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Formation of zinc phosphate coating by anodic electrochemical treatment

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Abstract

The formation of zinc phosphate coating by anodic electrochemical treatment is addrsed. The importance of the addition of nitrite, the extent of sludge formation and the eco-friendliness of the process is presented. Based on the amount of coating weight and change in potential—time measurements, a mechanism for the coating formation is proposed. The coating characteristics and corrosion resistance were evaluated. The study reveals that anodic electrochemical treatment, though enabling an acceleration of coating deposition, results in heavy sludge formation, making the process less eco-friendly. The coatings obtained by anodic phosphating are rich in phosphophyllite phase with a smaller proportion of hopeite phase and iron phosphate. Since the porosity of the anodically phosphated mild steel substrate is relatively higher, these coatings will suit applications which require higher oil-retaining capacity. The corrosion behaviour of anodically phosphated mild steel substrate in 3.5% sodium chloride solution reveals the ability of the phosphate coating to act as a barrier film towards the ingress of corrosive media.

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1. Introduction

Phosphating is the most widely used metal pretreatment process for the surface treatment and finishing of ferrous and non-ferrous metals. Due to its economy, speed of operation and ability to afford excellent corrosion resistance, wear resistance, adhesion and lubricative properties, it plays a significant role in the automobile, process and appliance industries [1–4]. Majority of the phosphating baths reported in literature require very high operating temperatures ranging from 90 to 98 °C. The main drawback associated with high-temperature operation is the energy demand, which is a major crisis in the present-day scenario. Besides, the use and maintenance of heating coils is difficult due to scale formation, which leads to improper heating

of the bath solution and require frequent replacement. Another problem is overheating of the bath solution, which causes an early conversion of the primary phosphate to tertiary phosphate before the metal has been treated which results in an increase in the free acidity of the bath and consequently delays the precipitation of the phosphate coating [5]. One possible way of meeting the energy demand and eliminating the difficulties encountered due to scaling of heating coils and overheating of the bath is through the use of low-temperature phosphating baths.

Though known to be in use since the 1940s [6], the low-temperature phosphating processes have become more significant today due to the escalating energy costs. However, low-temperature phosphating processes are very slow and need to be accelerated by some means. Acceleration of the phosphating process could be achieved by chemical, mechanical and electrochemical methods. However, each of them has some limitations and/or detrimental effects. Chemical accelerators are the preferred choice in many instances. However, nitrite, the most commonly used accelerator in low temperature phosphating baths, is likely to cause disposal problems [7]. Though electrochemical means of acceleration has been studied earlier [8–16], the detailed information regarding the mechanism of formation

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and the characteristics of the coating is lacking. Moreover, the choice of a preferable method of acceleration, cathodic or anodic, still remains ambiguous [11]. Our research work focuses on the electrochemical acceleration of the low-temperature phosphating process by both cathodic and anodic electrochemical treatment to ascertain the viability of these techniques for industrial applications. Our earlier papers [17,18] addressed the influence of cathodic electrochemical treatment on the formation of zinc phosphate coating and evaluation of its corrosion characteristics. The present paper addresses the formation of zinc phosphate coating by anodic electrochemical treatment.

2. Experimental details

The essential constituents of a zinc phosphating bath are a zinc salt, which is the source of zinc, *ortho*-phosphoric acid and an accelerator to speed up the rate of deposition [1–5]. Besides these basic components, a variety of special additives are also added to the bath to improve the quality and performance of the resultant coatings [5]. Since the present study focuses on the formation of zinc phosphate coating on mild steel substrates by anodic deposition process, the bath formulation was made using only the basic components to avoid the influence of any special additive. The composition of the baths and operating conditions used for the anodic phosphating process is given in Table 1, which is very similar to the one used by Sinha and Feser [16] for electrochemical phosphating. Sodium nitrite was used in these baths to avoid polarization of the cathode.

