International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Studying Corrosion and Adhesion Performance of a Phytic Acid Based Conversion Coating Post-Treated with Garlic Extract on Q235 Steel

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Received: 23 October 2020 / Accepted: 1 December 2020 / Published: 28 February 2021

A green phytic acid film was prepared on the steel surface before the natural garlic extract was used for the post-treatment of the conversion coating. Then scanning electron microscopy (SEM) equipped with X-ray energy dispersive spectrum (EDS) were adopted for micro-morphology and elemental composition determination of different samples. Atomic force microscopy (AFM) and contact angle measurement were used to assess the adhesion properties of the prepared coating. At last, the electrochemical characteristic of the coating on the Q235 steel was examined using electrochemical impedance spectroscopy (EIS) and polarization curves in a 3.5 wt. % NaCl. SEM and AFM studies have shown that a homogenous, flake-like coating with lower crack was deposited on the steel surface. Particularly, EIS studies have shown that the anti-corrosion performance of the coating that treated with the garlic extract was markedly improved. Simultaneously, the adhesion property with the subsequent coating adhesion was also increased.

Keywords: conversion coating; phytic acid; corrosion; garlic extract; adhesion

1. INTRODUCTION

Chemical conversion coating technology is widely used for metal surface treatment due to it not only can possess good anti-corrosion, but also further improve the adhesion ability to the subsequent coating layer. Therefore, conversion coating has been involved in many industries for decades such as automobile and household appliance manufacturing, hardware processing and many other industries. With the higher requirements for environmental protection and more attention to human health, the toxic chromium and phosphate conversion coating is gradually replaced by the chrome-free conversion coating. The development and application of green environment-friendly metal surface pre-treatment technology has become a very important research direction in the field of metal surface treatment.

Phytic acid (PA) is a natural, nontoxic, environmentally friendly macromolecule, which obtains from plants that contains six phosphonic acid groups giving its a powerful chelating capability to form stable metal-phytic complexes over a wide range of pH values with variety of metallic ions, such as Fe^{2+} , Fe^{3+} , Mg^{2+} , Ca^{2+} and Zn^{2+} [1]. The research demonstrated that phytic acid can be used to treat different metal surfaces and has the ability to protect metals in corrosive environment by the adhesion to subsequent coatings. Phytic acid based conversion coatings have been shown to protect magnesium alloy, as well as other alloy materials [2-5]. Nevertheless, there is a strong hydrogen evolution reaction in the micro cathode region during the film formation resulting in the loose structure and micro-cracks in the conversion coating (Schematic diagram of micro-cracks formation was shown in Fig.1). Finally, its deteriorated the binding force to the substrate and provided an efficient channel for corrosive medium, seriously weakening the protective effect of the coating. It is worth noting that the decrease of adhesion and delamination wad one of the main failure mechanisms of coating [6]. Consequently, it is very meaningful to prepare a pretreated conversion coating with less cracks and better corrosion performance.

In order to improve the corrosion resistance of conversion coating, various additives were mixed into the preparation process or the conversion coating was post-treated. Chen et al. [7] pretreated magnesium surface by alkaline and then covalent immobilized phytic acid molecules, forming a dense and homogenous protective coating. And then the authors immobilized heparin or bivalirudin in phytic acid coating by in-situ chemical method on Mg substrate. The results indicated that compared to PA-coated Mg sample, drug-loaded PA coating has the slower corrosion rate in phosphate buffered saline [8]. Zhang et al. [9] prepared the phytic acid coated magnesium alloy sample and heat treated the sample in the temperature range of 150°C-400°C. Due to the great crystallization of Mg₂P₂O₇, the sample heat-treated at 400°C displayed superior surface integrity, corrosion performance and crack healing. Gupta et al. [10] heat-treated the phytic acid coated magnesium alloy surface and obtained the same results. Gao et al.[11] and Mohammadloo et al.[12]prepared different composite conversion coating. Compare to the untreated sample and phytic acid conversion sample, composite sample has best corrosion resistance. Gao et al. [13] fabricated Zn^{2+} doped phytic acid coating on Q235 steels. The electrochemical measurements results indicated that the corrosion current density of Zn^{2+} doped phytic acid conversion coating was lower than that of phytic acid coating. SEM characterizations demonstrated that the PA coated sample was porous network structure consisting of needle-like crystals, but the Zn^{2+} doped PA coated sample was one uniform layer except some fine cracks. Yan et al.[14] added metal ions, such as Zn^{2+} , Ca^{2+} , Co^{2+} and Ni^{2+} to the phytic acid solution and prepared a series of phytic acid-metal complex coatings on iron substrate. Compared to the phytic acid coating, obtained phytic acid-metal ions coatings with much thicker and denser and possessed much stronger anti-corrosion performance.

