Enhancing Corrosion Resistance of Galvanized Steel by Phosphating and Silicate Post – Sealing

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Hot dip galvanized (HDG) coatings are widely used in various industrial fields for better corrosion protection of steels. Comparative study of the corrosion behavior of the phosphated hot-dip galvanized steel conversion coatings and post-sealing in sodium silicate solution were characterized in 3.5 \% NaCl solution by different techniques, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The surface morphology and elemental composition of hot-dip galvanized steel and post treated were characterized by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). The results showed that after phosphating the porous phosphate crystals formed on the surface of HDG steel and the phosphating followed by post-sealing samples in sodium silicate solution filled into the phosphate pores. The optimum silicate concentration ranged from (3-5 g/l), its morphology has fine crystal, compacted and dense uniform coating (zinc-silicate complex). Low silicate concentration (3-5 g/l) have better protection property and best corrosion performance than other high concentration (7-10 g/l) due to cracks formation in coating and bad protection.

**Keywords:** Hot-dip galvanizing steel process; phosphate conversion coatings; post-sealing silicate; corrosion resistance; potentiodynamic polarization; electrochemical impedance spectroscopy

1. **INTRODUCTION**

Steel is widely used as construction materials in various applications due to its excellent mechanical properties and low cost [1, 2]. Steel undergoes corrosion when exposed to different environments especially in high temperature and humidity that limit its practical application [3, 4]. To overcome this disadvantage there are different methods to prevent corrosion such as anodic protection, cathodic protection, addition of inhibitors and protective metallic coating. For corrosion protection of
steel, zinc or zinc alloys are most commonly used for coating by hot-dip galvanizing method [5-8]. By this method the material has the mechanical properties of steel enhanced with the corrosion protection of zinc.

Zinc coatings protected steel against corrosion through a galvanic effect and a barrier effect in which zinc acts as the sacrificial anode while steel acts as the cathode. However in most environments white rust (corrosion product of zinc) is easily deposit on the surface because of the high electrochemical reactivity of zinc [9-12]. Therefore the surface treatment is usually essential to protect the zinc itself and increase the corrosion resistance of zinc coatings. One of these treatments is chemical conversion coating process which provides more corrosion resistance by forming protective film and increase the adhesion between primer coatings and metal substrate [13, 14].

Phosphating is one of the most significant chemical conversion coatings that applied for corrosion protection by passivate the zinc surface and blocks the formation of zinc oxide. This type of treatment is commonly used as primer for painting to provide good adhesion property to the paint. However, phosphate coatings are crystalline and porous. Recently, effort concerned improving the corrosion resistance of phosphate coatings by varying the methods of post-sealing treatment after phosphating or by using additives in the treating solutions to decrease the coating porosity and improve the corrosion resistance [15-19].

Silicate conversion coating provides environmental friendly and effective corrosion protection coatings for hot dip galvanized steel [20-24]. Alkali silicate solutions enhance the corrosion protection by forming a thin passive transparent coating layer on metal surfaces which inhibit the corrosion reaction of metals [25].

In hot dip galvanizing process the corrosion performance and the durability of zinc coating could be developed with the addition of low amounts of certain alloying elements to the galvanizing zinc bath such as aluminum which enhance the corrosion resistance and improve the quality of the galvanizing coatings. Moreover the presence of aluminum in pure galvanizing zinc bath has a greater affinity with iron than zinc so instead of zinc–iron compound an aluminum iron intermetallic compound (Fe2Al5) developed. These alloys act as a barrier or inhibitor layer retards the zinc–iron reaction [26, 27].

In the present work an attempt is made to form zinc coatings containing 0.5 wt % aluminum with hot-dipping process on low carbon steel. The main objective is to improve and compare the corrosion resistance of hot-dip galvanized steel (HDG) in 3.5 % sodium chloride solution by phosphating treatment and post–sealing with variable concentrations of sodium silicate solutions. The structure and morphology of the galvanized layers has been investigated.