Mild steel substrates (composition: C: 0.16%; Si: 0.17%; Mn: 0.68%; P: 0.027%; S: 0.026%; Cr: 0.01%; Ni: 0.01%; Mo: 0.02% Fe: Balance) of 6 cm×5 cm×0.2 cm in size were used for the deposition of coatings by anodic phosphating process. The oil and the greasy matter present on the substrate material, which would otherwise inhibit the coating formation, were removed by wiping with cotton soaked in trichloroethylene. The degreased panels were pickled in 10% sulphuric acid at 70–80 °C for 5–10 min to remove the rust and mill scale. The pickled panels were rinsed thoroughly in deionized water to remove the acid residues present on it after pickling. The

Table 1 Chemical composition, control parameters and operating conditions of the baths used for anodic phosphating process

used for anodic pr	iospnating pr	ocess			
Bath composition				Baths A-	-E
ZnO				2.04 g/l	
H ₃ PO ₄ (85%)				16 ml/l	
NaOH				6.7 g/l	
NaNO ₂				0.5 g/l	
Time				60 min	
Current density				4, 5 and	6 mA/cm ²
Variables	Bath A	Bath B	Bath C	Bath D	Bath E
nН	2.90	2.60	3.20	2.90	2.90

Variables	Bath A	Bath B	Bath C	Bath D	Bath E
рН	2.90	2.60	3.20	2.90	2.90
FA value (points)	3.6	4.8	1.3	3.6	3.6
TA value (points)	29.0	31.0	21.0	29.0	29.0
FA/TA	1:8.06	1:6.46	1:16.15	1:8.06	1:8.06
Temperature (°C)	27	27	27	45	60

^{*}FA-Free acid value; TA-total acid value; FA/TA-free acid-to-total acid ratio.

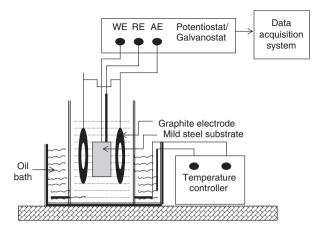


Fig. 1. The schematic of the experimental setup used for anodic phosphating process.

degreased, pickled and rinsed mild steel substrates were immediately immersed into the phosphating solution contained in the beaker cell, which is maintained at the temperature required for phosphating using a constant-temperature oil bath. Two sets of graphite disc electrodes (cathode) (6 cm diameter) were placed on both sides of the mild steel substrate (anode) as counterelectrodes. The graphite electrodes were suitably covered with a bag made of muslin cloth so that the fine graphite particles dislodged from the electrode did not contaminate the bath during deposition. The deposition of the zinc phosphate coating was carried out under galvanostatic conditions using a Potentiostat/Galvanostat (ACM Instruments, UK; Model: Gill AC). The schematic of the experimental setup is given in Fig. 1. Coating formation was allowed to proceed for the required period of time after which the coated substrates were removed. The effect of process variables such as applied current density, bath pH, temperature and processing time on the amount of coating formed and the extent of metal dissolution were studied [1-5]. Potential-time measurement during cathodic phosphating process was also carried out as a function of process variables such as current density, pH of the bath and temperature. The phosphated substrates were then rinsed with deionized water to remove the acid residues and the soluble salts left after phosphating. After rinsing, the coated substrates were subjected to drying using a stream of compressed air.

The surface morphology of the anodically phosphated mild steel substrate was assessed by scanning electron microscope (SEM) Cambridge Instruments (Model: Stereoscan 360). The corrosion resistance of the anodically phosphated mild steel substrates in 3.5% sodium chloride solution was evaluated based on the observations made after 12 h of immersion for the discolouration of the solution and rusting of the panels and the loss in weight measured after 24 h of immersion.

3. Results and discussion

3.1. Effect of process variables on coating weight

Coating weight is the prime factor widely used in industries to assess the quality of a phosphating bath and is strongly recommended by many specifications [19,20]. Further, based on the coating weight values, phosphate coatings have been classified into different categories and recommended for different end uses.

3.1.1. Effect of current density on coating weight

Current density is one of the major factors that influence the extent of phosphate coating formation. The effect of current density (4, 5 and 6 mA/cm²) on coating weight and iron dissolved during phosphating obtained using bath A are shown in Fig. 2a–c, respectively. The extent of metal dissolution and coating weight increases with increase in current density. However, compared to conventional phosphating process, the conversion ratio (ratio of coating weight to iron dissolved) is very low in the anodic phosphating process. A similar trend is also observed when the pH of the bath is varied to 2.60 (bath B) and 3.20 (bath C).

