OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 9, No. 11-12, Nov. – Dec. 2015, p. 1487 - 1490

The film forming mechanism of chromium-free passivation process in the tannic acid system for hot dip galvanizing coating

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In this paper, tannic acid, fluorine titanate and silane coupling agent passivation solution were used to prepare hot dip galvanized 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 galvanized 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 produce 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 galvanized steel sheet passivation coating or membrane.

(Received September 17, 2015; accepted October 28, 2015)

Keywords: Tannic acid, Hot Dip Galvanizing, Chromium free passivation liquid, Coating, Film forming mechanism

1. Introduction

Due to its advantages such as good corrosion resistance, high cost performance and simple technology, the application of traditional chromate passivation coating therefore is extensive [1, 2]. However, the hexavalent chromium in this passivation film leads to carcinogenicity, causing harm to environment and human body, hence this kind of passivation film has been gradually prohibited by countries [3-5]. In order to find the corresponding alternative products, researchers around the world have made a lot of investigations on the formula of environment-friendly passivation solution for hot dip galvanized steel sheets [6, 10]. In the field of the investigation of environment-friendly passivation solution for hot dip galvanized sheets [6], Parker (Japan), Henkel (Germany) have the leading technology; in the field of environment-friendly passive hot dip galvanized steel sheet manufacturing [7], JFE and Nippon steel (Japan) have developed series of corresponding products in 2003. In addition, in 2000 ~ 2005 Union Steel, Pohang Steel and Dongbu Steel (Korea) have successfully developed environment-friendly passive hot dip galvanized steel products, which has been widely used in home appliance manufacturing [8].

The relevant researches in China started late, although a lot of studies have been made, due to some problems such as corrosion resistance, process adaptability and cost, there is no industrial application. Thus, all Chinese manufactures use passive liquid imported from Parker and Henkel to produce environment-friendly hot dip galvanized steel products for home appliance application [9, 10]. In fact, the high price of imported passivation solution leads to the production costs of Chinese iron and steel enterprise significantly increasing; besides that, the raw materials of imported passivation solution are provided by foreign countries, then the preparation are conducted by domestic iron and steel companies with a simple fixed rules, therefore the mechanism of coating formation of passivation solution, drugs' names and their respective roles are unclear, which makes quality and stability of the products of domestic iron and steel enterprise are poor. Based on this, according to relevant results of current common trivalent chromium, molybdenum (tungsten) salts, titanium salts, zirconium salts, silicates, rare earth, tannic acid and silicon-based organic coatings [11, 14], this project investigated the film forming mechanism of chromium-free passivation process in the tannic acid system.

2. Experiment materials and methods

DK7716 wire cutting device was used to cut the hot-dip galvanized steel sheet into small sheets with size of 50 mm× 50 mm. Then deionized water were used to wash the sheets.

After removal of surface oil, acetone and deionized water were used to wash the small sheets again, and then air dried.

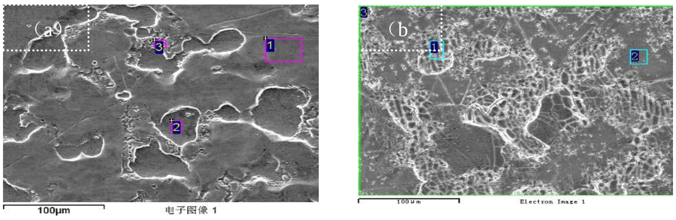
Tannic acid solution with a mass fraction of 2% to 7% was prepared at room temperature, then 2% fluotitanic acid and sol-like silane coupling agent were added, stirred rapidly to mix uniformly. The primary role of tannic acid solution is to form a three dimensional network structure, the role of the silane coupling agent to improve the corrosion resistance of the coating, and promoting the cross-linking between the elements in solution, the other important functions of silane coupling agent are to improve the film-forming property of coating, reduce the curing temperature and increase oxidation resistance, etc. [12, 13]. Finally, the pretreated hot dip galvanized steel sheet were immersed in the mixed solution for about 1 s, then taken out to solidify at about 80 °C [14].

JSM1600-LV (Ricoh, Japan) scanning electron microscope (SEM) was used to observe the surface morphology passivation of the passive coating. INCA EDS was used to analyze the microstructure and composition of the surface of coating. GDS-850A Glow Discharge Atomic Emission Spectroscopy was used to scan the elements in film layers. Magna IR-560 infrared spectrometer (Nicolet) was used to detect active ingredient and the molecular structure of the coating.

