

# The Film Forming Mechanism of Chromium-free Passivation in the Tannic Acid System for Electrogalvanized Coating

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**Abstract:** In this paper, tannic acid, fluorine titanate and silane coupling agent passivation solution were used to prepare hot dip 55% Al-Zn steel sheet passivation coating. And then the mechanism of film formation was studied. The microstructure, surface composition, layer by layer element distribution and molecular structure of 55% Al-Zn steel sheet passivation coating were revealed in scanning electron microscopy, X ray photoelectron spectroscopy, glow discharge atomic emission spectrometry and infrared spectrometry, respectively. The results show that: in one hand, using the silane coupling agent would generate many sol-gel particles in the passivation solution. On the other hand, tannic acid would produce spatial mesh structure. Therefore, passivation solution would generate a smooth, uniform and compact 55% Al-Zn steel sheet passivation coating or membrane.

## 1. Introduction

The traditional chromate passivation film has been widely used in industrial production because of its high corrosion resistance, high cost performance and simple process[1,2]. However,  $\text{Cr}^{6+}$  in the passivation film is carcinogenic and has great harm to the human body and environment. Therefore[3-5], the production containing  $\text{Cr}^{6+}$  has been gradually banned and eliminated by other countries. In order to find the corresponding substitute products, a great deal of research work has been done on the formulation of environment-friendly passivation liquid for hot-dip galvanized sheet at home and abroad[6-10]. Among them, hot galvanized plate and environment-friendly passivation liquid formulation of the field of [6], Japan, Germany Henkel Parker is a leading manufacturing field [7] environmental protection passivating hot galvanized plate, the Japanese iron and steel enterprises JFE, Nippon Steel in 2003 which has formed a series of products. In addition, South Korea, Pohang and the East have also successfully developed environment-friendly passivation hot-dip galvanizing products in 2000~2005, and have been widely used in home appliance manufacturing industry [8].

The related research and development work started late in our country. Although a lot of experimental studies have been carried out, there are still no industrial application achievements due to the problems of corrosion resistance, process adaptability and cost. Therefore, the domestic appliance manufacturers with galvanized steel are imported, the Chinese higher Parker passivation agent to produce environmentally friendly hot galvanized products [9,10]. In fact, using imported passivation liquid prices high, the production cost of the domestic iron and steel enterprises increased significantly,



and the import of passivation solution is all foreign to provide raw materials, according to the rules in the domestic fixed simple preparation, unclear mechanism of film and passivation liquid into the name of the drug formulation and their respective functions, making the domestic steel enterprise product quality stability. In summary, according to the current common trivalent chromium, molybdenum (tungsten) acid salt, titanium salt, zirconium salt and silicate, rare earth, tannic acid and silicon based organic coating related results of [11-14], this paper intends to study the tannic acid based chromium free passivation liquid film forming mechanism, provide a reference for the development of passivation solution.

## 2. Experimental materials and methods

D K7716 type wire cutting machine is used to heat the 55% Al-Zn alloy steel plate into 50 \* 50 \* 2 mm size, which then underwent accurate grinding by 240#, 360#, 400#, 600#, 800#, 1000#, 1200#, 1500#, 1800#, 2000# sandpaper, respectively, and wash with deionized water. Finally, rinse with acetone and deionized water and dry after removing the surface grease.

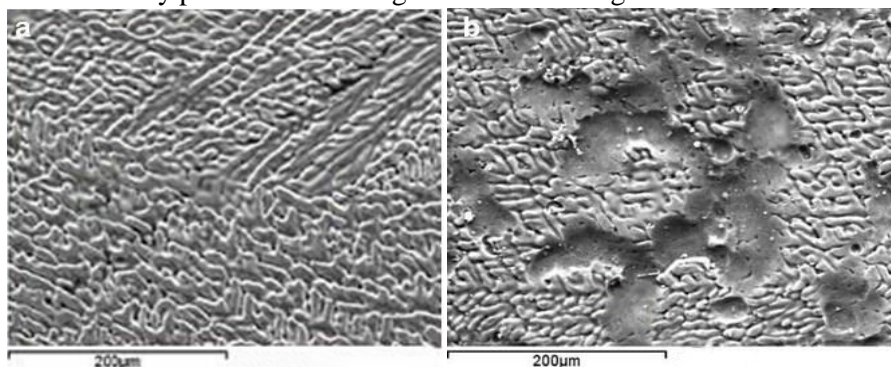
The tannic acid solution with mass fraction of 2%~7% is prepared at room temperature, and then the fluorine titanate and sol silane coupling agent with mass fraction of 2% is dripped in sequence, and the mixture is quickly stirred and evenly mixed. Among them, the main effect of tannic acid solution is the formation of the three-dimensional network structure, the effect of silane coupling agent to improve the corrosion resistance of the coating, promote the crosslinking between components in solution, another major effect of silane coupling agent is to improve coating film-forming properties, reduce curing temperature and increase the oxidation resistance of the coating [12, 13]. Finally, the heat treated 55% Al-Zn alloy steel plate is dipped in the mixed solution for about 1 s, and the coating [14] is cured at about 80 DEG C after taking out.