3.1.2. Effect of bath pH on coating weight

The effect of bath pH (2.60, 2.90 and 3.20) on coating weight and iron dissolved during phosphating obtained using baths B, A and C, at 6 mA/cm², are shown in Figs. 2c and 3a and b, respectively. Increase in bath pH leads to a decrease in iron dissolution and an increase in coating weight. Hence, the conversion ratio increases with an increase in pH of the bath. The decrease in coating weight observed at pH 3.20 at higher processing times is due to the spalling of the coating. A similar trend is also observed at 4 and 5 mA/cm².

3.1.3. Effect of temperature on coating weight

The effect of temperature (27, 45 and 60 °C) on coating weight and iron dissolved during phosphating obtained using baths A, D and E, at 6 mA/cm², are shown in Figs. 2a and 4a and b, respectively. Increase in temperature leads to an increase in extent of metal dissolution and coating weight. The conversion ratio also increases with an increase in temperature. The decrease in coating weight observed at higher temperatures at higher processing times is due to the spalling of the coating. A similar trend is also observed at 4 and 5 mA/cm².

During anodic phosphating, the substrate metal is made as anode and forced to dissolve due to the applied current density. The hydrogen evolution reaction is shifted to the cathode (counter-electrode).

Anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

Cathodic reaction:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$

A rise in interfacial pH is an essential prerequisite to deposit phosphate coating on the substrate. In anodic phosphating, the very high amount of ferrous ions available at the interface enables the displacement of the protons away from the interface and causes a rise in interfacial pH. Subsequently, phosphate coating is formed on the mild steel substrate. The extent of

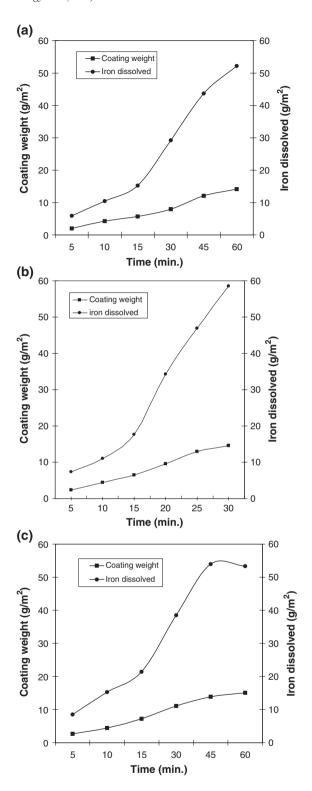


Fig. 2. Variation of phosphate coating weight and iron dissolved during phosphating as a function of time obtained using bath A (pH 2.9; temperature 27 °C) by anodic phosphating (a) 4 mA/cm²; (b) 5 mA/cm²; and (c) 6 mA/cm².

metal dissolution is extremely high with an increase in current density and temperature of the bath. However, the magnitude of increase in coating weight is much less. This is due to the regenerated phosphoric acid formed during the conversion of primary to tertiary phosphate (as shown in the equations) that

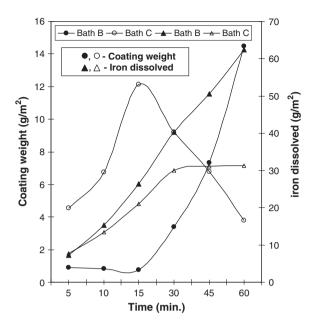


Fig. 3. Variation of phosphate coating weight and iron dissolved during phosphating as a function of time obtained using bath B (pH 2.6; temperature 27 °C) and bath C (pH 3.2; temperature 27 °C) by anodic phosphating at 6 mA/cm².

increases the local acidity at the interface, which might attack the base metal as well as the phosphate coating.

$$Zn(H_2PO_4)_2 \leftrightarrow ZnHPO_4 + H_3PO_4$$

$$3ZnHPO_4 \leftrightarrow Zn_3(PO_4)_2 + H_3PO_4$$

The continuous dissolution and precipitation of phosphate coating cause a very low increase in coating weight. An increase in pH of the bath decreases the extent of metal dissolu-

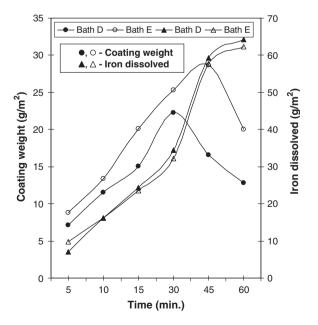


Fig. 4. Variation of phosphate coating weight and iron dissolved during phosphating as a function of time obtained using bath D (pH 2.9; temperature 45 °C) and bath E (pH 2.9; temperature 60 °C) by anodic phosphating at 6 mA/cm².

tion and increases the conversion ratio. This is due to the decreased metal attack and earlier attainment of PIP.

