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## Growth and corrosion behavior of molybdate passivation film on hot dip galvanized steel<sup>①</sup>

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**Abstract:** Hot dip galvanized steel sheets were passivated by molybdate aqueous solution containing 10 g/L  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , and the growth behavior and corrosion resistance of the passivation film were investigated. In the initial stage of passivation, the mass gain of film increases with passivation time proportionally. The film grows up more quickly and is apt to cracking at grain boundaries of zinc, then the cracks spread gradually on the whole surface of the film, and eventually the film will flake off with the increasing of film thickness. XPS results indicate that Mo compounds are present in Mo(VI) state on the surface of the film, and Mo(VI) and Mo(IV) states inside the film. NSS test shows that, the corrosion resistance of the passivation film decreases as the cracks occur, but in AASS test, the thicker the film is, the better the corrosion resistance is, the cracks of film have little effect on the corrosion resistance.

**Key words:** hot dip galvanizing; molybdate passivation film; corrosion resistance

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### 1 INTRODUCTION

Chromate conversion films have been applied as final anticorrosive treatments to galvanized steel for many years, their effectiveness in this application is widely acknowledged. However, with the advent of increasing environmental awareness, the toxic nature of chromium(VI) base treatment has made its use undesirable<sup>[1-3]</sup>, leading to the search for effective replacements<sup>[4-6]</sup>.

In this paper the molybdate-based passivation for hot dip galvanized steel is studied, the growth characteristic, chemical composition and corrosion resistance of the passivation film are investigated.

### 2 EXPERIMENTAL

Low carbon steel sheets (50 mm × 40 mm × 2 mm) were degreased, pickled, fluxed, dried and dipped in zinc bath at 450 °C for 2 min, withdrawn slowly, cooled in air for zinc freezing and quenched in water immediately. The thickness of every galvanized coating was about 50 μm. After the zinc coatings were applied, the galvanized samples were immersed immediately in the molybdate based passivation solution at 60 °C for different time from 1 to 25 min, then dried in air at room temperature. The passivation solution contains 10 g/L  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , some phosphate and has a pH value of 5.0.

Mass gains of the passivation films were weighed by an analytical balance with a precision of 0.1 mg. After

being dissolved the films in hydrochloric acid, Mo contents in the resultant solutions were analyzed with atomic absorption spectrophotometer to determine the Mo contents ( $\text{g/m}^2$ ) of the films. Surface morphologies of the films were observed by scanning electron microscopy (SEM). The distribution and valences of the elements in the films were analyzed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) respectively. Neutral salt spray test (NSS) and acetic acid salt spray test (AASS) were carried out in accordance with ASTM B117 and ASTM B287 respectively.

### 3 RESULTS

#### 3.1 Mass gain and Mo content of passivation film

The mass gain of the passivation film was almost proportional to the immersion time in the initial stage of immersion, and then it became to increase slowly after 10 min and turned to decrease after 20 min (Fig. 1). The relationship between the Mo content and immersion time is very similar to that between the mass gain versus immersion time (Fig. 2). Obviously, the mass loss after 20 min is resulted from the film flaking off, which is visible by naked eye.

#### 3.2 Surface morphology of passivation film

Surface morphology of the hot dip galvanized coating is shown in Fig. 3(a). The zinc grain boundaries and some shallow pits appear, the average size of the zinc

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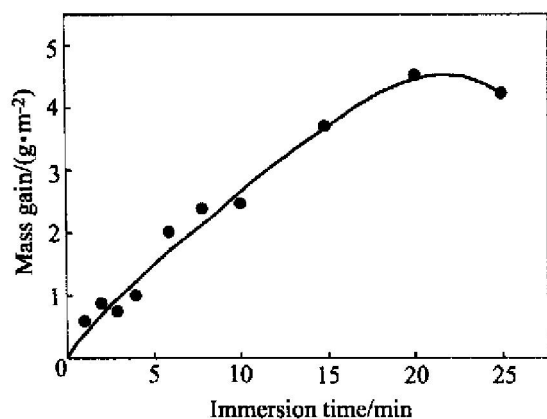