So as to improve corrosion resistance and bioactivity of AZ31 magnesium alloy, Zhang et al.[15] prepared a magnesium phytic acid/hydroxyapatite composite coating on magnesium alloy substrate. The results demonstrated that with the increase of hydroxyapatite content in phytic acid

solution, the cracks on the surface of the coatings gradually reduced, which subsequently improved the corrosion resistance of these coated magnesium alloy.

To the best of our current knowledge, however, there has been relatively few scientific study regarding the microstructure and anti-corrosion performance of phytic acid conversion coatings when post-treatment by green inhibitor, which was biodegradable, green and nontoxic. The corrosion inhibitor extracted from greenery contains N, O, S, P heteroatoms and heterocyclic compounds or π electrons that can adsorb on the metal surface [16]. The organic inhibitive ingredients in the garlic have been shown to be an effective corrosion inhibitor of metallic material in acid corrosive environment [17-19]. The extract contained different inhibitive ingredients such as amino acids, allicin and organic sulfide [17, 20]. It can be surmised that garlic extract could be applied to repair the cracks of conversion coating on the steel surface. At the same time, many functional groups contained in the organic compounds extracted from garlic, resulting in increase of adhesion between the top layer and steel substrate with strong hydrogen bond. In the present work, the effect of a post-treatment bath of garlic extract on the morphology, corrosion performance and adhesion properties of phytic acid-coated sample were investigated. The morphological and surface characteristics of the coating were observed by the surface analysis technologies of SEM-EDS, AFM and contact angle measurements, respectively. Furthermore, the corrosion resistance efficiency of the coated Q235 steel was assessed through electrochemical impedance spectroscopy (EIS) and polarization curves in a 3.5 wt. % NaCl.

2. EXPERIMENTAL

2.1 Materials

Q235 steel with the composition (in wt.%) C:0.17%, Mn:0.46%, Si:0.46%, S:0.017%, P:0.05%, Fe balance, measuring 10×10×3 mm prepared from China National Chemical Corporation.

Sodium chloride was provided by Sinopharm chemical reagent Co. Ltd. Sodium hydroxide was used to adjust pH values and was provided by Yantai ShuangShuang Chemical Co. Ltd. Phytic acid (PA) was provided by Aladdin Biochemical Technology Co. Ltd.

2.2 Garlic extraction process

Post-treatment bath of garlic extract was prepared with reference to literature [21]. The fresh garlic, which grows in the northwest of China, sliced, mashed to a slurry. A certain amount of mashed garlic was added to 100 mL deionized water, ultrasonically for an hour at room temperature and then filtered the residue with filter paper. Finally, we used the resulting solution for the post-treatment of conversion coating. Based on literature [19, 22-23] there are many organic compounds like allicin and alliin in the garlic extract. The chemical structure of some organic compounds are shown in Fig.2.

2.3 Surface treatment process

The steels plates were polished with a series of emery papers up to 2000 grade and then cleaned ultrasonically in distilled water, alcohol and acetone successively for 30 min, respectively, followed by

drying at 60°C. The cleaned steel samples were immersed in 20 g/L phytic acid solution at 60°C for 20 min and pH=5. And then the coated samples were rinsed thoroughly with deionized water and dried in an oven. In the next step, the phytic acid coated samples were immersed in a post-treatment bath of garlic extract containing mashed garlic for different concentrations of 2 g, 4 g and 8 g and times of 10min and 30 min. Again, the treated samples were washed with deionized water and dried in cold air for 2 h. Different concentrations and times treated samples are marked as GE-1(2 g: 10 min), GE-2(2 g: 30 min), GE-3(4 g: 10 min) and GE-4 (8 g: 10 min).