3. Experimental results

3.1 Analysis of microstructure

Fig. 1 shows the microstructure morphology of the sample with and without the treatment with chromium-free passivation process in the tannic acid system. As shown in figure (a), the untreated sample showed a uniform, dense, smooth surface. While figure (B) shows that the surface of the treated sample had many obviously uneven zinc layer structure, but the passive film formed through the reaction of passivation solution and Zn layer had good adhesion, and the phenomena that passivation film powdering, shedding defect did not appear. It can be concluded from figure (a) and (b) that, the passive coating of galvanized steel sheet after treated by chromium-free passivation process in the tannic acid system has better coverage and adhesion.



(a) untreated zinc layer (b) treated zinc layer

Fig. 1. Microstructure morphology of coating

3.2 Coating surface element analysis

In order to further explore the surface morphology and element distribution of the passive coating, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were applied to analyze microstructure and composition of the surface of the sample. According to Fig. 2, the surface of the sample after treated by chromium-free passivation process in the tannic acid system showed space network structure, the film was uniformly adhered to the surface of zinc layer with the appearance of corrosion pits. In addition, INCA EDS indicates that in addition to Zn, the elements in the surface film mainly were C, O,Ti and Si.

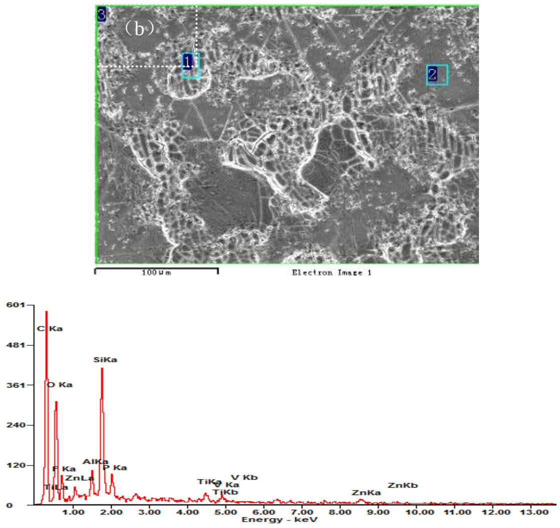


Fig. 2. SEM and INCA analysis results

3.3 Layer by layer elements scanning

The investigation of coatings element distribution layer by layer has great reference value to judge the existence form of films and the distribution state. GDS-850A glow discharge atomic emission spectrometer was used to scan the element distribution of the film layer by layer, the results shown in Fig. 3. The distribution of the elements indicates that: carbon decreased with the depth of film, which demonstrates that the organic film-forming material is mainly present in the surface layer. Moreover there was cross of passivation layer and galvanized layer, which indicates that the passive film and galvanized layer combined in the form of a chemical bond.

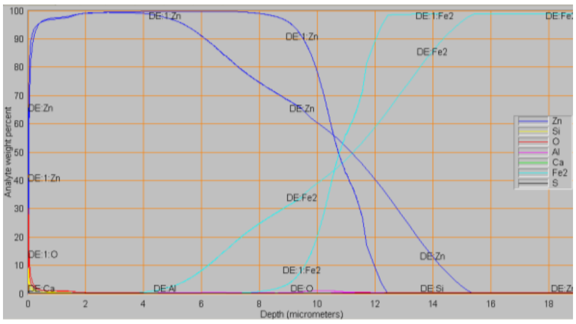


Fig. 3. Analysis results of film glow spectra

3.4 Infrared spectroscopy

The infrared spectrum of film can characterize the change of molecular structure during hydrolysis process. As shown in Fig. 4, with the increase of hydrolysis time, the strengths of Si- (CH_3) symmetric distortion absorption peaks at 453 cm-1, Si-O-C symmetric stretching peak at 702 cm-1 and asymmetric stretching peak at 1107 cm-1 dereased.

Within the range of 1000-1176 cm-1, Si-O-Si, Si-O-C and Si-O-Zn absorption peaks overlaped. The absorption peak at 1031 cm-1 strengthened, which resulted from the formation of Zn-O-Si bond through the reaction of silanol hydroxy and oxides on the surface of zinc layer. The peak at 1450 ~ 1608 cm-1 resulted from the bending vibration of C-C bond on the phenyl ring, the peak at 1735 cm-1 resulted from the stretching vibration of C = O group, and the strongest peak at 3000-3500 cm-1 resulted from the stretching vibration of -OH.

In addition, at 760 ~ 800 cm-1, the intensity of absorption peak of non-hydrolyzed group decreased with the increase of hydrolysis time. When the silane film layer on the surface of zinc layer solidified, the absorption intensity of the silanol (Si-OH) group located at 2870 ~ 3050 cm-1 reduced with aging time increased.

As shown in Fig. 4, with the extension of curing time, because of the mutual condensation of silanol groups, the absorption peak of silanol (Si-OH) at 3033 cm-1 gradually weakened, while the absorption peaks that formed siloxane (Si-O-Si) and zinc siloxane (Si-O-Zn) bonds (at 1000 ~ l176 cm) constantly widen and enhanced, which indicates that the bonding reaction of silane in passivation solution and Al-Zn alloy surface was substantially completed.

