



Formation and characteristics of zinc phosphate coatings obtained by electrochemical treatment: Cathodic vs. anodic

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ABSTRACT

Electrochemical treatment and galvanic coupling are some of the possible modes of acceleration of low temperature phosphating process. The cathodic and anodic treatments during phosphating influence the deposition mechanism, characteristic properties and the corrosion resistance of the resultant coatings in a different way. The present paper aims to compare these aspects and to identify the possible applications of phosphate coatings obtained by these treatments.

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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, phosphating plays a significant role in the automobile, process and appliance industries [1–4]. The energy demand, difficulty in maintaining heating coils and overheating of the bath [5] are some of the major concerns with the use of high temperature operated (90–98 °C) phosphating baths. Use of low temperature phosphating baths, though known to be in use for a long time, needs to be accelerated by chemical or mechanical or electrochemical methods. Our research work focuses on the modes of acceleration of low temperature phosphating process by cathodic and anodic treatments and by galvanic coupling to ascertain the viability of these techniques for industrial applications [6–12]. Our earlier papers [8–12] have addressed the influence of cathodic and anodic electrochemical treatments on the deposition of zinc phosphate coating on mild steel and evaluation of their corrosion behaviour. Both cathodic and anodic treatments influence the deposition mechanism, the characteristic properties and the corrosion resistance of the resultant coatings in a different way. A

comparison of these aspects and the possible applications of phosphate coatings obtained by these treatments will be of much help from industrial point of view, which forms the basis of this paper. The paper also aims to address the advantages and limitations of cathodic and anodic treatments and how effectively these treatments can be utilized to prepare phosphate coatings with desired characteristics.

2. Experimental details

The chemical composition of the bath, control parameters and operating conditions used for cathodic and anodic electrochemical treatments are given in Table 1. The bath constituents are essentially the same, except sodium nitrite, which is added in the phosphating bath during anodic treatment to prevent polarization of the cathode. Mild steel substrates (composition (in wt.%): 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. Graphite discs (6 mm diameter) served as the counter electrodes. The details of surface preparation of the mild steel substrates, experimental setup used for cathodic and anodic electrochemical treatments, etc., were given in our earlier papers [8–12]. Deposition of coatings was carried out under galvanostatic conditions at 4, 5 and 6 mA/cm² applied using a potentiostat/galvanostat (ACM Instruments, UK; Model: Gill AC). The structural characteristic of the coatings was evaluated by X-ray diffraction measurement using Cu K_α radiation.

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Table 1
Chemical composition of the bath, control parameters and operating conditions used for cathodic and anodic electrochemical treatments.

Variable	Cathodic treatment	Anodic treatment
ZnO (g/l)	2.04	2.04
H ₃ PO ₄ (85%) (ml/l)	16	16
NaOH (g/l)	6.7	6.7
NaNO ₂ (g/l)	–	0.5
pH	2.90	2.90
FA value (Points)	3.8	3.6
TA value (Points)	29.7	29.0
FA: TA	1: 7.82	1: 8.06
Temperature (°C)	27	27
Time (min)	60	60
Current density (mA/cm ²)	4, 5 and 6	4, 5 and 6

Bold values significant is pH of the phosphating solution. pH of the phosphating bath is an important parameter.

The surface morphology of the coatings was assessed by scanning electron microscope (SEM) (Cambridge Instruments; Model: Stereoscan 360). The corrosion resistance of phosphate coatings obtained by cathodic and anodic electrochemical treatment was evaluated by immersion test, salt spray test and, potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) studies. The details of the corrosion studies were given in our earlier papers [8–12].

The immersion, potentiodynamic polarization and EIS studies were performed to assess the corrosion protective ability of phosphate coatings prepared by cathodic and anodic treatment whereas the salt spray test was performed to assess the ability of these coatings to prevent underfilm corrosion. Before conducting the salt spray test, the phosphated steels were painted with synthetic enamel paint (white), the dry film thickness (DFT) of the double coat being 50 μm. The edges of the painted substrates were sealed with paraffin wax to avoid edge effect. The coated substrates were scribed to the base metal with a sharp needle so that the base metal is exposed to the salt mist in the salt spray chamber (ASTM B 117-03). The spreading of corrosion from the 'X'-scribe, after 96 h of exposure, was assessed and photographed.

3. Results and discussion

3.1. Mechanism of coating formation during cathodic and anodic electrochemical treatments

Conversion of soluble primary phosphate to insoluble tertiary phosphate following the rise in pH at the metal–solution interface accounts for the deposition of phosphate coating in cathodic as well as anodic treatments. However, depending on the type of treatment, other reactions also contribute to the coating deposition.

In cathodic treatment, during the initial stages a thin layer of zinc deposits on the surface of the mild steel substrate with a simultaneous hydrogen evolution reaction. The consumption of available H⁺ ions at the metal–solution interface results in a progressive rise in the interfacial pH and favours the conversion of soluble primary phosphate to insoluble tertiary phosphate. As a result, deposition of zinc phosphate occurs over the thin layer of zinc. The continued deposition of zinc and hydrogen evolution enables further deposition of zinc phosphate on adjacent areas. The available metallic sites (zinc) decrease with the progress in coating formation and it reaches almost a constant value. The continuous evolution of hydrogen (visually observed throughout the entire duration of deposition) suggests the availability of metallic sites (zinc) at the surface at any given time. It is presumed that the deposition of metallic zinc proceeds in the form of fixed channels surrounded by the non-metallic zinc phosphate throughout the thickness of the coating. Based on the above reactions, a pictorial model depicting

the mechanism of coating formation during cathodic treatment is proposed in Fig. 1.