Figure 1. Schematic diagram of conversion coting preparation process and micro-cracks formation

2.4 Characterization

2.4.1 Surface characterization

The chemical composition of garlic extract was measured using FT-IR technique (FT-IR, Nicolet 6700, USA) in the spectral range 4000-400 cm⁻¹ using KBr powder. The micro-morphology and the elemental composition of the samples treated by phytic acid conversion bath and post-treated with garlic extract were examined via SEM (Hitachi JSM-5600LV, JEOL, Japan) equipped with EDS. The surface roughness of the samples was observed by atomic force microscope (NanoScope III, VEECO, USA). Contact angle measurements were carried out by a contact angle apparatus (JC2000D3, from Shanghai Zhongchen digital technology apparatus Co., LTD. CHN). 1 μ L of deionized water was used as the probe liquid, which was placed on the surface of the sample and the contact angle was measured after 20 seconds.

2.4.2 Electrochemical corrosion measurements

Electrochemical experiments were conducted using a computer-controlled CHI660E electrochemical workstation. For this aim, the working electrode was immersed in 100 mL of 3.5 wt. % NaCl at 25 °C. EIS were carried out using a conventional three-electrode cell assembly including coated steel sheet as the working electrode with an exposed surface area of 1.0 cm² to contact the electrolyte solution, platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively. Prior to each sample for EIS test, the working electrode was

immersed in the electrolyte solution for 30 min to obtain the steady open circuit potential (OCP). EIS studies were performed over the frequency spectrum range from 100 kHz to 0.01 Hz with sinusoidal perturbation of 5mV amplitude at OCP. Using ZSimpWin software, the electrochemical impedance parameters obtained by fitting the experimental data were analyzed. The charge transfer resistance (R_{ct}) values were gained from Nyquist diagrams by measuring the difference in impedance values at low and high frequencies. Polarization test was implemented with a scan rate of 0.001V/s and potential range of -300 mV to +300 mV around OCP. Each test was performed using three specimens to ensure the reliability of results.

3. RESULTS AND DISCUSSION

3.1 Garlic extract characterization



Figure 2. FT-IR spectra of garlic extract and chemical structure of some organic ingredients extracted from garlic

Fig.2 showed the FT-IR spectrum of the garlic extract in the region of 400-4000 cm⁻¹. A series of broad absorption peaks around wave numbers of 3400 cm⁻¹ in the FT-IR spectrum are assigned to

stretching vibrations peak of hydroxyl. In this work, a strong characteristic peak of hydroxyl group (-OH) at 3351.1 cm⁻¹ was observed. The strong absorption band at 1637.5 cm⁻¹ belongs to C=O stretching vibration of the saturated aliphatic or esters [24]. The absorption peak at 1119.5 cm⁻¹ is a characteristic of the C-N stretching vibration of amines in alliin [25]. The absorption band at 1409.3 cm⁻¹ is probably correspond to the O-H bending vibration peak of carboxylates [26]. The absorption peak at near 1032.3 cm⁻¹ is belongs to S=O vibration peak of sulphoxide in allicin [27]. Consequently, it can be concluded that nitrogen and sulphur based ingredients present in the garlic extract. The garlic extract is likely consisted of amino acid and different functional groups of C-N, O-H, S=O and C-H. These results demonstrate convincingly that the presence of alliin and allicin in the garlic extract as reported in the literature [28].

3.2 Characterization of conversion coatings

3.2.1 Surface morphology analysis

3.2.1.1 SEM, EDS and AFM results.

The surface morphology of the untreated, PA and PA-GE treated samples and chemical composition of sample treated by PA or garlic extract post-treated were observed using SEM-EDS. The images are shown in Fig.3.