The coating weight values suggest only the amount of coating formed and do not provide any information regarding the kinetics of coating formation. Much information on the kinetics and mechanism of the phosphating process can be inferred from potential—time measurements rather than the coating weight measurements. Literature reports reveal that the kinetics of phosphate coating formation is best followed by measuring the changes in potential of the substrate as a function of time (potential—time measurements) [21–25].

3.2. Potential-time measurements

During anodic phosphating, the potential of the substrate is monitored continuously as a function of time for the entire duration of coating deposition. The potential—time curves obtained for all the baths chosen for the present study could be analyzed by dividing them in to two segments as follows:

Segment I change in potential from initial to maximum value Segment II change in potential beyond the maximum value

A typical potential—time curve depicting the classification of the above two segments is shown in Fig. 5.

3.2.1. Segment I

The change in potential from initial to maximum value is indicative of the nature of the metal surface during the initial stages of coating formation. In this segment, the potential of the mild steel substrate is shifted towards anodic direction. Shift in potential towards the anodic direction during the initial stages of coating formation is also observed in conventional phosphating process due to the corrosive attack by the free phosphoric acid present in the bath [22]. The extent of shift in potential in anodic phosphating is similar to the conventional phosphating process. However, the observed maximum potential is relatively more anodic to the initial/open circuit potential (–480 mV vs. SCE). This anodic shift in potential is due to the depletion of H⁺ ions in the electrode/electrolyte interface caused by the repulsive forces from the ferrous ions and the positive charge

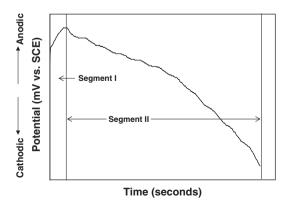


Fig. 5. A typical potential—time curve depicting the classification of the two different segments of the curve to analyze the changes that occur during anodic phosphating process.

on the substrate (Table 2). Though the potentials are relatively more anodic, metal dissolution is the predominant reaction during this segment.

3.2.2. Segment II

This segment represents the change in potential from a maximum value towards less negative values. Shift in potential towards less negative values is also observed in conventional phosphating processes, which can be accounted for the deposition of non-metallic zinc phosphate coating [21–25]. Hence, the shift in potential observed in this segment is due to the deposition of zinc phosphate coating on the substrate. The maximum potential represents the onset of conversion of soluble primary phosphate to insoluble tertiary phosphate (point of incipient precipitation), following the rise in interfacial pH. Further shift in potential towards less negative values represents the progressive buildup of the phosphate coating formation.

The extent of shift in potential towards less negative values is a function of current density, pH and temperature. Increase in current density, increase in temperature and increase in pH

Table 2
Potential values as a function of process variables derived from potential—time curves recorded during anodic phosphating process

Phosphating condition	Maximum potential (mV vs. SCE)	Time at which the maximum potential is reached (s)	Final potential (mV vs. SCE)	Extent of shift in potential from first stabilization potential to final potential (mV vs. SCE)
pH 2.9; 27 °C;	-140	90	-18	+122
4 mA/cm ²	100			. 101
pH 2.9; 27 °C;	-128	75	3	+131
5 mA/cm ²	110			
pH 2.9; 27 °C;	-118	65	16	+144
6 mA/cm ²	120	00	*	*
pH 3.2; 27 °C;	-130	80	*	*
4 mA/cm ²	110	70	*	*
pH 3.2; 27 °C;	-119	70	*	Ψ
5 mA/cm ²	110	60	*	*
pH 3.2; 27 °C; 6 mA/cm ²	-110	60	*	Ψ
	-160	105	-72	+88
pH 2.6; 27 °C; 4 mA/cm ²	-160	105	- 72	+88
pH 2.6; 27 °C;	-142	85	-41	+101
5 mA/cm ²	-142	83	-41	+101
pH 2.6; 27 °C;	-128	75	-15	+113
6 mA/cm^2	120	73	13	1113
pH 2.9; 45 °C;	-130	70	29	+159
4 mA/cm^2	130	70	2)	137
pH 2.9; 45 °C;	-118	65	54	+172
5 mA/cm^2	110	05	51	. 172
pH 2.9; 45 °C;	-106	55	74	+180
6 mA/cm^2	100		, ,	100
pH 2.9; 60 °C;	-116	60	*	*
4 mA/cm^2		- -		
pH 2.9; 60 °C;	-110	55	*	*
5 mA/cm^2		- -		
pH 2.9; 60 °C;	-100	50	*	*
6 mA/cm ²				

^{*}The final potential value shifts towards very high anodic value (around $\pm 1.9~\mathrm{V}$ vs. SCE).