In anodic treatment, the coating formation proceeds through two stages: 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 point of incipient precipitation (PIP). Further to this, both metal 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 reactions, a pictorial model depicting the mechanism of coating formation during anodic treatment is proposed in Fig. 1.

The mechanistic aspects associated with cathodic treatment resemble those of electrochemical deposition while the anodic

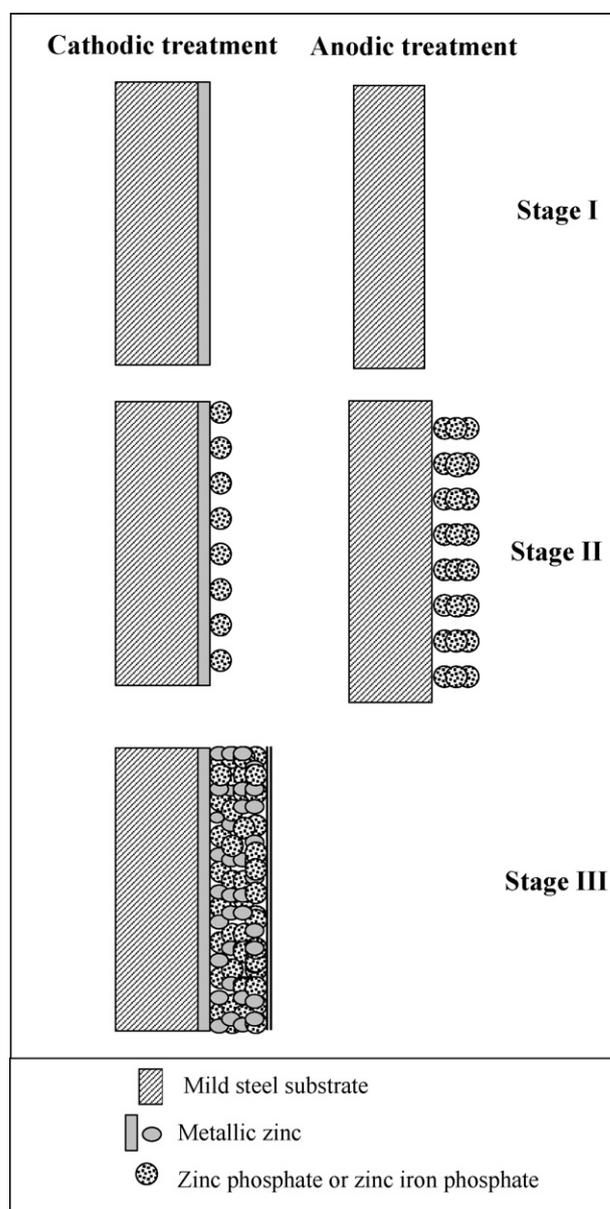


Fig. 1. Pictorial model depicting the various stages of coating formation during cathodic and anodic electrochemical treatments.

treatment resembles the conventional phosphating process but with accelerated metal dissolution. The cathodic treatment enables the formation of a zinc–zinc phosphate composite coating on mild steel whereas the anodic treatment leads to the deposition of zinc phosphate and zinc–iron phosphate. Similar to electrochemical deposition, the formation of zinc–zinc phosphate composite coating on mild steel continues as long as the current is applied in cathodic treatment. However, the magnitude of increase in coating weight is much less in anodic treatment. This is due to the fact that the regenerated phosphoric acid formed during the conversion of primary to tertiary phosphate increases the local acidity at the interface and attack the base metal as well as the phosphate coating. For depositing phosphate coating with a coating weight of 10 g/m^2 , it will take about 50 min by chemical deposition, whereas by using the same bath composition with anodic treatment, the processing time could be reduced to 30 min; a degree of acceleration of 40%. However, compared to conventional chemical treatment process, the conversion ratio (ratio of coating weight to iron dissolved) is very low in the anodic treatment process.

3.2. Characteristics of the coatings obtained by cathodic and anodic electrochemical treatments

The coatings obtained by cathodic treatment are gray in colour with bright metallic luster whereas those obtained by anodic treatment are grayish white with no metallic luster. Both of them are uniform and exhibit excellent adhesion to the mild steel substrate when evaluated by a pull-off test with a pressure sensitive adhesive tape. Adhesion of the paint film over the coatings obtained by cathodic and anodic treatments in the dry state is 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 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

