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Study of Nano Metal Oxide Incorporated Zinc Phosphate Coatings as Corrosion Inhibitors on Mild Steel

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Abstract

The existing corrosion prevention processes and methods are incapable of predicting all environmental conditions. On the other hand, the local metal coating and paint industries continue to suffer from a lack of appropriate advanced phosphating technology as a surface pre-coating technique. The incorporation of ceramic nanoparticles into the phosphate coating has improved the properties such as high corrosion resistance and secondary coating adhesion. As a result, the goal of this research was to create and improve a corrosion prevention method suitable for the metal coating industries by incorporating nano TiO_2 into a phosphate precoating. To facilitate the coating via chemical conversion, the cleaned mild steel specimens were dipped in the prepared phosphating bath containing the nano TiO_2. Under the given conditions, the optimum coating time was determined to be 90 minutes. Significant changes in coating weight, adhesion quality, surface porosity, and corrosion resistance were observed with the addition of nano TiO_2 (average particle size ~ 25 nm). X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and a gemmological microscope were used to investigate the crystal phases and surface morphology of zinc phosphate coatings. XRD data clearly showed that nano TiO_2 has successfully incorporated into the phosphate layer. The addition of nano TiO_2 to the zinc phosphate coating improved its properties, such as coating thickness and surface area, promising an improvement in corrosion resistance. With minor modifications aiming to lower the coating time, the findings of this study could be easily implemented in the metal coating industries and extended to other metals such as steel, aluminium, and alloys.

Keywords: Chemical Conversion, nano -TiO_2, Mild steel, Phosphating

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1. Introduction

Corrosion is a natural electrochemical reaction that transforms metal into a stable oxide, damaging its properties [1]. Metals including steel, aluminium, and alloys are commonly affected by corrosion [2]. Corrosion damages the physical and mechanical properties of metals. These include strength, toughness, ductility, appearance etc. Corrosion weakens structures, causes accidents, and leads to failures like pipeline cracks and bridge collapses. Therefore, constant monitoring and prevention of corrosion are crucial. For corrosion prevention, surface treatment processes can be applied to inhibit corrosion [2,19]. This involves treating metal parts before coating them to create a barrier against moisture and air [3]. Surface pretreatment includes mechanical, chemical, or electrochemical treatment before coating processes like electroplating, powder coating or painting [4].

Chemical conversion coatings are preferred surface treatments for metals due to their adherent nature, high coating formation rate, and cost-effectiveness. They can be formed using simple tools and without external electric potential [4]. Types of chemical conversion coatings include Chromate, Phosphate, and Oxalate coatings [5]. Phosphating is commonly used for metal surface treatment. Zinc phosphating, in particular, is widely employed in industries such as automobiles and household appliances. It is favoured for its low cost, easy formation, good corrosion protection, and adhesion [6].

Recent research indicates that nano coatings offer significant potential for enhancing surface corrosion performance compared to micromaterial coatings [7] Nanoparticle-enhanced coatings have demonstrated superior performance, including early-stage corrosion protection, increased resistance, improved control, and controlled inhibitor release [8]. Nano coatings, when applied, result in harder, thicker, tougher surfaces with better adhesive properties, fewer defects, and improved surface corrosion performance compared to micromaterial coatings [7,9].

The next advancement in phosphate coating involves incorporating ceramic nanoparticles to enhance the layer's properties, making it more effective for corrosion prevention and as a pre-coating. This highlights the significant potential for further development and optimization of nanoparticle-incorporated zinc phosphating methods. However, for a country like Sri Lanka, relying on imported phosphating solutions—composed of over 90% water—poses an economic challenge for the metal industry. Therefore, this research aims to develop and improve a nanoparticle-incorporated formulation for phosphate conversion coating, addressing future needs and local industrial requirements.

2. Experimental

2.1 Materials

Chemicals including Zinc oxide (ZnO) powder, Nano -titanium dioxide (TiO_2), 25% Phosphoric acid (H_3PO_4), Sodium nitrate ($NaNO_3$), Acetone (C_3H_6O), Hydrochloric acid (HCl), Sodium hydroxide ($NaOH$), Sodium chloride ($NaCl$), Potassium ferricyanide ($K_3[Fe(CN)_6]$), Agar powder, Bromophenol blue, and Phenolphthalein were used in this work and all the chemicals were in analytical reagent grade.

2.2 Methodology

The main steps of the phosphating include, metal surface cleaning, phosphating using chemical conversion bath, and characterization of the coating. In this work, we focused primarily on the phosphating step, in which a chemical conversion technique was used to form a phosphate layer on the metal substrates. The phosphate coating process and bath parameters were systematically adjusted to optimize the properties of the coated layers with and without TiO_2.