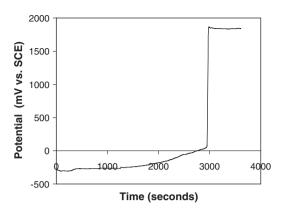


Fig. 6. Potential-time curve of anodically phosphated mild steel substrate depicting the sudden ennoblement of potential towards very high anodic potential.

result in greater shift in potential towards the less negative values. This can be attributed to the earlier attainment of PIP under these conditions (Table 2).

A sudden ennoblement of potential towards a very high anodic potential (around $+1.9 \, \text{V}$) is observed especially with baths C and E (Fig. 6). This can be attributed to the complete consumption of nitrite utilized for the oxidation of ferrous ions to ferric ions. The heavy amount of ferric phosphate sludge in anodic phosphating process supports such a possibility. The non-availability of nitrite to facilitate the hydrogen evolution reaction results in the polarization of the cathode and causes such behaviour.

3.3. Mechanism of coating formation

Coating weight measurements suggest that the increase in coating weight with increase in current density, increase in bath

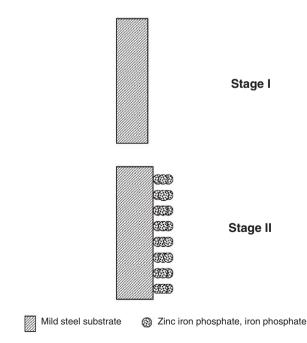


Fig. 7. Pictorial model depicting the two stages of coating formation during anodic phosphating process.

pH and increase in temperature is due to the earlier attainment of PIP due to the rise in interfacial pH. Potential-time measurements suggest the occurrence of iron dissolution as the predominant reaction during the initial period (Stage I), followed by the deposition of non-metallic zinc phosphate with a simultaneous metal dissolution through the pores of the coating in the second stage. Hence, it can be visualized that the onset of phosphate coating occurs following the initial metal dissolution, displacement of protons away from the interface and attainment of the PIP. Further to this, both iron dissolution and coating formation continue throughout the entire duration of deposition. Though a progressive increase in coating weight and iron dissolution is expected, the effect is observed only with iron dissolution and not with coating weight. The availability of regenerated phosphoric acid at the interface causes a drop in local pH, which attacks the base metal as well as the phosphate coating. Based on the above findings, a pictorial model for the mechanism of coating formation during anodic phosphating is proposed (Fig. 7).

Mild steel substrates anodically phosphated using baths A—E produce a coating consisting of iron-rich zinc phosphate. The coating may also contain a small amount of iron phosphate and zinc phosphate. Comparing the coating weight and quality of the coating obtained using the above baths, coatings obtained using bath A seem to possess a reasonable coating weight, uniformity and adhesion. Hence, evaluation of coating characteristics and corrosion resistance were carried out only for coatings prepared using bath A.

3.4. Evaluation of coating characteristics

The colour of the phosphate coating obtained using bath A is grayish white and is highly uniform. Adhesion of the phosphate coating on the mild steel substrate evaluated by the pull-off test with a pressure-sensitive adhesive tape is found to be good. Adhesion of the paint film over the anodically phosphated substrate in the dry state was found to be good since it mainly depends upon the cohesive failure of the paint film (topcoat) and it has very little influence on the nature of the phosphate coating underneath the paint film.