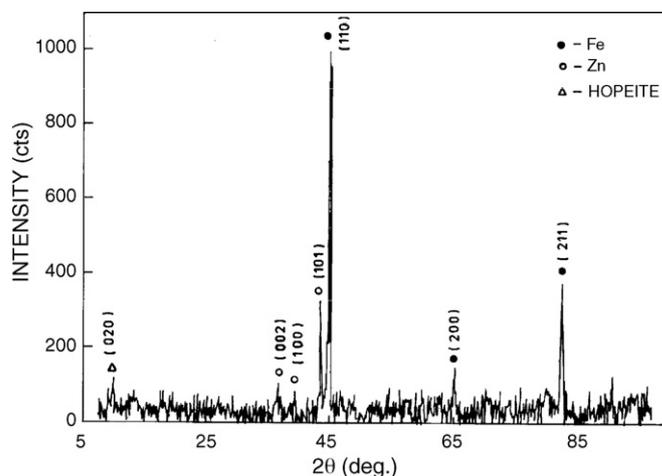


Fig. 2. X-ray diffraction pattern of zinc–zinc phosphate composite coating obtained by cathodic treatment at 6 mA/cm^2 .

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 for coatings obtained using anodic treatment whereas no blue spot is observed over the entire area for coatings obtained using cathodic treatment. This indicates the absence of ferrous ions (from the mild steel substrate) at the surface of the phosphate coating to react with the ferricyanide ions to form the Prussian blue colour as it is covered by a layer of zinc. The electrochemical method, which measures the oxygen reduction current density at -550 mV vs. SCE indicates the amount of porosity involved. The oxygen reduction current density values for coatings obtained by anodic treatment are in the range of $15\text{--}20 \mu\text{A/cm}^2$, which indicates that coatings are relatively more porous than those obtained by chemical treatment.

The coatings obtained by cathodic treatment are rich in hopeite phase $\{\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ with elemental zinc. Unlike the phosphate coatings obtained by chemical treatment, they are mostly free from phosphophyllite phase $\{\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$. X-ray diffraction measurement confirms the presence of zinc and the hopeite phase (Fig. 2). Based on the phase constituents, the coatings obtained by cathodic treatment can be classified as zinc–zinc phosphate

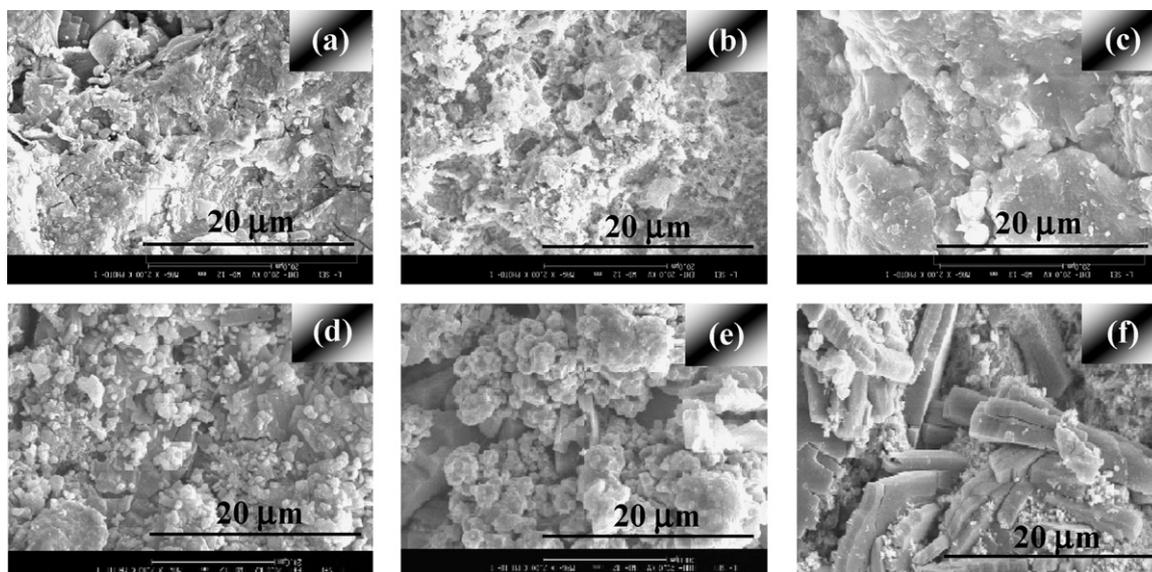


Fig. 3. Surface morphology of phosphate coatings obtained by cathodic (a–c) and anodic (d–f) electrochemical treatments at different current densities (a and c) 4 mA/cm^2 ; (b and d) 5 mA/cm^2 ; and (e and f) 6 mA/cm^2 .

Table 2
Corrosion resistance of phosphate coatings obtained by cathodic and anodic electrochemical treatments in 3.5% NaCl evaluated by immersion test, potentiodynamic polarization and EIS studies.