2.2.1. Surface cleaning of mild steel

Mild steel specimen was cut into the dimension of 6.0 x 1.0 x 0.4 cm. Then, it was abraded with a series of emery papers up to 400 grits. Then, mild steel sample was degreased and cleaned using a series of chemicals including 10 wt.% $NaOH$, 10% HCl, acetone and deionized water respectively, to remove oil, dust, and the remaining rust.

2.2.2. Phosphating bath

The bath composition was originally derived from published research articles [3,8-10,16,20,21,24,25]. Typically, the bath consists of phosphoric acid and zinc oxide as the primary components in an aqueous medium, with sodium nitrate acting as an accelerator. In this study, nano-titanium dioxide was incorporated into the phosphating bath, and a systematic investigation was conducted to determine the optimal bath conditions for achieving an enhanced nano-TiO_2 incorporated zinc phosphate conversion layer.

2.2.3. Phosphating

The dip-coating method was used to coat a layer of zinc phosphate on the steel specimens via chemical conversion. Initially, the dipping time was optimized for the coating in a given bath, without introducing TiO_2 into the bath. The used phosphating bath consists of 0.550 g of zinc oxide mixed with 3.74 ml of phosphoric acid followed by diluting with 100 ml of deionized water. After optimizing the dipping time for a given composition of the bath, different amounts of nano TiO_2 were systematically introduced into the phosphating bath to prepare nano TiO_2 incorporated Zinc phosphate layers. The pH of the phosphating bath was measured and obtained to be 2.98.

2.2.4. Characterization of phosphate coating

The effects of introducing nano TiO_2 into the optimized phosphating bath on composition, coating weight, surface morphology and corrosion resistance were assessed through various methods. A destructive method was employed to evaluate coating weight with respect to immersion time. Two sets of phosphate-coated samples were used to compare the corrosion resistance of specimens with and without TiO_2 incorporation. The specimens were immersed in a Ferroxyl reagent test to evaluate surface porosity and monitor corrosion progression on both coated and uncoated areas. Additionally, X-ray diffraction (XRD) analysis was performed to determine the crystal phases present in the phosphate coating. The XRD analysis covered a diffraction angle range of 2θ from 0° to 100° using Cu Kα radiation ($\lambda = 1.5406$ Å) and was conducted using the Ultima IV X-Ray Diffractometer. The surface morphology of the zinc phosphate coatings was examined using scanning electron microscopy (SEM) and a gemmological microscope.

3. Results and Discussion

3.1. Optimum bath composition

Chemical composition and relevant control parameter that were used to obtain an optimum nano-TiO_2 incorporated zinc phosphate conversion layer is tabulated in the Table-1. Here, the calculations are shown for a total bath volume of 100 ml.

Table 1
Chemical composition and control parameters

Chemical Composition	
25.0 % H_3PO_4	3.74 ml
ZnO	0.550g
$NaNO_3$	0.147g
$Nano\ TiO_2$ (25 nm)	0.200g
Deionized water	100.0ml
Control Parameters	
pH	2.98 ± 0.1
Temperature	27.0℃ ± 3.0℃
Immersion time	1. 30 $hours$
Free acid value (FA)	1.4 cm^3
Total acid value(TA)	16. 2 cm^3
FA: TA	1: 11.6