2. EXPERIMENTAL

2.1 Sample preparation

The samples were prepared by cutting low carbon steel sheet into 30 x 30 x 2 mm pieces. The chemical composition of steel used in this study is listed in Table 1.
Table 1. Chemical composition of low carbon steel used as substrate for galvanizing process (wt. %).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.23</td>
<td>0.045</td>
<td>0.14</td>
<td>0.035</td>
<td>0.03</td>
<td>balanced</td>
</tr>
</tbody>
</table>

2.2 Hot dip galvanizing process

Surface preparation is the most important step in the HDG process. For mechanical treatment, all the surfaces of samples were wet ground using emery papers up to 1200 grit to produce smooth surface, rinsed with distilled water then ultrasonically cleaned in acetone and finally dried in steam of warm air. For chemical treatment, the specimens were degreased for 3 min in 15 g/l Na₂CO₃ and 15 g/l Na₃PO₄ at 80°C to remove oil and greasy substance. The specimens were pickled in 10 % HCl for 10 s at an ambient temperature to remove any oxides from the steel surface, and then fluxed in a mixed solution with 20 g/l ZnCl₂ and 30 g/l NH₄Cl at 60°C for about 10 min to activate the surface. Finally the specimens were dried at 120°C before dipped in molten zinc bath containing 0.5 wt % aluminum at 460°C for 60 s. After that the specimens withdrawal slowly at a controlled rate (2 cm/s) and quenched in water immediately. The galvanizing process was carried out in a laboratory electric furnace inside ceramic crucible, the thickness of galvanized layer was determined [1, 5, 26, 28].

2.3 Surface thickness of coatings

Surface thickness is important to evaluate the performance of the coating and determine its application. In this work, the thickness of the coat layer was determined by gravimetrically (striping method) and microscopically using SEM.

**Gravimetric method** (striping method) is a widely used to obtain the thickness of coating. Here the measurements are made of the sample dimensions and the weight of the sample with coat and without the coat after immersed in inhibited HCl solution (sp.gr.1.16) (500 ml HCl + 500 ml H₂O+3.2 g antimony trichloride SbCl₃) were noted. These measurements are then combined with the knowledge of the coating density to drive an average coating thickness [29].

\[
\text{Coating thickness} = \frac{M_1 - M_2}{D \times A}
\]  

Where M₁ and M₂ are the mass in gram of the sample before and after striping, respectively. A is the area of the film on the sample (cm²) and D is the density of the coat (g/cm³).

The thickness of the galvanized coatings was checked microscopically by scanning electron microscope on the cross cut section of the sample after polishing and measures its thickness. The average value of thickness was taken by measuring the thickness in three different places of the surface.

2.4 Preparation of the coatings

For post-treatment the HDG samples were ultrasonically treated for ~ 5 min rinsed with deionized water and then immersed in passivation solutions. The passivation solutions were prepared
from reagent grade chemicals and deionized water. The composition of the solution and the process parameters for bath coatings are shown in Table 2. After immersion process the samples were rinsed and dried.

Table 2. Formulations and process parameters for post treatment of HDG steel.

<table>
<thead>
<tr>
<th>Phosphating</th>
<th>Silicate post-sealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO 1.2 g/l</td>
<td>Na silicate (3-10 g/l)</td>
</tr>
<tr>
<td>NaNO₃ 15 g/l</td>
<td>T: 85°C</td>
</tr>
<tr>
<td>85 % H₃PO₄ 11 ml/l</td>
<td>pH: 11.7</td>
</tr>
<tr>
<td>T: (45°C), pH: 3.0, t: (60-600 s)</td>
<td>t: 60 s</td>
</tr>
</tbody>
</table>

2.5 Surface morphology and characterization

The surface morphology and microstructure characterization of the coated samples were investigated before and after treatment using scanning electron microscope (SEM) JEOL JSM 5410, Japan equipped with an energy dispersive spectroscopy unit (EDX). For the examination of microstructure cross-sections the galvanized sample have been cut, mounted in conventional Bakelite and polished to remove about 0.5 mm of the materials.

2.6 Electrochemical tests

The electrochemical measurements were operated in a conventional three electrode cell containing 3.5% NaCl solution using computerized potentiostat/Galvanostat (Auto LAB PGSTAT 302). The working electrode was a piece of HDG steel or treated samples, while platinum wire and Ag/AgCl electrodes were used as auxiliary and reference electrodes respectively. Before the electrochemical measurements the samples were immersed in 3.5% NaCl solution for 30 min to attain the steady state open-circuit potential (OCP). Electrochemical impedance spectroscopy (EIS) was carried out at frequencies ranged from 100 KHz to 10 mHz with the amplitude of 5 mV. The potentiodynamic polarization measurements were performed at scanning rate of 1 mV/s in a range from -200 mV to +200 mV from (OCP) value. The corrosion potential (E₉₉) and corrosion current density (I₉₉) were derived from the polarization curves by Tafel extrapolation method.