System studied	Loss in weight ^a (g/m ²) after 24 h of immersion	Corrosion potential E_{corr} (mV vs. SCE)	Corrosion current density i_{corr} ($\mu\text{A}/\text{cm}^2$)
Uncoated mild steel	24.2 ± 0.21	–	–
Phosphate coating on mild steel obtained by chemical method	13.12 ± 0.12	–680	21
Phosphate coating on mild steel obtained by cathodic electrochemical treatment at 4 mA/cm ²	1.7 ± 0.06	–1016	24
Phosphate coating on mild steel obtained by cathodic electrochemical treatment at 5 mA/cm ²	1.4 ± 0.05	–1061	35
Phosphate coating on mild steel obtained by cathodic electrochemical treatment at 6 mA/cm ²	1.3 ± 0.08	–1087	101
Phosphate coating on mild steel obtained by anodic electrochemical treatment at 4 mA/cm ²	11.4 ± 0.13	–652	9
Phosphate coating on mild steel obtained by anodic electrochemical treatment at 5 mA/cm ²	12.1 ± 0.11	–663	16
Phosphate coating on mild steel obtained by anodic electrochemical treatment at 6 mA/cm ²	12.9 ± 0.14	–706	21

^a Average of 5 measurements.

composite coating. Coatings obtained by anodic treatment though consists of both hopeite $\{\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ and phosphophyllite $\{\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ phases similar to those obtained by chemical treatment, they are rich in phosphophyllite phase. The formation of a phosphophyllite-rich coating in anodic treatment process is further supported by the process conditions, which facilitate

higher amounts of ferrous ions at the interface. The better thermal and chemical stabilities of the coatings obtained by anodic treatment also support the view that they are rich in phosphophyllite phase.

The surface morphology of coatings obtained by cathodic treatment exhibits the formation of plate-or-flower-like crystals, which

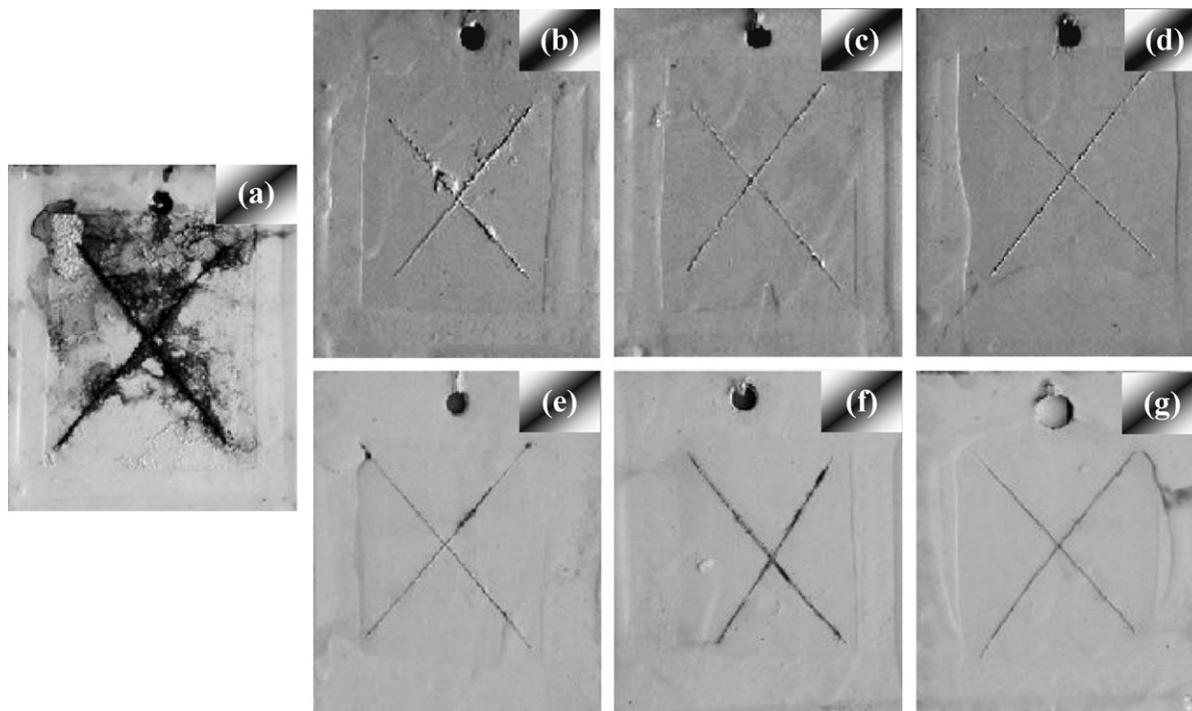


Fig. 4. Performance of phosphated and painted mild steel substrates after 96 h of salt spray test (a) unphosphated mild steel; (b–d) mild steel phosphated using cathodic electrochemical treatment; (e–g) mild steel phosphated using anodic electrochemical treatment at various current densities (b and e) 4 mA/cm²; (c and f) 5 mA/cm²; (d and g) 6 mA/cm².