Fig. 1 Effect of immersion time on mass gain of passivation film

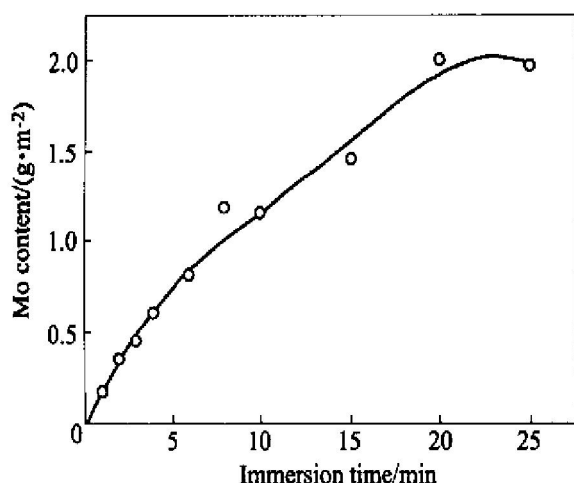


Fig. 2 Effect of immersion time on Mo content of passivation film

grains is about hundreds of micrometers. After immersion for 1 min, the surface became more flat and the zinc grain boundaries became clearer, there were some wrinkles nearby the grain boundaries because of quicker growth of the passivation film on the active grain boundaries, as shown in Fig. 3(b). After immersion for 3 min, the surface morphology of the passivation film changed enormously: in the flat surface area the grain boundaries of zinc and shallow pits disappeared and some fragments distributed in reticulation with size compared to that of original zinc grains, as shown in Fig. 3(c). In higher magnification, these fragments were cracked passivation films. After immersion for 5 min, the cracks had already occurred on the whole surface of the passivation film, like 'dried river bed' pattern (Fig. 4(a)). The width of the cracks increased with increasing passivation time as well. After immersion for 10 min, some secondary cracks appeared and local passivation film warped (Fig. 4(b)). After immersion for 15 min, the passivation film warped seriously and the tendency for the film to flake off was increased (Fig. 4(c)).

### 3.3 Distribution and valance of elements in passivation film

The AES composition profile of passivation film of a sample after immersion for 2 min is illustrated in Fig. 5. This profile shows that the zinc content increases steadily while the contents of Mo, P and O decrease gradually along the depth direction of the film, and there is a little of C on the surface as a contamination element. The Auger signal for Na is at the same position as zinc, the sodium content cannot be quantitatively determined, but using XPS it is shown that there is about 3% Na on the surface of the film. According to the rate and the time of argon ion sputtering, the thickness of the film is within the range from 60 to 100 nm.

The results of XPS show that the binding energies of the Mo peaks before argon ion sputtering are 232.7 and 235.7 eV, corresponding respectively to the Mo3d<sub>5/2</sub> (232.6 eV) and Mo3d<sub>3/2</sub> (235.8 eV) peaks<sup>[7]</sup> (Fig. 6(a)). It can be concluded that Mo(VI) (MoO<sub>3</sub>) exists on the surface of the film. The spectrum for Mo after 100 s argon ion sputtering is obtained and deconvoluted by computer analysis (Fig. 6(b)), the peak can be resolved into four peaks representing the Mo compound in the Mo(VI) and Mo(IV) states with the binding energies of 235.7 eV, 232.6 eV and 233.4 eV, 230.2 eV peaks<sup>[7, 8]</sup> in the inner of the film. Moreover, XPS results show that P compound and Zn compound are always presented in P(V) and Zn(II) states both on the surface and in the inner of the film respectively.