Japanese Ricoh JSM1600-LV scanning electron microscope (SEM) was used to observe the coating surface microstructure and composition by INCA, EDS analysis, the film was scanned by layer element GDS-850A glow discharge atomic emission. Molecular structure of Nicolet Magna coating type was detected by ir-560 infrared spectrometer.

## 3. Results and discussion

### 3.1. Microscopic morphology analysis

Figure 1 shows the microscopic morphology of the sample treated with chromate free passivation solution and without any passivation solution. As can be seen from figure 1 (a), the surface of the sample is uniform, dense and smooth without using passivation liquid. figure 1 (b) using tannic acid without surface chromium passivation liquid samples despite many obvious uneven Al-Zn structure, but the passivation membrane reaction passivation solution and Al-Zn layer after the formation of a good adhesion, no passivation powder, loss and other defects. From the figure 1 (a) and figure 1 (b) we can found that the use of tannic acid system chromium free passivation solution after the heat treatment, 55% Al-Zn alloy passivation coating has better coverage and cohesiveness.

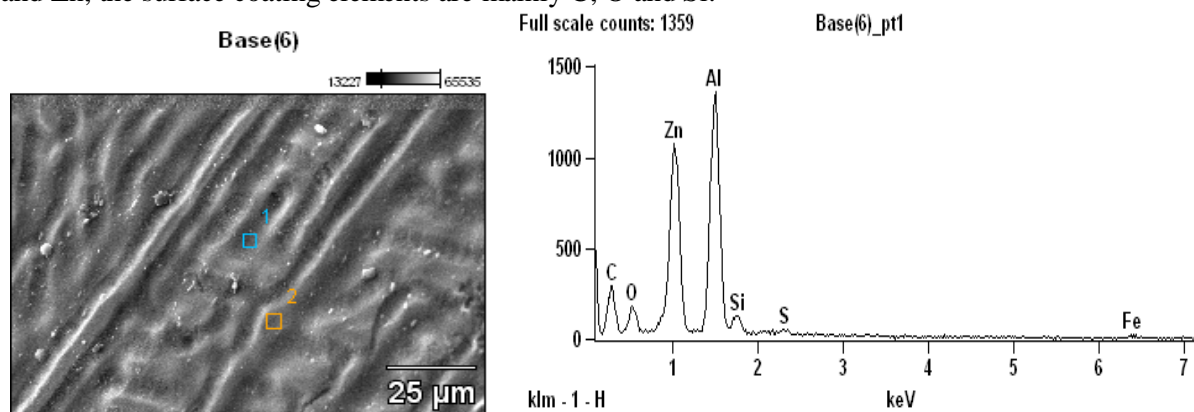


**Figure 1** Microstructure morphology of coating (a) 55% Al-Zn alloy coating (b) Compared with a galvanized coating.

### 3.2. Coating elements and surface analysis

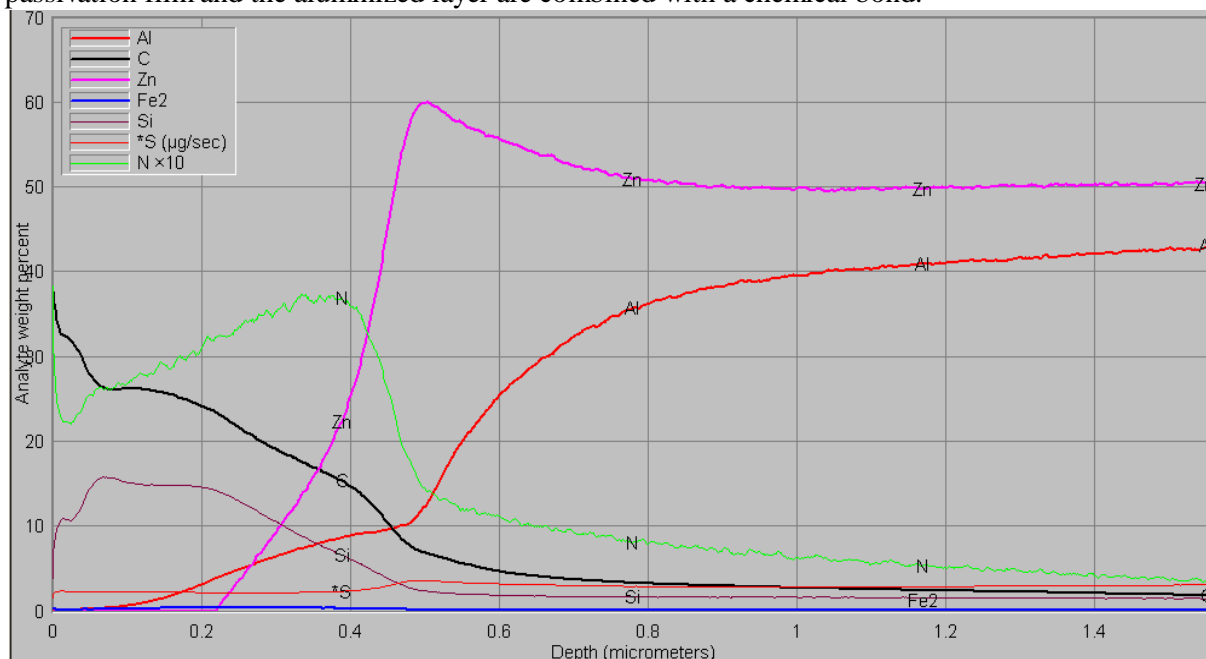
In order to further investigate the surface morphology and element distribution of the coating, the microstructure and composition of the sample surface were analyzed by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). The results were shown in figure 2.

As can be seen from the diagram, there is a network structure on the surface of the sample when treated with chromate chrome free passivation solution. The film is uniformly adhered to the surface of Al-Zn coating and has a corrosion pit. In addition, INCA spectrometer points out that except for Al and Zn, the surface coating elements are mainly C, O and Si.



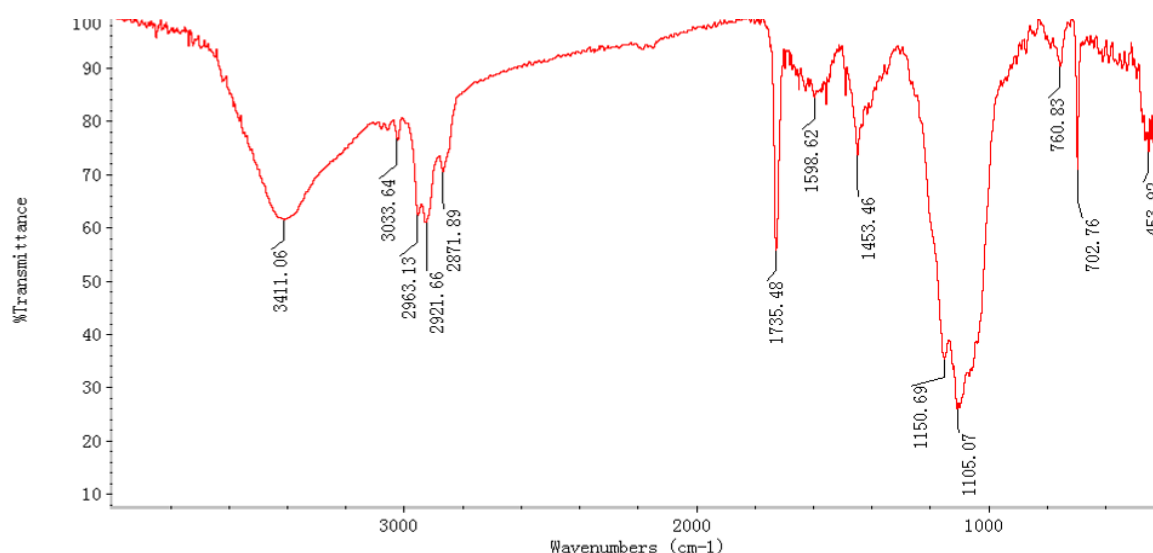
**Figure 2** SEM and INCA analysis results.