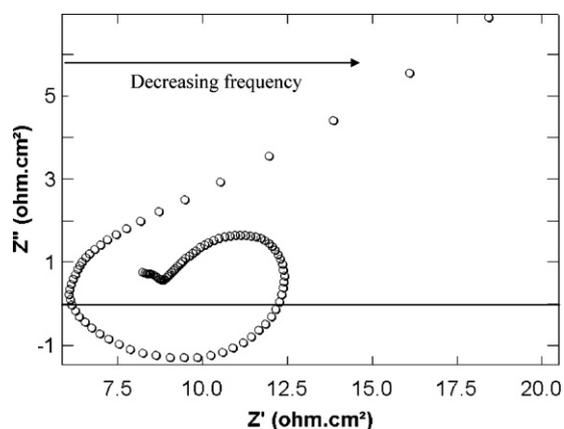


Fig. 5. Nyquist plot of cathodically phosphated (4 mA/cm^2) mild steel substrate in 3.5% sodium chloride solution during the initial periods.

is characteristic of the hopeite phase $\{\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ (Fig. 3). The crystallite size of the coating increases with increase in current density. For coatings obtained at 6 mA/cm^2 , where the zinc content of the coating is high, the morphology of the coating resembles that of electrodeposited zinc [13]. The surface morphology of coatings obtained by anodic treatment exhibits the formation of needle-like crystals, which is characteristic of the phosphophyllite phase $\{\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ (Fig. 3). The refinement of crystals observed in the morphology of the coating is due to the continuous dissolution and re-precipitation of the phosphate coating by the regenerated phosphoric acid under the influence of anodic current.

3.3. Corrosion resistance of the coatings obtained by cathodic and anodic electrochemical treatments

3.3.1. Immersion test in 3.5% NaCl

The zinc–zinc phosphate composite coatings obtained by cathodic treatment exhibit excellent stability in 3.5% NaCl solution; they last for a week with no red rust formation. The composite layer of zinc and zinc phosphate provides both sacrificial and barrier layer protection and significantly increases the corrosion resistance. The corrosion behaviour of these coatings resembles that of electrodeposited and hot dipped galvanized zinc coatings, in terms of white rust formation—characteristic of zinc based corrosion product. The corrosion behaviour of phosphating coatings obtained by anodic treatment resembles those obtained by chemical treatment. The loss in weight due to corrosion after 24 h of immersion in 3.5% NaCl solution is 24.12 g/m^2

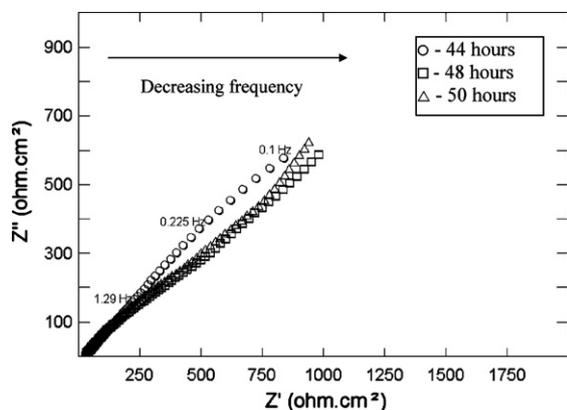


Fig. 6. Nyquist plot of cathodically phosphated (5 mA/cm^2) mild steel substrate in 3.5% sodium chloride solution as a function of immersion time (44–50 h).

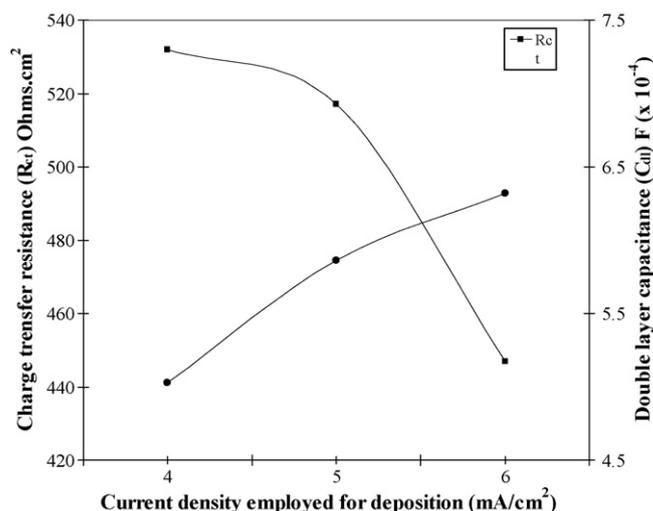


Fig. 7. Variation in the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of phosphate coatings prepared by anodic treatment as a function of current density employed for deposition.

for uncoated mild steel, 13.12 g/m^2 for chemically phosphated mild steel, $1.3\text{--}1.7 \text{ g/m}^2$ for mild steels phosphated using cathodic treatment and $11.4\text{--}12.9 \text{ g/m}^2$ for mild steels phosphated using anodic treatment (Table 2).

3.3.2. Salt spray test

The ability to prevent underfilm corrosion is best measured by assessing the spreading of corrosion from the 'X'-scribe (scribed to the base metal) made on the phosphated and painted mild steel substrate subjected to salt spray test. The spreading of corrosion from the 'X'-scribe after 96 h of salt spray test is relatively less for mild steel substrates phosphated by cathodic and anodic treatments compared to that of unphosphated mild steel (Fig. 4) and demonstrate the effectiveness of phosphate coatings obtained by these treatments in resisting alkaline attack. However, the type of corrosion product formed in the scribed region is quite different for coatings obtained by cathodic treatment; a white corrosion product is seen in the scribed region of these coatings as opposed to the red rust in scribed region of the coatings obtained by anodic treatment. The formation of white corrosion product is due to the preferential dissolution of metallic zinc present in the coating.