3. RESULTS AND DISCUSSION

3.1 Coating thickness and composition

The coat thickness of the galvanized steel obtained by immersing in molten zinc bath containing 0.5 wt % Al operated at 460°C for 60 s as immersion time was determined by measure the weight of the sample with coat and again after stripped using an acid solution. The thickness was then calculated using equation 1 and is found to be ~ 30.5 μm.
Figure 1. (a) SEM micrograph illustrating the measurements of the coat thickness (b) EDX cross-sectional mapping analysis of the zinc coating formed after 60 s immersion of steel at 460ºC in zinc + 0.5 wt.% Al bath.

Figure 1a show the cross sectional structure which measuring the coat thickness of the galvanized steel. The micrograph reveals that the morphology of the coating is relatively compact, defined and adheres on the surface, the average value of coat thickness was taken by measuring the thickness in three different places of the surface and the average thickness was ~32.27 μm which is in great consistent with the calculated value by gravimetric method. Fig.1b represents the EDX cross sectional analysis of the zinc coating layer. The surface element composition of the sample coating layer is composed clearly of 98.91 wt. % Zn, 0.58 wt. % Al and 0.52 wt. % Fe.

3.2 Cross-sectional and composition of the coating layers after treatment

Figure 2 (a-e) illustrates the SEM and EDX analysis of the alloy layers of galvanized coating developed after treatment at optimal condition (600 s phosphated HDG steel and post-sealing with 5 g/l sodium silicate for 60 s). The chemical composition of the layers was determined from the EDX analysis. It can be observed that distribution between Zn and Fe, the concentration of Si and P ions gradually increased from the bulk to the surface of the sample (higher near the surface and decreased gradually through the layer of the sample) as seen in Table 3. Therefore it can be concluded that the formation of coating increased near the surface which acts as effective corrosion inhibitors.

Table 3. EDX cross-sectional analysis of the alloy layers of galvanized coating developed after treatment at optimal condition

<table>
<thead>
<tr>
<th>Layer number</th>
<th>Fe%</th>
<th>Zn%</th>
<th>Al%</th>
<th>P%</th>
<th>Si%</th>
<th>O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94.77</td>
<td>0.56</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>4.57</td>
</tr>
<tr>
<td>2</td>
<td>17.24</td>
<td>36.59</td>
<td>6.31</td>
<td>3.84</td>
<td>-</td>
<td>35.83</td>
</tr>
<tr>
<td>3</td>
<td>15.17</td>
<td>36.62</td>
<td>1.28</td>
<td>0.95</td>
<td>0.94</td>
<td>45.04</td>
</tr>
<tr>
<td>4</td>
<td>7.48</td>
<td>58.38</td>
<td>0.37</td>
<td>-</td>
<td>0.37</td>
<td>33.44</td>
</tr>
</tbody>
</table>
Figure 2. (a) SEM micrograph, (b-e) EDX mapping analysis of the alloy layers of galvanized coating developed after treatment at optimal condition (600 s phosphated HDG steel and post-sealing with 5 g/l sodium silicate for 60 s).

Figure 3. (a) SEM micrograph, (b) EDX concentration (distribution) profile for the element through thickness of HDG steel and (c) Elemental mapping of the coat after treatment at optimal condition (line analysis)
For further evidence of the formation of conversion coating Fig. (3a, b) illustrate the SEM and EDX analysis through thickness of HDG steel after treatment. From the figures the main elements were Zn, Fe, Al, P, Si and O. This indicating that the all element participated in the formation of coating layer. Fig. 3c shows the changes in the distribution of chemical composition from the inner to outer layer of the coating of the treated HDG. It is seen that from the line analysis of the base metal Fe is gradually decreased while Zn and Al are increased and P, Si, O appeared form the outer coating layer [26, 30].