The study of the element distribution of coating layer by layer is of great reference value to the existing form and distribution state of the coating. GDS-850A glow discharge atomic emission spectrometry was used to scan the film by layer by layer element. The scanning results were shown in figure 3. From the distribution of elements, it is found that the carbon decreases with the depth of the film. This shows that organic film forming material mainly exists on the surface of film. In addition, there is a cross between the passivation layer and the aluminized layer, which indicates that the passivation film and the aluminized layer are combined with a chemical bond.



**Figure 3** Analysis results of film glow spectra.

The infrared spectrum of the film can characterize the change of molecular structure during hydrolysis. As shown in figure 4, with the increase of hydrolysis time, the symmetric distortion absorption peak of Si- (CH<sub>3</sub>) at 453 cm<sup>-1</sup>, the symmetrical stretching peak of Si-O-C at 702 cm<sup>-1</sup> and the intensity of asymmetric stretching peak at 1107 cm<sup>-1</sup> gradually decrease. In the range of 1000-1176 cm<sup>-1</sup>, the absorption peaks of Si-O-Si, Si-O-C and Si-O-Al overlap each other. The absorption peak at 1031 cm<sup>-1</sup> is continuously enhanced, which is the Al-O-Si bond formed by the effect of the silanol hydroxyl group on the surface oxide of the aluminum alloy. The peak at 1450~1608 cm<sup>-1</sup> is the result of bending vibration of the C-C bond on the benzene ring. The peaks at 1735 cm<sup>-1</sup> are produced by stretching vibrations of the C=O group. The strongest peak at 3000-3500 cm<sup>-1</sup> is the stretching vibration peak produced by -OH. In addition, at 760~800 cm<sup>-1</sup>, the absorption peak strength of the hydrolysis group decreases with the increase of hydrolysis time. The absorption strength of silanol group (Si-OH) at 2870~3050 cm<sup>-1</sup> at the silane film layer of aluminum alloy decreases with the increase of aging time. It is shown that with the prolonging of curing time, the condensation of the silanol groups, silicon alcohol at 3033 cm<sup>-1</sup> (Si-OH) absorption peak gradually weakened, and the formation of siloxane (Si-O-Si) and aluminum (Si-O-Al) siloxane bond absorption peak (1000 ~ 1176 cm) continuously variable width reinforced, and showed that silane the surface of Al-Zn alloy in the passivation solution of the basic completion of the bonding reaction.