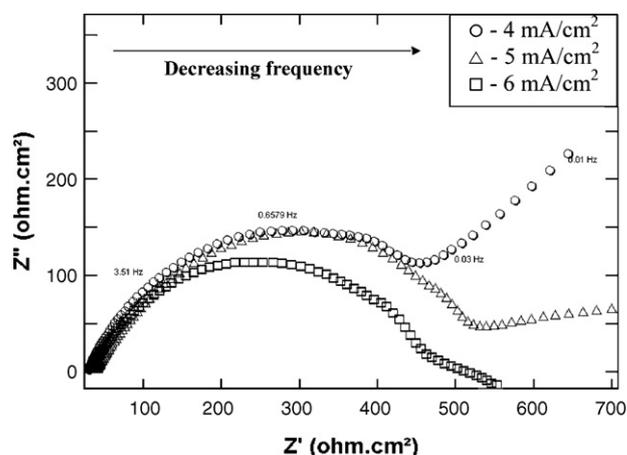


Fig. 8. Nyquist plot of phosphated mild steel substrate obtained by anodic electrochemical treatment in 3.5% sodium chloride solution.

3.3.3. Potentiodynamic polarization and EIS studies

Potentiodynamic polarization studies reveal that the corrosion resistance offered by the zinc–zinc phosphate composite coatings obtained by cathodic treatment is very low. This is due to the dissolution of zinc from these coatings. EIS studies confirm the zinc dissolution as the predominant reaction during the initial stages of immersion (inductive loop in the Nyquist plot) (Fig. 5). However, with increase in immersion time, the non-metallic nature of the coating is progressively increased due to the formation of zinc corrosion products, which imparts resistance to the charge transfer process and enables an increase in corrosion resistance (Fig. 6). The zinc corrosion products formed may consist of zinc oxide and zinc hydroxychloride.

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of phosphate coatings obtained by anodic treatment at 6 mA/cm^2 are quite similar to those obtained by chemical treatment (Table 2). The cathodic shift in E_{corr} and the increase in i_{corr} suggest that with increase in current density employed for the deposition of phosphate coating from 4 to 6 mA/cm^2 , the resultant coating becomes more porous due to the dissolution of the coating under the influence of anodic current. The decrease in R_{ct} and increase in C_{dl} further confirms the increase in porosity or discontinuity of the coatings with increase in current density (Fig. 7). The Nyquist plot of phosphate coatings obtained by anodic treatment exhibit a semi-circle in the high frequency region followed by a diffusion tail in the low frequency region (Fig. 8). The appearance of a diffusion tail in the low frequency region is characteristic of Warburg impedance behaviour and suggests that the corrosion of phosphate coating obtained by anodic treatment in 3.5% sodium chloride solution is a diffusion controlled process.

3.4. Advantages and limitations of cathodic and anodic electrochemical treatments

The deposition of zinc phosphate coatings on mild steel by cathodic and anodic electrochemical treatments has several advantages and limitations. A comparison of the salient features of the cathodic and anodic treatment processes is given in Table 3. Unlike the chemical treatment, the coating weight increases with increase in treatment time during cathodic treatment, since the electrochemical reduction of zinc ions and evolution of hydrogen enable a rise in pH at the metal solution interface and facilitate the deposi-

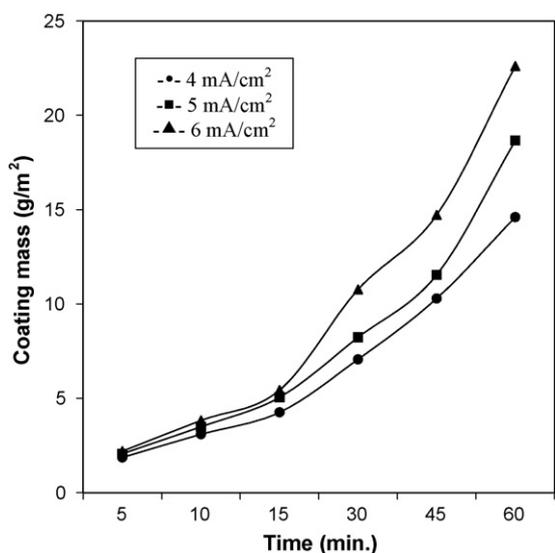


Fig. 9. Effect of applied current density (4 to 6 mA/cm^2) on phosphate coating weight obtained by cathodic treatment.

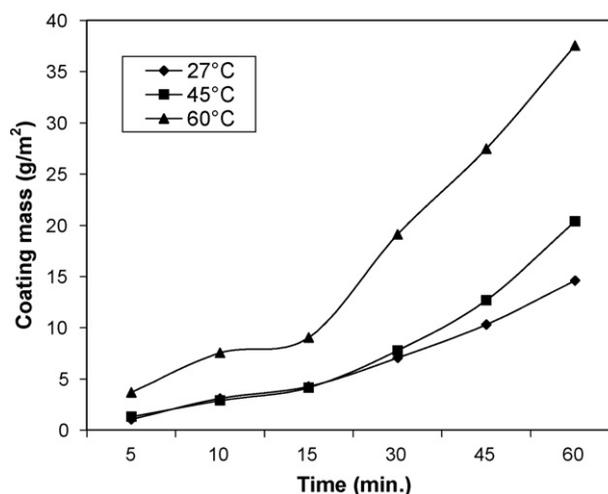


Fig. 10. Effect of bath temperature on phosphate coating weight obtained by cathodic treatment at 4 mA/cm^2 .