Wet adhesion measurements performed after 240 h of immersion in deionized water at 45 °C reveals that there is no blister formation, indicating that the permeability of the paint film is low. The extent of adhesion measured by a pressure-

Table 3 Porosity of anodically phosphated mild steel substrates estimated in terms of oxygen reduction current density at $-550~\rm mV$ vs. SCE in 0.1 N sodium hydroxide solution

System studied	Current density at -550 mV vs. SCE ($\mu\text{A/cm}^2$)
Mild steel substrate anodically phosphated at 4 mA/cm ²	15
Mild steel substrate anodically phosphated at 5 mA/cm ²	18
Mild steel substrate anodically phosphated at 6 mA/cm ²	20

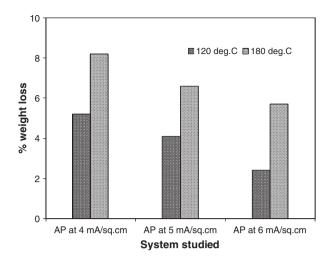


Fig. 8. Thermal stability of anodically phosphated mild steel substrates when subjected to thermal treatment at 120 and 180 °C for 30 min.

sensitive adhesive tape, after making scribes to the base metal, revealed that the wet adhesion is consistently good. The wet adhesion behaviour is rated as 5B as per ASTM D 3359-02.

The porosity of phosphate coatings assessed by the chemical method based on Prussian blue colour formation as a result of the interaction between the ferrous ions in the uncoated areas and the ferricyanide present in the test solution showed the appearance of a few blue spots per square centimeter. However, the more reliable electrochemical method, which measures the oxygen reduction current density, clearly indicates the amount of porosity involved. The current density values measured at $-550~\rm mV$ vs. SCE are in the range of $15-20~\rm \mu A/cm^2$ (Table 3), indicating that the porosity of the anodically phosphated mild steel substrate is relatively higher than that of conventionally phosphated ones.

The percentage weight loss obtained for anodically phosphated substrate, when subjected to thermal treatment at 120 and 180 °C for 30 min, is given in Fig. 8. The measure of the percentage residual coating weight obtained for anodically phosphated substrates from immersion treatments at mild acidic, neutral and alkaline conditions are given in Fig. 9. The increase

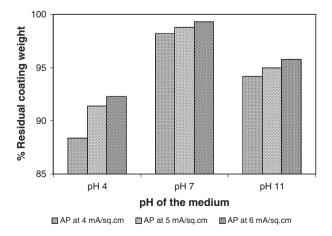
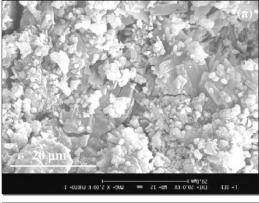
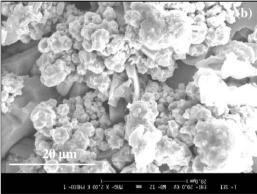


Fig. 9. Chemical stability of anodically phosphated mild steel substrates subjected to immersion at mild acidic (pH 4), neutral (pH 7) and alkaline (pH 11) conditions for 30 min.





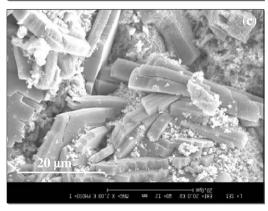


Fig. 10. Surface morphology of the anodically phosphated mild steel substrates using bath A at different current densities (a) 4 mA/cm²; (b) 5 mA/cm²; and (c) 6 mA/cm².

in the percentage loss in weight following thermal treatment at 120 and 180 °C is due to the loss of associated water molecules from the two phases of the zinc phosphate coating, namely, hopeite $\{Zn_3(PO_4)_2\cdot 4H_2O\}$ and phosphophyllite $\{Zn_2Fe(PO_4)_2\cdot 4H_2O\}$. At 120 °C, hopeite loses two molecules of water, while at 180 °C, it loses the remaining two molecules, whereas phosphophyllite loses only two molecules of water of hydration even at this temperature [26]. The observed trend in the relatively lesser percentage loss in weight in thermal treatment and the higher residual coating weight in chemical treatment suggest that a phosphophyllite-rich coating is formed in all the cases of anodically phosphated substrates. The formation of a phosphophyllite-rich coating in anodic phosphating process is further supported by the process conditions, which facilitate higher amounts of ferrous ions at the interface. Thermal and

chemical stability of the phosphate coatings obtained by anodic phosphating process resembles that of the conventional zinc phosphate coating deposited on steel substrate.