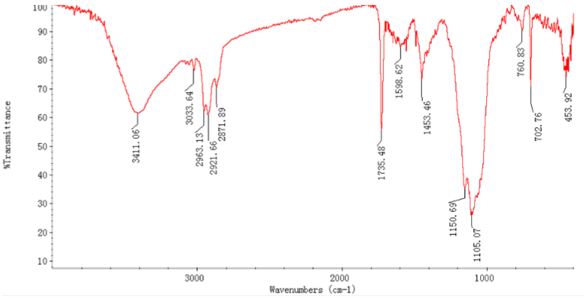


Fig. 4. IR spectrum analysis of the film

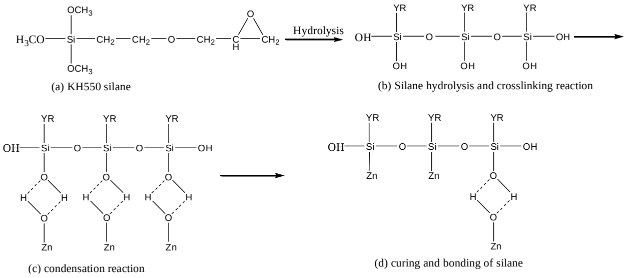
4. Analysis and discussion

According to the above analysis results, it can be speculated that the film forming mechanism of chromium-free passivation process for hot dip galvanizing coating is:

The reactions of chromium-free passivation process in the tannic acid system occured sequentially as figure 5 (a), (b), (c), (d). With the process of hydrolysis, the concentration of SiOH increased, the concentration of hydrogen ions in the solution concentration increased, and SiOH condensation or the generation of large molecular through oxygen bond went faster.

Subsequently, in the frequency range of 1000-1176 cm-1, the absorption peaks of various groups of significantly changed. For example, the absorption peak of Si-O-Si bond at 1110cm-1 gradually moved to high frequency band, this movement caused the film forming a linear siloxane chain during crosslinking process. Moreover, in the frequency range of 1000 ~ 1105 cm-1, the absorption peak grown, meanwhile zinc siloxane (Zn-O-Si) and siloxane (Si-O-Si) bonds started to form a complete space network structure at the interface and sub-interface of zinc layer. Because a steady state did not reach, with the formation of the network structure of zinc siloxane and siloxane in the film layer, crosslinking density increased, the impedance of fingerprint-resistant film increased, namely the corrosion resistance constantly increased.

On the other hand, due to the increase of the cross-linking density of the film, meanwhile nano-phenylpropyl resin and nano-colloidal SiO_2 particles filled in these gaps of the crosslinked spatial network, making film porosity, permeability and swelling degree significantly reduced, and the uniformity of the film started to increase. With the process of the irreversible hydrolysis of unhydrolyzed ester group and the condensation reaction of silanol groups, the crosslinking density of film constantly increased, and the hydrophilic groups (Si-OH) gradually reduced, which led to the strengthen of film's density and hydrophobicity, thereby the film can effectively prevent the infiltration of electrolyte and the impedance further improve, namely corrosion resistance increase again.



(a) KH550 silane

(b) Silane hydrolysis and crosslinking reaction

(c) condensation reaction

(d) curing and bonding of silane

Fig. 5. Mechanism of formation of chromium-free passivation solution

5. Conclusion

1) The main function of the components of chromium-free passivation process in the tannic acid system is: tannic acid solution is used for the formation of three-dimensional network structure, the role of fluotitanic acid is to improve the corrosion resistance of the coating and promote the crosslinking of each components in solution, the role of silane coupling agent is to improve the film forming properties of the coating, reduce the curing temperature and increase oxidation resistance.

2) The film forming mechanism of chromium-free passivation process in the tannic acid system for hot dip galvanizing coating is: Firstly, the three-dimensional network structure form under the action of tannic acid solution, then the reaction of sol-like silane coupling agent produce sol - gel particles to fill in the three-dimensional network structure, finally smooth, uniform and dense passive coating forms.

3) The application of tannic acid, fluotitanic acid and sol-like silane coupling agent in the preparation of chromium-free environment-friendly hot dip galvanizing coating, has good passivation effect, the surface of the passive coating is uniform, dense and smooth, which provides a reference for industrial manufacturing of environment-friendly hot dip galvanized steel sheet (already used in the actual production).

Acknowledgement

One of the authors (Mr. Xu Zhefeng) gratefully acknowledges financial support from Ministry of Science and Technology of the People’s Republic of China, through 863 Project (No.2009AA03Z529). The authors wish to acknowledge Prof. Yan Chuanwei, Institute of Metal Research, Chinese Academy of Sciences, for providing Electrochemical measurement system facility.

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