tion of zinc phosphate on the substrate (Fig. 9). Similarly, cathodic treatment does not alter the chemical equilibrium of the phosphating bath with increase in bath temperature which would otherwise cause precipitation of zinc phosphate in the bath solution, a common phenomenon in chemical treatment. In fact, increase in bath temperature enables an increase in coating weight and it is possible to obtain a coating weight of 45 g/m^2 at 60°C in 60 min (Fig. 10). Formation of a zinc–zinc phosphate composite coating is a special feature of cathodic treatment. It is possible to change the nature of cations and/or the anodes so that a variety of composite coatings can be prepared using this methodology. Since the substrate serves as the cathode it is possible to deposit the zinc–zinc phosphate coatings over a variety of metallic substrates. This attribute is particularly beneficial for depositing coatings on materials which are difficult to be phosphated by chemical treatment. Being a cathodic process, the possibility of hydrogenation of steel during cathodic treatment cannot be ruled out. It is particularly crucial if the substrate used is high-carbon or high-alloy, hardened, high strength steels. In fact, this is the major limitation of this methodology. It is recommended to perform a hydrogen embrittlement relief heat-treatment after deposition of the zinc phosphate coating, which would otherwise affect the mechanical properties of

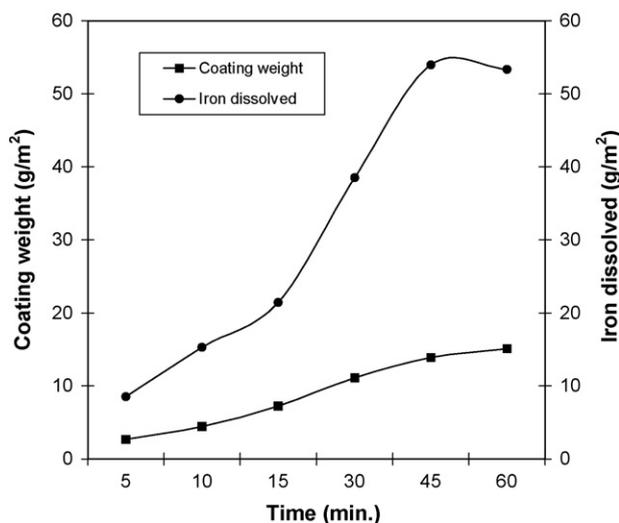


Fig. 11. Variation of phosphate coating weight and iron dissolved during phosphating as a function of time obtained by anodic treatment at 6 mA/cm^2 .

Table 3
Comparison of cathodic and anodic electrochemical treatment processes.

Parameter	Cathodic treatment	Anodic treatment
Bath constituents	Essential constituents—ZnO, H ₃ PO ₄ and NaOH	Essential constituents—ZnO, H ₃ PO ₄ , NaOH and NaNO ₂
Special additive	No special additives	No special additives
Requirement of accelerator	No accelerator is necessary	Accelerator addition is essential to prevent polarization of the cathode
Energy requirement	Capable of producing good quality coatings even at low temperature	Capable of producing good quality coatings even at low temperature
Eco-friendliness	More eco-friendly	Less eco-friendly
Operational problems	Disintegration of graphite cathode; use of anode bag is essential to get good quality deposits being a cathodic process, it might induce hydrogen embrittlement—desirable to adopt a post-baking operation to relieve the hydrogen	Deposition of metallic zinc at the graphite cathode
Iron dissolution	No iron dissolution	Heavy iron dissolution
Coating weight	High; permits to build the desired coating weight by increasing the deposition time	Medium; similar to conventional phosphating process
Sludge formation	No sludge formation	Heavy sludge formation
Reactions at Mild steel	Deposition of zinc and zinc phosphate; hydrogen evolution;	Iron dissolution; phosphate deposition
Means of attainment of PIP	Proton consumption for H ₂ evolution reaction	Drifting of protons away from the electrode vicinity
Coating composition	Zinc phosphate (hopeite phase); Metallic zinc	Zinc–iron phosphate (phosphophyllite) zinc phosphate (hopeite); Iron phosphate
Colour and appearance	Gray with bright crystalline luster	Grayish white with no metallic luster
Uniformity of the coating	Uniform	Uniform
Surface morphology	Plate/flower-like crystals	Needle-like crystals
Adhesion	Good	Good
Porosity	Very low porosity	More porous than conventional phosphating process
Thermal stability	Comparable with anodic and conventional phosphating processes	Comparable with cathodic and conventional phosphating processes
Chemical stability	Relatively lower than conventional and anodic phosphating processes	Relatively higher than cathodic phosphating process Resembles that of conventional phosphating process
Immersion test	No red rust formation after 12 h of immersion; solution remains colourless Weight loss after 24 h is considerably lower than conventional and anodic phosphating process	No red rust formation after 12 h of immersion Solution remains colourless Weight loss after 24 h is lower than conventional phosphating; relatively higher than cathodic phosphating Formation of red rust leading to further corrosion
Salt spray test	Formation of zinc based corrosion products (white rust) which resist further corrosion Prevents spreading of corrosion from the scribe White rust formation at the scribe	Prevents spreading of corrosion from the scribe Red rust formation at the scribe
Potentiodynamic Polarization studies	Greater shift in E_{corr} values towards cathodic values compared to uncoated mild steel (–1000 to –1100 mV Vs. SCE) With increase in immersion time the E_{corr} values shift towards more anodic values	A slight shift in E_{corr} values towards anodic values compared to uncoated mild steel –680 to –700 mV Vs. SCE) Behaves like conventionally phosphated mild steel
Electrochemical impedance studies	Nyquist plot exhibits a small semicircle and an inductive loop in the initial period Improvement of corrosion resistance with time	Nyquist plot exhibits a semicircle and a diffusion tail; semi-infinite and finite length diffusion behaviour Behaves like conventionally phosphated mild steel
Galvanic corrosion	Protects the uncoated mild steel substrate during the initial periods of immersion With increase in time, the corrosion of uncoated steel is accelerated	Accelerates the corrosion of uncoated mild steel during the initial periods of immersion With increase in time, the corrosion of uncoated steel will proceed further
Cathodic delamination	Mean delamination distance is less than 1 mm	Mean delamination distance is less than 1 mm
Corrosion of phosphated and painted steel	Prevents the corrosion of the base metal for a long time. R_{ct} values are in the range of $10^5 \Omega \text{ cm}^2$	Prevents the corrosion of the base metal for a reasonable time. R_{ct} values are in the range of 10^4 – $10^5 \Omega \text{ cm}^2$