3.3 Mechanism of conversion coatings

During the immersion of galvanized steel in the phosphating solution, the anodic reaction is zinc dissolution and cathodic reaction is the reduction of protons leading to an increase in the pH near the electrode surface which facilitate the dissolution of the $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ ions. When the pH is high enough near the electrode $\text{Zn}^{2+}$is precipitates as a corrosion protection layer (conversion coating) [31, 32]. The reactions might occur as follows:

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \quad (2) \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 \quad (3) \\
\text{H}_2\text{PO}_4^- & \rightarrow \text{HPO}_4^{2-} + \text{H}^+ \quad (4) \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn (OH)}_2 \quad (5) \\
3\text{Zn}^{2+} + 2\text{PO}_4^{3-} + \text{H}_2\text{O} & \rightarrow \text{Zn}_3(\text{PO}_4)_2.4\text{H}_2\text{O} \text{ (hopeite)} \quad (6)
\end{align*}
\]

Protective crystalline coating shows good adhesion on the galvanized steel but the irregular crystals results in open pores which lead to corrosion. The corrosion resistance of the phosphate HDG sample can be improved by post-sealing with variable concentrations of sodium silicate solution. The pores among zinc phosphate crystals are sealed with film containing Si, P, O and Zn lead to formation of coating on galvanized steel surface [33].

When the HDGS was immersed in sodium silicate solution the pH value was about 11.7. The anodic oxidation of zinc and cathodic reduction of oxygen occurred at the zinc surface lead to formation of $\text{Zn(OH)}_2$ on the surface which react with silicate anions by removing of water molecules and forming zinc silicates [34]. The reactions might occur as follows:

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad (7) \\
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \quad (8) \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn (OH)}_2 \quad (9)
\end{align*}
\]

The reactions between Zn–OH groups and orthosilicate monomers may be written as:

\[
\begin{align*}
\text{Zn}^-\text{OH} + \text{HO}^-\text{Si}^-\text{OH} & \rightarrow \text{Zn}^-\text{O}^-\text{Si}^-\text{OH} + \text{H}_2\text{O} 
\end{align*}
\]
The reactions of two orthosilicate monomers may be written as:

\[
\text{SiOH}_2 + \text{SiOH}_2 \rightarrow \text{SiO}_2\text{OH} + \text{H}_2\text{O} \quad (11)
\]

3.4 Electrochemical corrosion of the coatings

The potentiodynamic polarization curves of HDGS and phosphated samples for different immersion times (60, 180, 300 and 600 s) in 3.5 % NaCl solution are shown in Fig. 4. As the phoshating time is increased the anodic and cathodic branches for samples are shifted towards the direction leading to a decrease in the corrosion current (I_{corr}) value, this may be due to formation of more protective film with an increase in phosphating time [7].

Generally it is well known that, the polarization resistance is related to the corrosion current through Tafel slopes by Stern–Geary equation

\[
R_p = \frac{\beta_a \beta_c}{2.3 I_{corr} (\beta_a + \beta_c)} \quad (12)
\]

Where (\beta_a) and (\beta_c) are the anodic and cathodic Tafel slopes.

The potentiodynamic polarization curves of phosphated samples with and without silicate post-sealing in 3.5 % NaCl solution are shown in Fig. 5.

**Figure 4.** Potentiodynamic polarization curves for phosphated HDG steel samples for different time immersed in 3.5% NaCl solution.
Silicate coatings were obtained by 60 s immersion in different concentration of sodium silicate solution (3, 5, 7, 10 g/l). It is clear from curves that the performance of silicate coatings was dependent on their concentration. The corrosion resistance of the coating increases by increasing sodium silicate concentration up to 5 g/l, which is related to the formation of zinc silicate complex (coatings) at this concentration forming dense, compact and homogeneous layer at the surface. On the other hand any further increasing in concentration more than 5 g/l decreases the corrosion resistance due to formation of some cracks on the surface giving inhomogeneous coatings with bad appearance as (this can be consistent with SEM-EDX analysis in Fig. 11).

The corrosion protection efficiency $P_e$ % of the phosphate coatings for HDG steel immersed in 3.5% NaCl solution were calculated from corrosion current densities value using the following equation [30, 35]:

$$P_e \% = 1 - \frac{i_{\text{corr}}}{i_{\text{corr}^*}} \times 100$$  \hspace{1cm} (13)

Where $i_{\text{corr}^*}$ and $i_{\text{corr}}$ are the corrosion current densities of the HDG steel before and after phosphated respectively (Table 4). The $P_e$ values for coated samples were calculated and represented as a function of phosphating times in Fig. 6. The $P_e$ values increase as the phosphating immersion time increase up to 300 s and then appeared to be reaching a limited value.