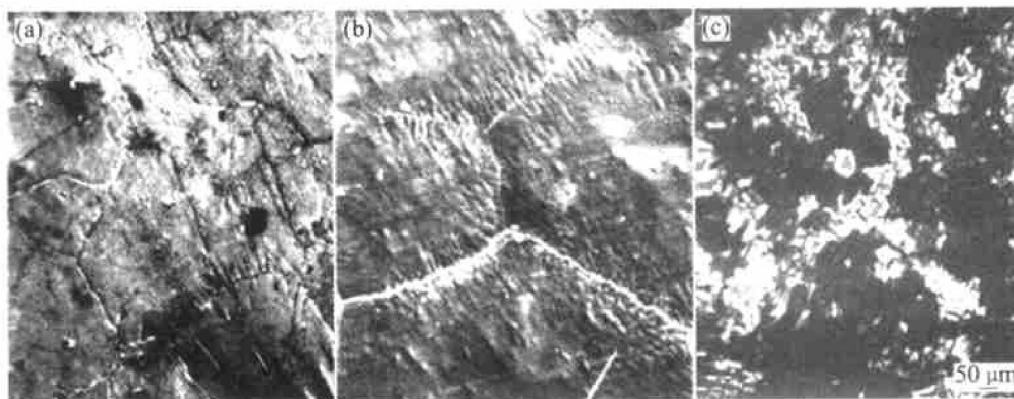
### 3.4 Corrosion test

Table 1 indicates the results of NSS and AASS tests for passivated samples, in which the corroded area means where metallic luster of zinc was lost and the white rust clearly occurred.

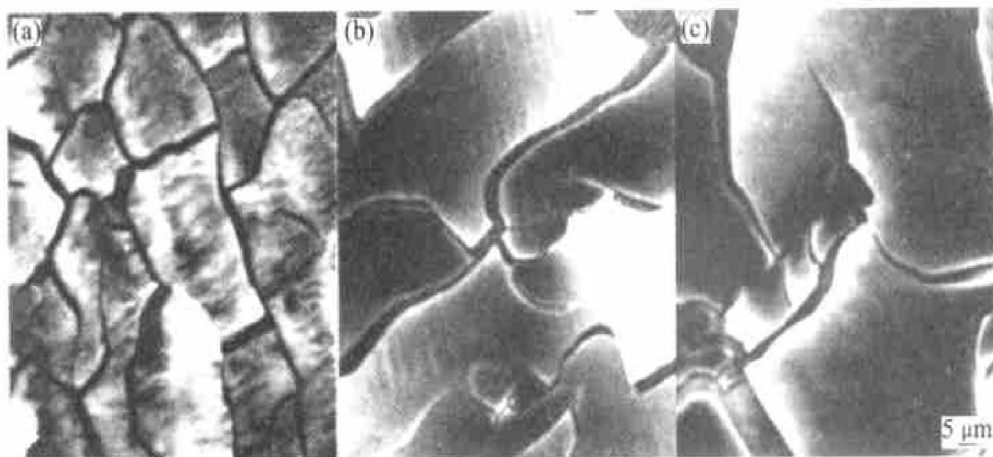
Table 1 Corroded area ratio of passivated samples after NSS and AASS (%)

Test	Spray time/ h	Passivation time/ s					
		10	20	40	60	120	300
NSS	6	0	0	0	0	0	5
	12	3	0	0	0	0	10
	24	5	2	2	2	7	15
AASS	6	2	1	1	1	1	0
	12	15	8	8	8	8	1
	24	25	15	10	10	8	1

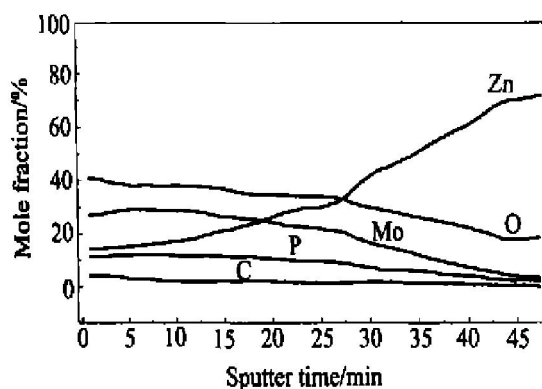
The corrosion resistance of the passivation film is enhanced steadily by increasing passivation time from 10 to 20 s and is not changed by increasing passivation time from 20 to 60 s both in NSS



**Fig. 3** Surface morphologies of hot dip galvanized steel without (a) and with immersion for 1 min (b) and 3 min (c) respectively



**Fig. 4** Microcracks of molybdate conversion films after various immersion time (a) -5 min; (b) -10 min; (c) -15 min

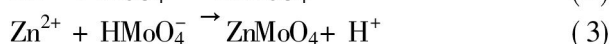
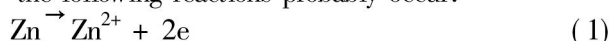


**Fig. 5** Auger depth profile of molybdate conversion film

and AASS. However, increasing passivation time from 60 to 300 s, the corrosion resistance in NSS is decreased but the corrosion resistance in AASS is still enhanced.