the steel. Use of pulsed current instead of direct current during cathodic treatment would reduce the extent of hydrogenation of steel.

Anodic treatment significantly increases the extent of metal dissolution during phosphating and increase the porosity of the resultant coatings. Increased metal dissolution during anodic treatment decreases the conversion ratio (ratio of coating mass/mass of metal dissolved during phosphating) (Fig. 11). Higher porosity of the coatings obtained by anodic treatment reduces their corrosion protective ability (Table 2). Disconnecting the current source after a few minutes will be a viable option to get phosphate coatings with better characteristics. The higher porosity of

the coatings obtained by anodic treatment though is not beneficial in terms of corrosion resistance, will suit for most applications that require higher oil- or lube-retaining capacity, particularly in tube and wire drawing operations. Increased metal dissolution though considered as a limitation of deposition of zinc phosphate coating by anodic treatment, will be beneficial in depositing manganese phosphate coatings on steel since one of the constituent of manganese phosphate coating on steel is $(\text{Mn-Fe})_5\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, which requires higher concentrations of ferrous ions at the metal solution interface. Experimental work has proved that this attribute is true, the details of which will appear in a future publication.

4. Conclusions

A comparison of the deposition mechanism, characteristic properties and corrosion resistance of phosphate coatings obtained by cathodic and anodic treatments during phosphating is addressed. The advantages and disadvantages of the cathodic and anodic treatments in terms of energy efficiency, eco-friendliness, processing problems, sludge formation, possible application of the coatings obtained by these treatments for different end uses, limitation of the process, etc. are also addressed. The comparative study provides an insight on how best the cathodic and anodic treatments can be manipulated to produce tailor made coatings with the desired characteristics. The possibility of formation of various types of metal/alloy-phosphate based composite coatings using cathodic treatment and manganese phosphate coating at ambient temperature will open up new avenues in surface pretreatment of steel.

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References

- [1] D.B. Freeman, *Phosphating and Metal Pretreatment—A Guide to Modern Processes and Practice*, Industrial Press Inc., New York, 1986.
- [2] W. Rausch, *The Phosphating of Metals*, Finishing Publications Ltd., London, 1990.
- [3] Guy Lorin, *Phosphating of Metals*, Finishing Publications Ltd., London, 1974.
- [4] T.S.N. Sankara Narayanan, *Rev. Adv. Mater. Sci.* 9 (2005) 130.
- [5] T.S.N. Sankara Narayanan, M. Subbaiyan, *Met. Finish* 93 (1) (1995) 30.
- [6] K. Ravichandran, H. Sivanandh, S. Ganesh, T. Hariharasudan, T.S.N. Sankara Narayanan, *Met. Finish* 98 (9) (2000) 48.
- [7] K. Ravichandran, T.S.N. Sankara Narayanan, *Trans. Inst. Met. Finish.* 79 (4) (2001) 143.
- [8] S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, *Surf. Coat. Technol.* 200 (2006) 4117.
- [9] S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, *Electrochim. Acta* 51 (2) (2005) 247.
- [10] S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, *Surf. Coat. Technol.* 200 (2006) 6014.
- [11] T.S.N. Sankara Narayanan, S. Jegannathan, K. Ravichandran, *Prog. Org. Coat.* 55 (2006) 355.
- [12] S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, *Progress Organic Coatings* 57 (2006) 392.
- [13] C. Cachet, F. Ganne, S. Joiret, G. Maurin, J. Petitjean, V. Vivier, R. Wiat, *Electrochim. Acta* 47 (2002) 3409.