The corrosion protection efficiency $P_e$ % of the phosphate coatings for HDG samples post–sealed in different concentrations of sodium silicate solution were calculated and represented in Fig. 7 as a function of silicate concentration. It is values evident that post sealing of samples enhances the corrosion protection efficiency of phosphated galvanized steel up to 5 g/l sodium silicate solution and any further increase in the concentration reduce the protection efficiency.
Figure 6. Corrosion protection efficiency of phosphated HDG steel samples as a function of phosphating time.

Figure 7. Corrosion protection efficiency of phosphated HDG steel samples post–sealed with sodium silicate solution as a function of silicate concentration.

The corresponding corrosion parameters such as corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), polarization resistance ($R_p$) and protection efficiency ($P_e$) were derived directly from the polarization curves and listed in Table 4.
Table 4. Electrochemical parameters and corrosion rates obtained by polarization tests.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$E_{\text{corr}}$ / V</th>
<th>$I_{\text{corr}}$ / $\mu$A/cm$^2$</th>
<th>$R_p$ / K$\Omega$</th>
<th>$R_i$ / mm/y</th>
<th>$P_e$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDG</td>
<td>-1.009</td>
<td>26.9</td>
<td>0.85</td>
<td>0.401</td>
<td>-</td>
</tr>
<tr>
<td>60 s phos</td>
<td>-0.980</td>
<td>24.9</td>
<td>0.95</td>
<td>0.372</td>
<td>8</td>
</tr>
<tr>
<td>180 s phos</td>
<td>-0.999</td>
<td>14.3</td>
<td>1.99</td>
<td>0.213</td>
<td>47</td>
</tr>
<tr>
<td>300 s phos</td>
<td>-1.023</td>
<td>9.2</td>
<td>3.85</td>
<td>0.138</td>
<td>66</td>
</tr>
<tr>
<td>600 s phos</td>
<td>-1.015</td>
<td>7.5</td>
<td>4.39</td>
<td>0.112</td>
<td>71</td>
</tr>
<tr>
<td>600 s phos + 3 g/l Si</td>
<td>-1.009</td>
<td>5.3</td>
<td>9.59</td>
<td>0.079</td>
<td>80</td>
</tr>
<tr>
<td>600 s phos + 5 g/l Si</td>
<td>-1.005</td>
<td>4.3</td>
<td>12.91</td>
<td>0.065</td>
<td>85</td>
</tr>
<tr>
<td>600 s phos + 7 g/l Si</td>
<td>-1.010</td>
<td>16.1</td>
<td>2.60</td>
<td>0.240</td>
<td>40</td>
</tr>
<tr>
<td>600 s phos + 10 g/l Si</td>
<td>-1.062</td>
<td>18.0</td>
<td>1.47</td>
<td>0.268</td>
<td>33</td>
</tr>
</tbody>
</table>

Figure 8. Electrochemical impedance curves for phosphated HDG steel samples for different time immersed in 3.5% NaCl solution.

Figure 9. Electrochemical impedance curves for phosphated HDG steel samples post-sealed with variable concentration of sodium silicate solutions for 60 s and immersed in 3.5% NaCl solution.
EIS measurements were recorded to confirm the anticorrosion behavior of treated HDG steel. Fig. 8 shows the Nyquist plots of HDG steel and phosphated samples for different time (60, 180, 300 and 600 s) immersed in 3.5 % NaCl solution. The Nyquist plots are characterized by well defined one capacitive loop indicating one time constant at phosphating time (0, 60 and 180 s) but at high phosphating time (300 and 600 s) Nyquist diagram consists of two capacitive loop representing (two time constants), which indicate the occurrence of two process during corrosion. The total impedance values of the phosphated samples were higher than HDG steel, and increased with increasing the phosphating time [36].