Figure 3. SEM images, a) not-treated steel, b) PA coated, c) garlic extract post-treated, EDS spectra and elemental composition of sample treated by d) PA and e) garlic extract post-treated.

Int. J. Electrochem. Sci., 16 (2021) Article ID: 210448

Fig.3 a–c shows the SEM micrographs of the different samples. Based on the Fig.3 a, it is clear that the surface of the polished steel was smooth, but there are some scratches. Nevertheless, there are some cracks and uncovered surface in the phytic acid-coated sample, which are easily seen. It is clear that PA coated sample was post-treated by garlic extract bath resulted in the more uniform, continuous and compact coating was produced. At the same time, flake-like morphology is observed on the garlic extract post-treated surface, it may be that organic inhibitor which extracted from garlic adsorbed on the uncovered surface. Meanwhile, hydrogen bond exists between inhibitor and hydroxyl group in the phytic acid molecule, which promoted the adsorption of inhibitor on phytic acid coating. However, there are still some micro-cracks formed, which may be related to the loss of water in the coating during the later drying process. Fig.3 d-e showed the EDS spectra and elemental composition of the PA treated and garlic extract treated sample, respectively. As seen in the Fig.3 d, the phytic acid coated sample is mainly composed of Fe, C, P and O. And the presence of P in the phytic acid coating enables the phytic acid to better adsorb onto the metal surface to deposited a chemical conversion coating. After treatment with the extract, S and N were detected on the steel surface. This observation indicates that inhibitor has been located within the phytic acid coating structure. The increase of O after treated with garlic extract may be another reason proving the insertion of organic inhibitor into phytic acidcoated structure. As can be seen from EDS results, the decrease of Fe concentration on the sample treated with garlic extract may signify that the more inhibitor molecules absorbed on the steel surface. leading to the increase of surface coverage.

The nano-scale surface morphology of no-treated steel and steel treated with PA or PA-GE-4 was studied by AFM (Fig.4).



Figure 4. Surface morphology of the steel, PA and PA-GE (a) optical images; (b) AFM images

The nano-scale surface morphology of bare steel, steel treated with PA and PA-GE-4 were depicted in Fig.4. The untreated steel surface is relatively smooth with obvious scratches resulting from the SiC polishing step. The AFM images in Fig.4 b confirm the presence of phytic acid on the steel compared to the bare steel sample. It is evident from the AFM micrographs that the phytic acid deposition on the steel substrate resulted in an obviously increase of sample surface roughness in compare with bare steel. (R_a : average roughness and R_{max} : the max surface height). The phytic acid-coated steel exhibited a non-uniform surface morphology. The optical images showed that low-aggregate particles covered the steel surface when that treated with phytic acid bath. Results obtained from Fig.4 PA-GE-4 indicated that when phytic acid coating was post-treated with garlic extract, the size of the particles became finer and a more homogenous and smoother surface is observed, as seen in Fig.4 c PA-GE-4. The coating exhibits a uniform coverage and the roughness of coating is considerably reduced when post-treated. The surface of PA-GE-4 is almost smooth without cracks or defects, and the surface roughness parameters (R_a and R_{max}) were decreased to 21.85 and 285.1 nm, respectively. These observations are consistent with the SEM analysis.

3.2.1.2 Contact angle results

One important outcome of using conversion coatings on steel substrates is to enhance the organic coating adhesion to the substrate. The surface free energy of the steel surface is affected by the composition and texture of the conversion coating. When the surface free energy of coating is increased, the adhesion of the coating to the substrate and subsequent coatings is correspondingly enhanced [29]. In consequence, it becomes very important to evaluate the variation of the surface energy of the substrate post-treated with garlic extract. So as to evaluate the effect of post-treatment on the surface energy of steel substrate, the surface chemistry of different coatings was investigated using static contact angle measurements.