**Figure 4** IR spectrum analysis of the film.

### 3.3. Experimental results are discussed

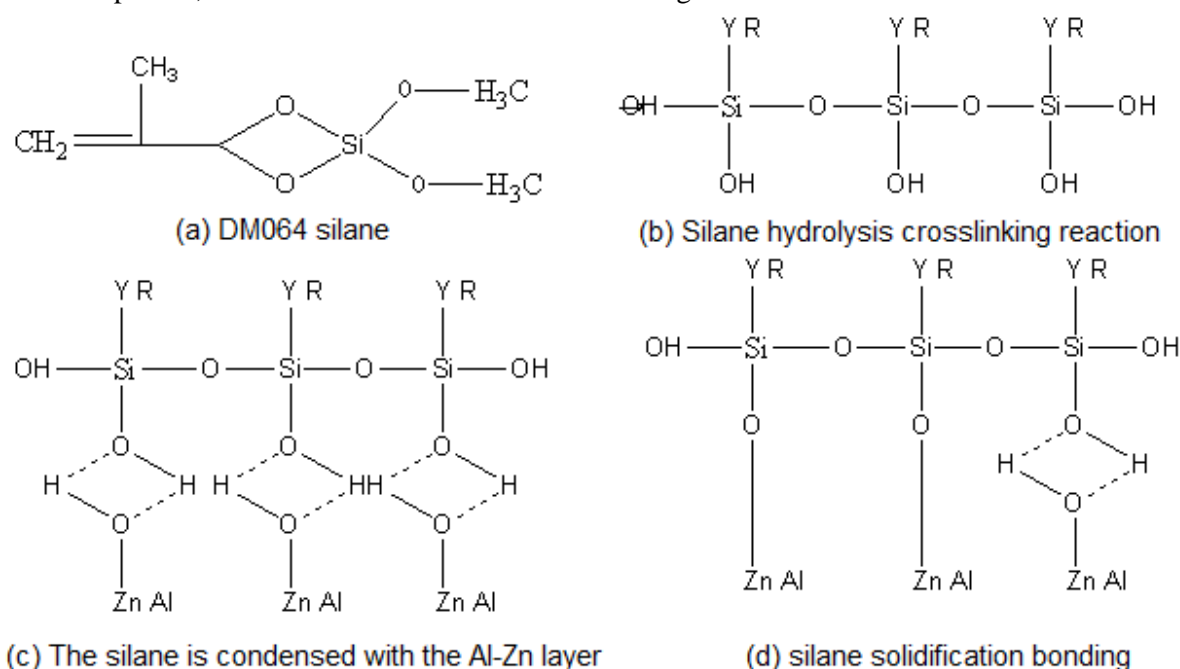
According to the above analysis results, it can be inferred that the film forming mechanism of the hot dip aluminized chromate free passivation liquid is as follows:

The chromate free chromate passivation solution in turn occurs in figure 5 (a), (b), (c), and (d) reactions. With the development of hydrolysis, the concentration of SiOH increases continuously. The concentration of hydrogen ion in solution increases, and the condensation of SiOH or the binding of oxygen to macromolecule will accelerate.

Subsequently, in the range of 1000-1176 cm<sup>-1</sup> band, the absorption peaks of different groups have changed significantly. For example, the absorption peak of the Si-O-Si bond at 1110 cm<sup>-1</sup> moves gradually to the high frequency band, which results in the formation of linear siloxane chains during cross-linking and curing. Moreover, in the range of 1000 ~ 1105 cm<sup>-1</sup> band, the absorption peak is continuously enhanced. At this time, the aluminum siloxane (Al-O-Si) and siloxane (Si-O-Si) bonds form a complete spatial network structure at the aluminum alloy interface and sub interface. Because has not reached a steady state, so as to gradually form the film in silicone and aluminum siloxane

network structure, crosslinking density increasing, the impedance of fingerprint resistant film is also increasing, the corrosion resistance of continuous improvement.

On the other hand, due to the increase of crosslinking density in the films, and nanometer styrene acrylic resin and nano colloidal  $\text{SiO}_2$  particles filled into the void space mesh of these cross-linked, the coating porosity, permeability and swelling degree were significantly decreased, the film began to increase the uniformity. With the condensation reaction between the film without hydrolysis of the ester irreversible hydrolysis reaction and the silanol groups of the time, the film crosslink density increasing, the hydrophilic group (Si-OH) also decreased, resulting in film density and hydrophobic coating which can prevent the increasing infiltration of electrolyte effectively impedance, has been further improved, and the corrosion resistance increased again.



**Figure 5** Mechanism of formation of chromium free passivation solution.

#### 4. Conclusions

- 1) The main effect of tannic acid zinc coating system components of chromium in the passivation solution: tannic acid solution is the role of the formation of the three-dimensional network structure, 2tif6 role is to improve the corrosion resistance of the coating, promote the crosslinking of each element between the solution and the effect of silane coupling agent is the film-forming properties of the coatings to improve, reduce the curing temperature and increase antioxidation.
- 2) Tannic acid based hot aluminium zinc chromium free passivation liquid film forming mechanism is as follows: first to form three-dimensional network structure in the tannic acid solution, then sol type silane coupling agent reaction sol gel particles and filled in the three-dimensional network structure, finally the formation of smooth, uniform and compact combination of passivation coatings.
- 3) By using aluminium zinc fluoride solution and tannic acid, titanate sol silane coupling agent prepared by non chromium passivation solution has better passivation effect, surface passivation coating is uniform, dense and smooth, for industrial manufacturing environmentally friendly hot aluminium zinc plate provides a reference (has been applied in actual production).

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