Fig. 9. Shows the Nyquist plots of the phosphated samples with silicate post-sealing. EIS was measured in 3.5 % NaCl solution, the changing of solution conductivity with changing concentration of silicate solution results in different impedance responses at high and low frequency range. The obtained Nyquist diagram consists of two time constants at silicate concentration (3 g/l) but at higher silicate concentration (5, 7 and 10 g/l) the obtained Nyquist diagram consists of one time constant. It's clear from the curves that, the impedance values of silicate-coated samples is higher than those of the HDG samples for concentrations (3, 5 g/l) and impedance values lower than those of the HDG samples for concentrations (7, 10 g/l). The coating resistance increased in order of: 10 g/l < 7 g/l < HDG < 3 g/l < 5 g/l. Therefore the best concentration of silicate passivation bath is 5 g/l due to formation of zinc-silicate complex which is highly resistance to corrosion and it would decrease the active sites of substrate. Otherwise any further increase in the silicate concentration (7 and 10 g/l) leads to formation of cracks which increase the interaction between NaCl and the investigated sample and decrease the corrosion resistance [30].

**Figure 10.** Equivalent circuits used for modeling of experimental EIS data (a) with one time constant and (b) with two time constant.
To interpret these data the proposed equivalent circuits corresponding to the EIS spectra is given in Fig. 10 (a, b) and the fitted parameters listed in Table 5. The model in Fig.10a represents the equivalent circuit for phosphating time (0, 60 and 180 s) and for the phosphated samples post-sealing in silicate concentration (5, 7 and 10g/l). It is simple model consists of a constant phase element (CPE) which is parallel to the polarization resistance of the surface film (R_p) both of them are in series with solution resistance (R_s).

The model in Fig.10b represent the equivalent circuit with two RQ couples to explain the corrosion process for phosphating time (300 and 600 s) and for post-sealing in silicate concentration (3 g/l) which includes the solution resistance (R_s) between the reference electrode and the surface of working electrode in series combination of two resistance (R_1) and (R_2) correspond to the polarization resistance of coating and the substrate/coating interface, respectively, both of them are in series with constant phase element (CPE). Constant phase element is included in circuits instead of capacitance give more accurate fit due to the non-homogeneity of the electrode surface and is defined by two values Q, α.

The CPE is a special element whose value is a function of the angular frequency and expressed as:

\[ Z_{CPE} = Q \left( i \omega \right)^{-\alpha} \]  

(14)

Where \( i \) is the imaginary number, \( i = (-1)^{1/2} \), \( \omega \) is angular frequency in rad s\(^{-1}\), \( \omega = 2\pi f \) and \( f \) is the frequency in Hz = s\(^{-1}\), the factor \( \alpha \) is an adjustable parameter introduced to account for the deviation from the ideal capacitive behavior due to the roughness of the electrode surface. The smaller value of \( \alpha \) the higher surface roughness. If \( \alpha \) equals one, the impedance of CPE is identical to that of a capacitor, \( Z_c = (i\omega C)^{-\alpha} \), and in this case \( Q \) gives a pure capacitance (C) [37, 38].

**Table 5.** Electrochemical impedance parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs/Ω</th>
<th>R1/Ω</th>
<th>CPE1/µF</th>
<th>α1</th>
<th>R2/Ω</th>
<th>CPE2/µF</th>
<th>α2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDG</td>
<td>700</td>
<td>1540</td>
<td>3.0</td>
<td>0.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60 s phos</td>
<td>870</td>
<td>1890</td>
<td>2.3</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>180 s phos</td>
<td>940</td>
<td>2208</td>
<td>2.1</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300 s phos</td>
<td>820</td>
<td>565</td>
<td>8.3</td>
<td>0.79</td>
<td>3475</td>
<td>1.5</td>
<td>0.81</td>
</tr>
<tr>
<td>600 s phos</td>
<td>1075</td>
<td>2710</td>
<td>1.9</td>
<td>0.81</td>
<td>3515</td>
<td>1.4</td>
<td>0.86</td>
</tr>
<tr>
<td>600 s phos + 3 g/l Si</td>
<td>1096</td>
<td>5405</td>
<td>1.2</td>
<td>0.85</td>
<td>6450</td>
<td>1.0</td>
<td>0.84</td>
</tr>
<tr>
<td>600 s phos + 5 g/l Si</td>
<td>1200</td>
<td>18500</td>
<td>0.6</td>
<td>0.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600 s phos + 7 g/l Si</td>
<td>780</td>
<td>3200</td>
<td>1.5</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600 s phos + 10 g/l Si</td>
<td>660</td>
<td>2800</td>
<td>1.8</td>
<td>0.76</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Comparison of the coating performance offered by phosphated HDG sample and post-sealed with sodium silicate solution at optimum condition and other similar coatings are given in Table 6.
Silicate conversion coating is a very effective and economic way to increase the protection efficiency, which is in accordance with results previously reported [30, 39-41].