We can calculate the surface free energy and work of adhesion values (W_a) according to the equations of Neumann (Eq.1) and Young (Eq.2) [30]:

$$W_{\rm a} = \gamma_{\rm 1V} (1 + \cos\theta) \ (1)$$

 $W_{\rm a} = 2(\gamma_{\rm 1v} \cdot \gamma_{\rm sv})^{1/2} \exp[-\beta(\gamma_{\rm 1v} - \gamma_{\rm sv})^2] \quad (2)$

In Eq.1 and 2, the variables θ and γ_{sv} are the contact angle of sample and the surface free energy of the substrate, respectively. Constant γ_{lv} is the surface tension of water (72.0 mJ/m²) and β is 0.0001247 ± 0.000010 (mJ/m²)². Three parallel samples were prepared in parallel for different sample and taken the average of the three values as the final result, the calculated results are listed in Fig.5.

The contact angle of the untreated steel substrate was approximately $71.5\pm1.8^{\circ}$, indicating substantial hydrophilic properties. Fig.5 demonstrates that the deposition of phytic acid on the steel surface compared to the untreated steel decreased the contact angle. The results also show the increase in γ_{sv} and W_a of the coated samples after treatment by PA. The decreased contact angle after PA deposition is attributed to the phosphate groups that bear two hydroxyl groups and four hydrogen atoms. On the other hand, the inhibitor absorbed in the cracks and sealed the cracks of the PA coating and provided a smooth surface with excellent wettability. The hydrophilic nature of inhibitor enables

strong adhesion [31]. The lowest contact angle is observed in the PA-GE-4 sample. Post-treated with garlic extract results in smaller contact angle and higher surface free energy value than absence of post-treatment. The change in surface morphology combined with the higher surface free energy of the surface improves the coating wettability of the metal surface. These observations indicate that post-treated with green inhibitor not only make the obtained coating more uniform, but also increase the adhesion values with the subsequent coating.



Figure 5. Contact angle diagram of different samples and the relationship between contact angle, surface free energy and work of adhesion values

3.2.2 Corrosion performance

3.2.2.1 Electrochemical impedance spectroscopy measurements

The anti-corrosion performances of the bare steel, PA bath treated and different concentrations of garlic extract post-treatment bath treated samples was evaluated by EIS and polarization measurements. The electrochemical impedance spectra of the different coated samples which dipped in 3.5 wt.% NaCl solution are displayed in Fig.6.



Figure 6. Impedance diagrams of bare steel, PA coating and post-treated with garlic extract

According to the characteristics of the impedance spectra, the equivalent circuits for studies are listed in Fig.7.



Figure 7. The equivalent circuit models for data fitting

In this equivalent circuit, R_s is the resistance of the electrolyte resulting from the ohmic or uncompensated resistance of the solution between the working electrodes and reference electrodes. R_1 and Q_a are the resistance and capacitance, respectively, of the micro-pores in the coating formed on the surface of the steel [32]. Q_{dl} is a constant phase element (CPE) that was included in the fitting instead of an ideal capacitor to simulate the double-layer capacitance at the steel/solution interface. R_{ct} represents the charge transfer resistance at the interface between electrolyte and iron substrate at the crack location of the coating, which is in parallel with the double-layer capacitance at the steel/solution interface. To quantitatively evaluate the corrosion inhibition effect of the coating, ZSimpWin software was used to simulate and analyse the EIS spectrograms. The parameters of different samples obtained from the fitting parameters of the experimental impedance spectra are summarized in Table 1.

Table 1. Equivalent circuit parameters of different coated samples

	-	-	-	-	-	
Sample	$R_{\rm S}/(\Omega \cdot {\rm cm}^2)$	$R_1/(\Omega \cdot \mathrm{cm}^2)$	$Q_{ m a}/{ m uFcm^2}$	$R_{\rm ct}/(\Omega \cdot {\rm cm}^2)$	$Q_{\rm dl}/{ m uFcm^2}$	P.E.(%)
Bare steel	3.898			170.3	645.4	
PA	4.685	22.1	532.0	273.6	64.6	37.8
coating						
GE-1	3.613	42.9	330	480.2	188.2	64.5
GE-2	5.496	61.0	158	530.4	174.6	67.9
GE-3	5.269	70.3	120	562.7	168.4	69.3
GE-4	12.10	101.1	89	964.1	140.4	82.3