#### 4 DISCUSSION

Immersing the zinc coating in the passivation solution, the following reactions probably occur:

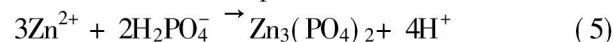


In weak acid solution, the molybdate may be re-

duced as



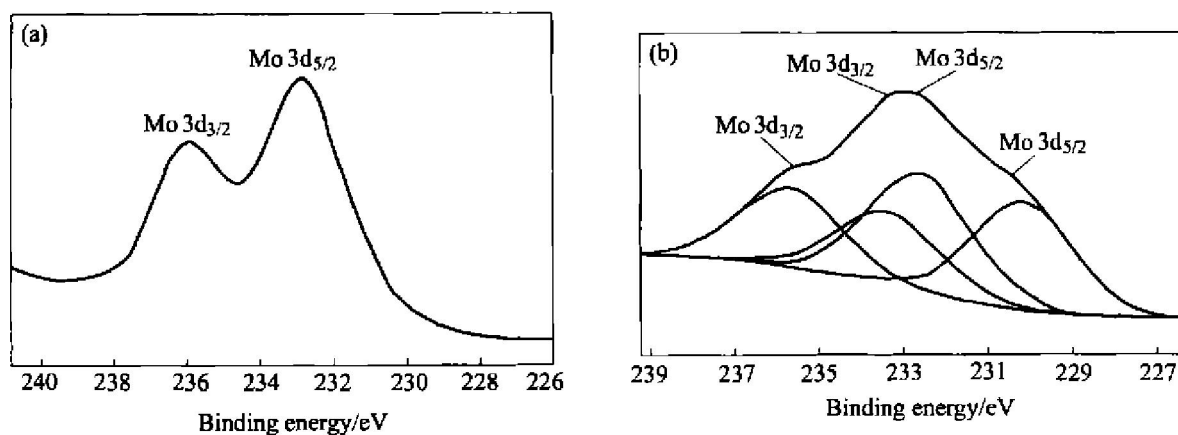
According to the Hagg diagram for the ortho phosphate system<sup>[9, 10]</sup>, phosphate mostly exists in the form of  $\text{H}_2\text{PO}_4^-$  in a solution with pH 5, so



Therefore, the passivation film contains  $\text{Zn}^{2+}$ ,  $\text{Mo}^{6+}$ ,  $\text{Mo}^{4+}$ ,  $\text{P}^{5+}$ ,  $\text{O}^{2-}$ , etc. X-ray diffraction (XRD) analysis shows that the film may be amorphous. Kurosawa et al<sup>[11]</sup> reported similar results for molybdate passivation film on steel.

The formation process of the passivation film may induce growth stress in the film, which increased progressively with the growing of the film, therefore resulting in the formation of cracks in the film for releasing stress. The crack formation during molybdate passivation on hot-dip galvanized coating is the same as that on electroplated zinc and zinc alloy coating<sup>[4, 12]</sup>.

Supposing that the density of the passivation film is 3 ~ 6 g/cm<sup>3</sup> and according to the data in Fig. 1, the thickness of the film obtained by immersion for 10 min should be 0.5 ~ 1 μm. Therefore, the thickness of the film that has best corrosion resistance against NSS is about 0.1 μm. Along with increasing the



**Fig. 6** High resolution XPS spectra of Mo after sputtering different time  
(a) -0 s; (b) -100 s

thickness of the film and the formation of cracks, the corrosion resistance against NSS decreases, but the corrosion resistance against AASS increases continuously, it seems that the corrosion resistance against AASS mainly depends on the film thickness and is little affected by the cracks in the film.

## 5 CONCLUSIONS

1) Molybdate passivation films on hot dip galvanized steel sheets were obtained by simple immersion in a molybdate aqueous solution.

2) In the initial stage of the film growth, the thickness of the film was proportionally increased with immersion time. The film grew up more quickly on the zinc grain boundary and was apt to cracking, then the cracks spread progressively on the whole surface of the film and resulted in the film flaking off.

3) The corrosion resistance of the film without cracks is enhanced with increasing the film thickness. However, as the cracks of the film occur, the corrosion resistance of the film against NSS decreases, but that against AASS seems not being affected.

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