**Table 6. Coating performance compared with others**

<table>
<thead>
<tr>
<th>Coatings</th>
<th>$I_{corr}$ $\mu$A/cm$^2$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_{VI}$</td>
<td>55.2</td>
<td>[40]</td>
</tr>
<tr>
<td>Cr$_{III}$</td>
<td>7.6</td>
<td>[41]</td>
</tr>
<tr>
<td>Phos/Si</td>
<td>4.3</td>
<td>This work</td>
</tr>
</tbody>
</table>

![Figure 11. SEM micrographs and EDX analysis before and after corrosion of HDG steel sample (a, b), 600 s phosphated HDG steel sample (c, d), phosphated HDG steel post-sealed with 5 g/l silicate solution (e, f), phosphated HDG steel post-sealed with 10 g/l silicate solution (g, h).](image-url)
The surface morphology of samples before corrosion represent in Fig. 11(a, c, e and g) which show the SEM of HDG steel sample, 600 s phosphated HDG, sample after post-sealing with sodium silicate at 5 g/l and 10 g/l respectively.

It's clear in Fig.11c zinc phosphate crystals deposit on the surface with pores among the crystals. After sealing with 5 g/l sodium silicate solution the surface morphology appears homogeneous Fig. 11e and further increasing in sodium silicate concentration 10 g/l lead to formation of some cracks on the surface giving inhomogeneous coating with bad appearance and facilitate electrolyte diffusion as seen in Fig 11g. In Fig.11 (b, d, f and h) show the SEM micrographs after corrosion of the same samples. The corrosive medium (3.5 % NaCl solution) affect the HDG samples and attack is clearly appeared but after treated sample especially at optimum treatment condition (600 s phosphated and post-sealed with 5 g/l sodium silicate solution ) there is good protective coating layer which has the best corrosion resistance with high protection ability and suppressed the effect of the corrosive medium.

The EDX results of the same samples are listed in Table 7, which verify the change of chemical composition of the coating. The pores among zinc phosphate before the sealing composed of Zn, P and small amount of O whereas, after the silicate post-sealing Si, P, Zn and high content of O appears which indicate new compound and strong coating are formed on the surface of HDG steel which is responsible for the protection of the treated samples.

Table 7. lists the EDX results of the samples before and after corrosion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before corrosion Composition</th>
<th>After corrosion Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Fe</td>
</tr>
<tr>
<td>GS</td>
<td>98.91</td>
<td>0.52</td>
</tr>
<tr>
<td>GS+P</td>
<td>89.61</td>
<td>-</td>
</tr>
<tr>
<td>GS+P+5g/l Si</td>
<td>92.11</td>
<td>-</td>
</tr>
<tr>
<td>GS+P+10g/l Si</td>
<td>95.25</td>
<td>-</td>
</tr>
</tbody>
</table>

Finally the results in this investigation from all techniques showed that the improved coatings with best corrosion performance was obtained by optimum condition through phosphated HDG steel for 600 s followed by post-sealing with 5 g/l sodium silicate solution for 60 s.

4. CONCLUSIONS

Based on results obtained in this investigation, the following conclusion is derived:

1- The conversion coating is added to metal surface to increase the functionality and corrosion protection ability.
2- The change in morphology of the zinc coatings due to surface treatment influenced the corrosion resistance property towards the external aggressive media of the investigated samples.

3- The electrochemical tests show that, the post treatment of galvanized steel in phosphate solution reduce the corrosion in 3.5% NaCl. The better performance by increasing the phosphating time due to formation of protective film (coat) on the surface which retards the permeation and destructive action of chloride ions in solution.

4- The corrosion resistance confirms the synergism between the phosphate coatings and silicate -post sealing, the sodium silicate solution sealed the pores among the zinc phosphate crystals. The improved coating with optimal corrosion resistance are obtained for phosphating time 600 s and post – sealing with sodium silicate for 60 s up to 5 g/l

5- Any further increasing in sodium silicate concentration will decrease the corrosion resistance due to formation of some cracks on the surface with bad appearance as (as confirmed by SEM- EDX analysis)

6- The corrosion protection efficiency P_e % of the coatings increases greatly when the phosphate HDG samples were post-sealing with 5 g /l sodium silicate solution for 60 s.

References


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