Fig. 6 shows the impedance as a single semicircle, the radius of which enlarges with increased garlic extract concentration. This demonstrates that the corrosion reaction charge transfer resistance

increases and the corrosion rate decreases. Compared with the bare steel and PA coated steel sample, the GE-4 coating exhibited the best corrosion resistance. The data presented in Table 1 suggest that the coating resistance and charge transfer resistance increase with increasing garlic extract concentration, indicating that the sample treated with GE-1 had a higher corrosion resistance to corrosive ions. This increase is consistent with the reduced porosity seen when phytic acid based coating was treated with post-treatment bath. Generally speaking, the coating layer with high charge transfer resistance and low capacitance has good corrosion resistance to the metal substrate [33]. Notably, the R_{ct} value of the GE-4 sample is approximately six times that of bare steel, suggesting that the corrosion process is significantly impeded. Meanwhile, the protection efficiency (P.E.) of different sample was calculated from the R_{ct} using the following equation:

P. E. (%) =
$$\frac{\text{Rct} - \text{R'ct}}{\text{Rct}} \times 100\%$$
 (3)

where R_{ct} and R'_{ct} denote the charge transfer resistance values of coated sample and bare steel, respectively. It is apparently concluded that post-treated coatings exhibited the higher protection efficiencies compared with the phytic acid coated. The effect of conversion time on protection efficiency is not obvious. However, it is obvious that the corrosion rate decreases and inhibition efficiency increases with the increase of concentration of the garlic extract, which is attribute to the more inhibitor molecules adsorb on the Q235 steel surface to form a shielding layer and hinder the diffusion of corrosive ions to metal surface.

3.2.2.2 Potentiodynamic polarization curve of different conversion coatings

The polarization measurement was also tested on the coated samples to investigate the corrosion protection mechanism. Polarization curves of different conversion coating are presented in Fig.8. The electrochemical corrosion kinetic parameters such as polarization resistance (R_p), corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are summarized in Table 2.



Figure 8. Potentiodynamic polarization curves of bare steel, PA coating and samples post-treated with garlic extract

sample	$I_{\rm corr} ({\rm A} \cdot {\rm cm}^{-2})$	$R_{\rm P}\left(\Omega\cdot{\rm cm}^{-2} ight)$	$E_{\rm corr}$ (V vs.SCE)
Bare steel	142.6	238.3	-0.632
PA coating	49.57	642	-0.674
GE-1	11.54	2600	-0.656
GE-2	9.175	2991	-0.639
GE-3	8.343	3152.2	-0.678
GE-4	6.208	3810.9	-0.678

Table 2. Polarization parameters for the different samples exposed to 3.5wt. % NaCl

It is obvious from the Table 2 that steel samples treated with phytic acid solution and posttreatment bath resulted in a lower corrosion current density (I_{corr}) and a higher polarization resistance (R_p) compared to the untreated steel sample. It is clear from the potentiodynamic polarization curves presented in Fig.8 that the anodic and cathodic current of the PA-GE conversion coating is lower than that of the bare steel and phytic acid coated sample, meaning that both the cathodic and anodic branches were suppressed and it significantly increases the corrosion resistance of the steel sample. The corrosion protection of the PA-GE conversion coating is concerned with adsorption of organic corrosion inhibitor on steel surface. The adsorption of more corrosion inhibitor molecules is beneficial to reduce the available sites for the anodic and cathodic reactions and further block the transportation of corrosive ions, thereby retarding the corrosion rate. The GE-4 treated coating shown a corrosion current density more than 8 and 24 times lower than phytic acid coating and bare steel, respectively. Simultaneously, the polarization resistance of garlic extract coated steel was approximately 6 times larger than that using phytic acid alone. This finding demonstrates that the corrosion rate of the steel samples was significantly retarded by the conversion coatings. And this is consistent with the results of electrochemical impedance result.

