5)} The addition of phosphoric acid resulted in good corrosion resistance outdoors exposure trials.⁵⁾

The structure of the molybdate conversion coatings has been investigated by XPS (X-ray photoelectron spectroscopy) because of its non-crystalline structure, and XPS analysis shows that the presence of Mo(IV) and Mo(VI) states), Mo(V) and Mo(IV) states or Mo(V) state only.¹⁰⁾

But the agreement has not been reached yet.

In this study, effects of Al addition to molybdate conversion coatings on anticorrosive property and the structure of molybdate conversion coatings were investigated using electrochemical experiments and Raman spectroscopy, respectively.

2. Experimentals

Conversion coatings were performed by dipping zinc electrode in various solutions, and the compositions of treatment solutions are listed in Table 1. Prior to dipping, zinc electrode of 1 cm² was polished with 2000 grit SiC sand paper. After the conversion coating, samples were rinsed with distilled water and dried in air. Electrochemical experiments are performed in the borate buffer solution using potentiostat/galvanostat (EG&G Parc 273A) which was coupled with the rotator (EG&G 616). A saturated calomel electrode (SCE) was used as the reference electrode and graphite rod as a counter electrode, and borate buffer solution is composed of 0.15M Na₂B₄O₇ and 0.3M H₃BO₃ with pH of 8.8. To control the concentration of the dissolved oxygen in borate buffer solution, the solution was continuously bubbled by N₂ or O₂ gas during experi-

Table 1. The composition of treatment solution

Bath	Mo50	MoA	Ch30
pH	5.0	3.0	3.0
Composition (concentration)	Na ₂ MoO ₄ (0.1M)	Na ₂ MoO ₄ (0.1M) Al ₂ (SO ₄) ₃ (0.05M)	KCr ₂ O ₇ (0.05M)

ments, and the concentration was measured by dissolved oxygen meter. (Istek 215D)

The saturated concentration of the dissolved oxygen is approximately 39 ppm during continuous oxygen bubbling to and 0.2 ppm during continuous nitrogen bubbling. Raman spectra were obtained using Raman spectrophotometer (Jobin-Yvon Model T64000). The composition-depth profiles of Al added molybdate conversion coatings were obtained by combining AES (Perkin-Elmer, Physical Electronic Inc.; Model 660), and the amounts of Mo in conversion coatings were obtained by ICP-AES analysis (Shimadzu ICPQ 1000)

3. Results and Discussion

3.1 Appearance of conversion coatings

The appearances of conversion coatings obtained with Mo50 solution bath show colorful transparent film with time, ranging from a golden/blue to green film when the treatment time does not exceed about 1 minute. But if the treatment time exceeds 1 minute, dark-orange colored film is formed, and the thickness increases with time, which results in characteristic dried 'river-bed' cracked surface structure. But the rate of film formation reactions of conversion coatings obtained with MoA solution bath, which Al is added, is much slower than that of conversion coatings obtained with Mo50 solution bath. The appearances of conversion coatings obtained with MoA treatment bath show metallic luster even after 5 minutes of immersion.

Table 2 summaries the Mo content of conversion coatings with a variation time and treatment bath, and reveals that Mo content of conversion coatings with Mo50 exceeds 20 times than that of conversion coatings with MoA treatment bath, which also indicates the rate of film formation reactions is much faster than that of conversion coatings obtained with MoA treatment bath.

Figure 1 shows the depth profile of conversion coatings obtained with MoA treatment bath for 30 sec. Al content in the film is about 6-8 at %, and also Zn content is about 8 at %. The deposition of Al and Zn species in the film is probably due to a local increase in pH caused by the cathodic reduction of molybdate near the surface of the substrate during the treatment.

Table 2. The Mo content with a variation of time and treatment bath.

Bath	Mo50	Mo50	Mo50	Mo50	Mo50	MoA	MoA
Immersion time (sec)	2	10	30	60	300	30	300
Amount of Mo deposited (10^{-7} mol/cm 2)	0.81	2.4	4.7	7.2	29.0	0.21	0.39

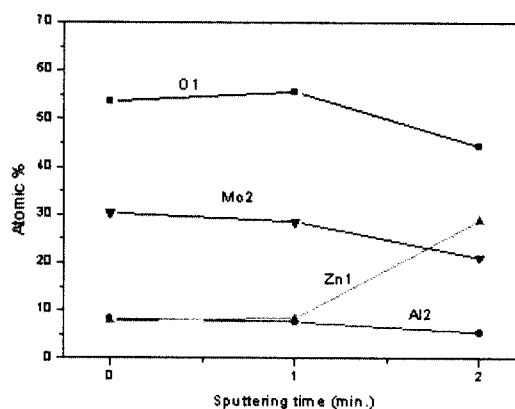


Fig. 1. AES depth profiles of Al added molybdate conversion coatings.