The surface morphology of anodically phosphated steel substrates, obtained using bath A at 4, 5 and 6 mA/cm², are shown in Fig. 10a–c, respectively. The formation of needle-like crystals is characteristic of the phosphophyllite phase $\{Zn_2Fe(PO_4)_2\cdot 4H_2O\}$. The refinement of crystals revealed in the morphology of the coating is due to the continuous dissolution and re-precipitation of the phosphate coating by the phosphoric acid formed during the anodic phosphating process.

3.5. Evaluation of corrosion performance

Immersion in 3.5% NaCl solution provides an insight into the corrosion behaviour of phosphated mild steel substrates. The extent of corrosion is assessed by visual observation after 12 h of immersion and by measuring the loss in mass due to corrosion after 24 h of immersion. Observations made after 12 h (Table 4) reveal that the anodically phosphated mild steel substrate remains good and shows no rust formation. However, discolouration of the solution occurs in the case of uncoated mild steel substrate, indicating a higher amount of iron dissolution, in this case. The formation of a yellowish orange precipitate of ferric hydroxide following the hydrolysis of iron(II) chloride formed by the attack of chloride ions at the uncoated areas indicate greater corrosion and discolouration of the solution in the case of uncoated steel. The absence of red rust on the surface of phosphated steel indicates that the anodically phosphated mild steel substrates are more uniform besides possessing a good corrosion resistance. The improvement in corrosion resistance compared to uncoated mild steel substrate is also reflected in the loss in weight due to corrosion measured after 24 h (Table 4). This is due to the ability of the phosphate coating to act as a barrier film towards the ingress of corrosive media.

Table 4 Corrosion resistance of anodically phosphated mild steel substrate subjected to immersion in 3.5% sodium chloride solution for 24 h

System studied	Observations after 12 h	Loss in weight (g/m ²) after24 h
Uncoated mild steel	Discolouration of the solution	24.2
	Red rust formation on the surface of the substrate	
Mild steel substrate anodically phosphated	No discolouration of the solution	11.4
at 4 mA/cm ²	No red rust formation on the surface of the substrate	
Mild steel substrate anodically phosphated	No discolouration of the solution. No red rust	12.1
at 5 mA/cm ²	formation on the surface of the substrate	
Mild steel substrate anodically phosphated	No discolouration of the solution. No red rust	12.9
at 6 mA/cm ²	formation on the surface of the substrate	

4. Conclusions

The study on the formation of zinc phosphate coating by anodic electrochemical treatment leads to the following conclusions. The anodic phosphating process requires the addition of a minimum amount of sodium nitrite to prevent polarization of the cathode and to realize the coating formation. The baths used for the anodic phosphating process are capable of producing good-quality coatings even at low temperature, offering benefits in terms of energy savings, a decrease in processing cost and improvement in plant life. Being an anodic process, there is significant iron dissolution, which in turn gets oxidized by nitrite and precipitated as ferric phosphate sludge. The heavy sludge formation and the environmental impact of toxic nitrite compounds render the anodic phosphating process less eco-friendly. The phosphate coating weight and iron dissolved during phosphating increases with an increase in current density, pH of the bath and temperature. Compared to conventional phosphating processes, the conversion ratio (ratio of coating weight to iron dissolved) is very low in the anodic phosphating process. Potential-time measurements reveal that the coating formation proceeds through two stages in which metal dissolution and deposition of phosphate coating are the predominant reactions during the first and second stages, respectively. The onset of phosphate coating occurs following the initial metal dissolution, displacement of protons away from the interface and attainment of the PIP. Further to this, both metal dissolution and coating formation continue throughout the entire duration of deposition. The mechanistic aspects associated with the anodic phosphating resemble those of a conventional phosphating process but with accelerated metal dissolution. For obtaining a coating weight of 10 g/m² using the bath composition of the present study, it will take about 50 min by chemical deposition, whereas by anodic electrochemical treatment, the processing time is reduced to 30 min. indicating a degree of acceleration of 40% by the anodic electrochemical treatment. The coatings obtained by the anodic phosphating process are rich in the phosphophyllite phase with a smaller proportion of hopeite phase and iron phosphate. The porosity of the anodically phosphated mild steel substrate is relatively higher than that of conventionally phosphated ones. Hence, the anodic phosphating process will suit applications which require higher oil-retaining capacity. The corrosion behaviour of anodically phosphated mild steel substrate in 3.5% sodium chloride solution reveals the ability of the phosphate coating to act as a barrier film towards the ingress of corrosive media.

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