The deposition of phytic acid resulted in the corrosion potential (E_{corr}) being shifted towards a more negative value compared to the bare steel, demonstrating that the phytic acid coating affected the cathodic reaction more intensely than anodic reaction. The GE-post-treatment phytic acid coating also affected both the anodic and cathodic reactions. Simultaneously, the cathodic reaction was markedly slowed down via arresting the reduction of water, which was transported mainly through the micro-cracks in the coating. Since the reduction of water was prevented, the cathodic reaction was significantly retarded. However, the corrosion potential (E_{corr}) shifted towards a more negative direction (from -0.632 V to -0.678 V) compared to that when using the phytic acid coating. These finding demonstrates that post-treatment bath enhanced the anticorrosion performance of the phytic acid based coating through further blocking the transport of corrosive ions to the active sites, particularly the cathodic sites on the steel surface. Because corrosion inhibitors extracted from garlic filled the cracks or pores in the phytic acid based conversion coating, post-treatment provided much better protection against corrosion [27].

4. DISCUSSION

The electrochemical measurement results have demonstrated that post-treated with the garlic extract resulted in a markedly improvement of the anticorrosion performance of phytic acid based conversion coating. Additionally, post-treatment changed the structure and morphology of the prepared phytic acid based coating. The precipitation of phytic acid coating on the Q235 steel substrate can be explained by the following reaction:

 $Fe \to Fe^{2+} + 2e^{-}$ $RH_{10}^{2-} + Fe^{2+} \to FeRH_{10}$ $RH_{10}^{2-} + H_2O \to RH_9^{3-} + H_3O^{+}$ $RH_9^{3-} + Fe^{3+} \to FeRH_9$ $R = C_6H_6O_6(PO_3)_6$

The active groups of phytic acid can react with Fe^{2+}/Fe^{3+} in the conversion bath to form chelate compounds, which were then deposited on the steel surface [34]. The SEM/EDS and AFM analyses showed that post-treated with garlic extract bath vanished the crack. The phytic acid conversion coating is mainly composed of phytic acid complexes. Meanwhile, after the post-treatment, fewer micro-cracks were observed, because of the inhibitor absorbed in the cracks and sealed the cracks of the PA coating. This rationale is schematically illustrated in Fig.9. Inhibitors such as amino acids, allicin and organic sulfide extracted from garlic contains N, O, S heteroatoms in their structure, which highly tend to conjugated with empty d orbital of Fe on the steel surface that was not covered with phytic acid and form coordinate bond, resulting in adsorb on the metal surface and form a protective coating which separates the corrosive medium from the metal surface [35].

The extract contained different inhibitive ingredients All of these observations revealed that green inhibitor was able to enhance the anticorrosion resistance of the phytic acid based conversion coating through two central mechanisms. First of all, inhibitor increased the phytic acid coating barrier performance by reducing the porosity of the coating. Secondly, hydrogen bond exists between inhibitor and hydroxyl group which promoted the adsorption of inhibitor on phytic acid coating. To some extent, the protective inhibitor layer protects the phytic acid coating.



Figure 9. Schematic of the mechanism of the effect of garlic extract

5. CONCLUSION

Post-treatment bath prepared from garlic extract was used to treat the phytic acid conversion coating. Simultaneously, the effects of garlic acid on the adhesion properties of the phytic acid based conversion coating were studied on the Q235 steel surface. The results revealed that the steel coated with phytic acid and garlic extract had better corrosion resistance. The anticorrosion efficiency of the phytic acid conversion coating increased with the increase of mashed garlic concentration. The SEM, EDS and AFM results indicated that phytic acid could deposit on the steel surface to form a protective film. At the same time, the adhesion property with the subsequent coating was improved after the posttreatment. The phytic acid coating in this study would constitute a first line treatment (primer) on the steel surface with the aim of reducing micro-cracks, improving corrosion performance and adhesion property. Increasing attention will be given to not only improving the protective efficiency of the conversion coating, but also to endow it with self-healing ability. And a final top coat will be crucial to obtain adequate corrosion protection.

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CONFLICTS OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

This research was financially supported by China's Ministry of Science and Technology "Project for science and technology personnel service enterprise" (No.2009GJG10041).

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