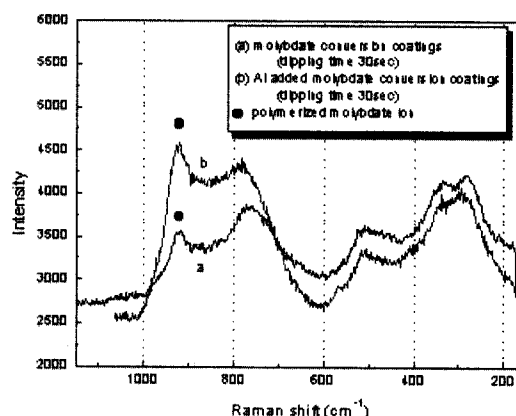


Fig. 2. Raman spectra of molybdate conversion coatings and Al added molybdate conversion coatings.

3.2 Reduction of molybdate ion in the film

Figure 2 shows the Raman spectra of conversion coatings obtained in both MoA and Mo50 bath. The broad Raman bands at 760 cm^{-1} , 510 cm^{-1} , 340 cm^{-1} can be assigned as MoO_2 (760 cm^{-1} , 505 cm^{-1} , 365 cm^{-1})¹² and 748 cm^{-1} , 510 cm^{-1} , 360 cm^{-1})¹³, and the broadness implies that MoO_2 is amorphous. The Raman band at about 928 cm^{-1} implies that the polymerized and octahedral cluster ion ($\text{Mo}_7\text{O}_{24}^{6-}$ raman band at 934 cm^{-1})¹⁴ or $\text{Mo}_8\text{O}_{26}^{4-}$ raman band at 963 cm^{-1})¹⁴ exists in the film. Considering that the major molybdate ion is $\text{Mo}_7\text{O}_{24}^{6-}$ at $\text{pH}=5.0$ in the treatment bath,^{10,14-15} $\text{Mo}_7\text{O}_{24}^{6-}$ is trapped in the film during the formation of the film. So, the film is composed of amorphous MoO_2 , trapped $\text{Mo}_7\text{O}_{24}^{6-}$, and Zn oxides or hydroxides.

Since the self-healing effect was observed during corrosion in chromate coatings,¹⁶ the possibility of reduction reaction of molybdate conversion coatings was investigated, Figure 3 presents the ex-situ Raman spectra obtained by controlling the potential of the electrode at -1.1 V for

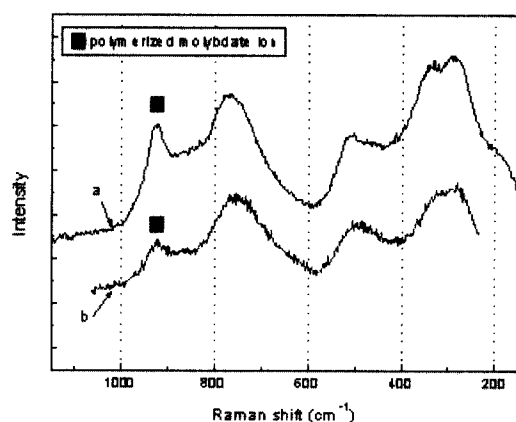


Fig. 3. (a) Raman spectra of molybdate conversion coatings obtained with Mo50 bath for 30 sec and (b) ex-situ Raman spectra of the electrode with electrochemical reduction of (a) by control the potential at -1.1 V for 1 hr in N_2 atmosphere.

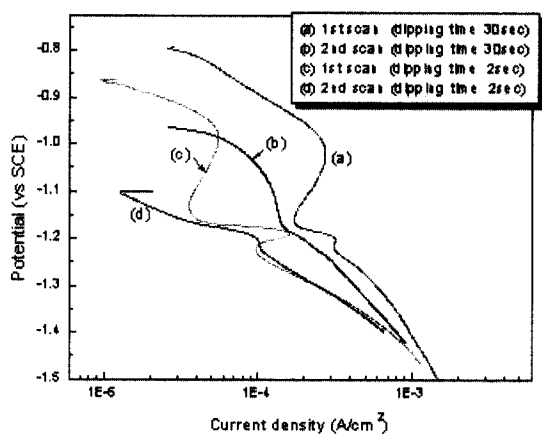


Fig. 4. Potentiodynamic curves with molybdate conversion coatings obtained with Mo50 bath for 30 sec, and with Mo50 bath for 2 sec, in N_2 bubbled borate solution. Scan rate is 2 mV/sec

1 hr in N_2 bubbled borate buffer solution.

The intensity of Raman band of polymerized molybdate ion is reduced in Figure 3, which indicate that polymerized molybdate ion participated in cathodic reaction.

Figure 4 shows potentiodynamic curves of molybdate conversion coatings with a scan rate of 2mV/sec in the borate buffer solution bubbled by N_2 . The rest potential of molybdate conversion coatings increases with the Mo content of the film, it shows a broad hump about -1.0 V.

The cathodic current in Figure 4 (a)(Mo content = 4.7×10^{-7} mol/cm²) is larger than that of Figure 4 (c) (Mo content = 4.7×10^{-7} mol/cm²). The rest potential and the current of hump decrease during the second scan. Although oxygen reduction and hydrogen evolution reactions occurring during the cathodic polarization will be discussed in

next section, the above facts indicate that the molybdate ions in the film are also reducing during the cathodic reduction process.

3.3 Hydrogen evolution reaction and reduction reaction of dissolved oxygen

It is well known that the chromate layer can hinder the cathodic and anodic reactions.¹⁷⁾

As mentioned above, hexavalent molybdenum ions also can be reduced during the cathodic reaction, potentiostatic experiments at -1.2 V were performed in advance to minimize the reduction of molybdate ions in the film.

Figure 5 shows the hydrogen evolution reaction on various substrates.

Tafel slope for hydrogen evolution is almost constant as -0.15 (0.02 V/decade regardless of substrates, and the current density of hydrogen evolution on molybdate conversion coatings increases with the Mo content in the film and exceeds the current density of hydrogen evolution reaction on Zn. But the current density of hydrogen evolution on Al added molybdate conversion coatings decreases with the Mo content in the film.

The increasing of the current density of hydrogen evolution on molybdate conversion coatings implies that the conversion coatings did not act as diffusion barrier to the cathodic reaction rather act as active sites for electrochemical reduction reaction and also implies that the sites of reaction is not necessarily to be surface of Zn, which is beneath the film. And this is confirmed by the fact that MoO_2 has some electronic conductivity.¹⁸⁾

Figure 6 illustrates the potentiodynamic curves of oxygen reduction on different conversion coatings obtained in O_2 bubbled borate buffer solution.

In the potential range of between -1.1 V and -1.2 V,

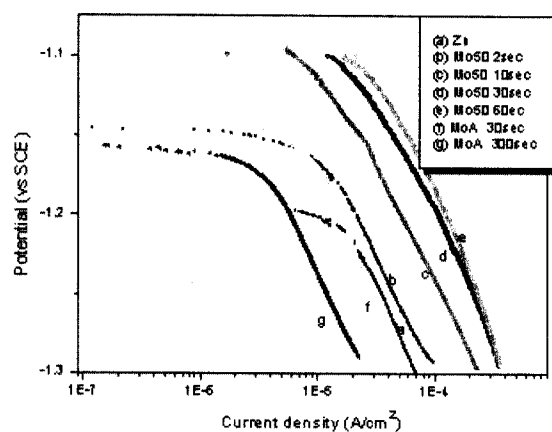


Fig. 5. Potentiodynamic curves of conversion coatings obtained with various treatment bath and time in N_2 bubbled borate solution. Scan rate is 0.166 mV/sec.

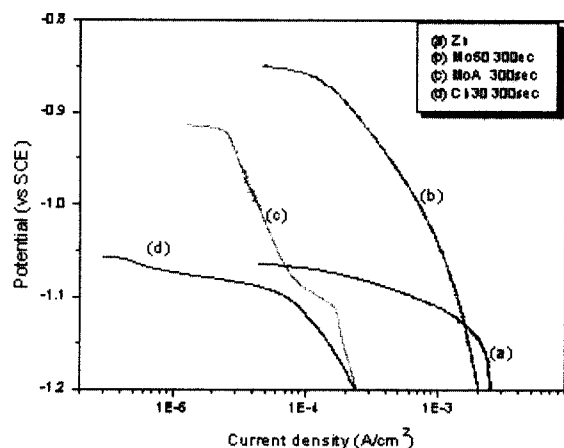


Fig. 6. Potentiodynamic curves of conversion coatings obtained with various treatment bath and time in O_2 bubbled borate solution. Scan rate is 0.166 mV/sec.

current density shown in Figure 6 (c) is very large in comparison with the current density shown in Figure 4 (g), which indicates that the major species that participate in the cathodic reaction is dissolved oxygen.

Figure 6 shows that the reduction current of oxygen on Zn in the potential range of -1.15 V ~ -1.2 V, is the largest among the tested electrodes. Although electrochemical reduction of oxygen on molybdate conversion coatings obtained with Mo50 is not effective, in comparison with conversion coatings obtained with Ch30 or MoA. And, the oxygen reduction reaction on chromate coating is most slowed among the conversion coatings as expected.

3.4 Anticorrosive properties

As discussed above, the reduction rate of dissolved oxygen on molybdate conversion coatings is lower than that on Zn which we can expect the reduction of the corrosion rate.

To test the anticorrosive property, the conversion coatings obtained with MoA and Mo50 treatment bath for 30 sec, was immersed in NaCl 5 wt% solution for 10 hr, and the amounts of produced white rust was compared. In Al added molybdate conversion coatings obtained with MoA bath, the amounts of produced white rust is below 10 %, but molybdate conversion coatings obtained with Mo50 bath, that of produced white rust is as much as 40%, which means that Al adding to molybdate conversion coatings much more enhance the anticorrosive properties

considering that the Mo content of Al added molybdate conversion coatings is lower than a twentieth of that of molybdate conversion coatings.

4. Conclusions

The structure and electrochemical properties of molybdate conversion coatings were characterized with Raman spectroscopy and potentiodynamic polarization techniques, respectively. The film formed on Zn substrate was found to be amorphous MoO_2 and also it contains polymerized molybdate ions. The addition of Al into the film shows better corrosion resistance and this effect is explained in terms of hydrogen reduction and oxygen reduction.

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