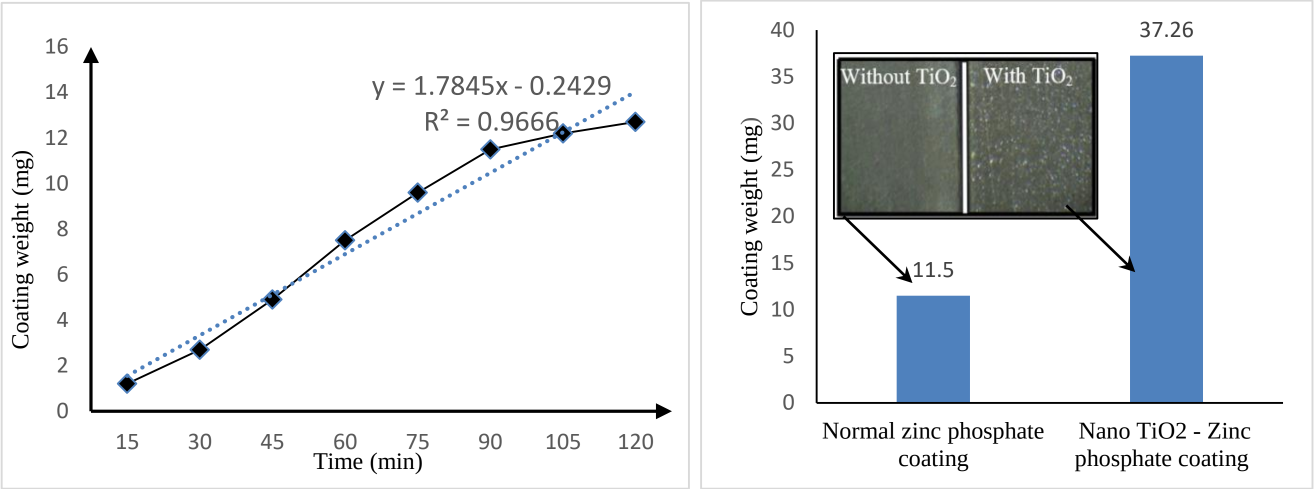

Fig. 1. (a) Depicts the effect of growth time on coating weigh, coating area is 11.6 cm^2, (dashed line represent a liner fit to the graph of weight vs time), (b) Comparison of the phosphate coating weight without (coating area 11.6 cm^2) and with TiO_2 (coating area 9.8 cm^2), (inset image of the Fig. 1 (b) shows the microscopic images of the prepared phosphate specimens)

3.2. Coating weight vs time

Fig. 1 exhibits the phosphate coating over time for time-series samples without TiO_2 incorporation. Under these conditions, the optimal coating time was observed as 90 minutes. After about 90 minutes under these conditions, the growth or the coating thickness reaches its maximum. This may be attributed to the obstruction of the active metal surface by the deposited layer. Alternatively, it could result from the equilibrium between growth and dissolution reactions, influenced by the substantial presence of free acid in the solution. The phosphate coating amount was assessed by comparing the apparent weight before and after coating of a given area. The calculated average coating weight of the samples (without TiO_2) is about 11 mg (coating area 11.6 cm^2). The samples prepared with the addition of nano-TiO_2 into the bath and after 90 minutes of coating, showed a coating weight of about 37 mg (coating area 9.8 cm^2). It represents approximately a fourfold increase in coating weight and thickness compared to standard zinc phosphate coatings per unit area. The presence of white material in the microscopic image (inset Fig. 1 (b)) indicates the incorporation of TiO_2 particles into the phosphating layer. For optimal adhesion and corrosion resistance, zinc phosphate coatings serve as an effective pre-coating before secondary applications like powder coating, with a desired thickness of 5 to 15 µm. This study highlights that using a bath containing nano-TiO_2 can achieve the minimum target thickness in approximately 12 minutes of growth.

3.3. Surface morphology of normal and nano TiO_2- zinc phosphate coating - SEM

Fig. 2(a) and (b) exhibit SEM images of phosphate coating on mild steel without TiO_2 at magnifications of 500x and 4500x, respectively. Fig. 2(c) and (d) show the SEM images of specimens with TiO_2, at magnifications of 500x and 1000x, respectively. These SEM images provide valuable insights into the nucleation and growth process of phosphate coatings on the mild steel substrate. The visible crystals in Fig. 2(a) and 2(c) are identified as phosphate compounds within the coatings. Without nano-TiO_2 in the bath large crystals exceeding 10 µm in size, with an average dimension of approximately 20 µm × 30 µm, and distinct 3D particle edges are clearly observed on the surface. This suggests that long-range, three-dimensional growth is more favourable when foreign materials or impurities such as nano-TiO_2 are absent in the bath. However, the crystals formed in this condition are randomly oriented on the metal surface. Conversely, with the introduction of nano-TiO_2 into the phosphating bath, only a few rod-like crystals exceeding 10 µm in length are clearly visible on the surface, while most other crystal formations appear smaller than 10 µm in size. The distinct modification in the formed crystals in the presence of TiO_2 suggests significant changes in the nucleation and growth mechanisms. In the presence of nano-TiO_2, the nucleation density has increased significantly, while the crystal size is restricted to a few micrometres, effectively limiting three-dimensional growth. The resulting coating exhibits, higher thickness with a more homogeneous surface and well-defined, small rod-like crystals.

Similar studies reveal that incorporating various additives, such as cations (Ni^{2+}, Mn^{2+}) [11], TiO_2 [10,30], CeO [12], and nano-SiO_2 [13,17,27], significantly modify the properties of phosphate conversion coating layers. These modifications result in improved layer uniformity, increased thickness and growth rate, fewer defects, and refined crystal structures with minimal porosity. The addition of nanoparticles or suitable additives is believed to influence the growth mechanism by increasing nucleation density and reducing large 3D crystal growth. The physical adsorption of nanoparticles (e.g., TiO_2, ZnO) onto the metallic surface forms cathodic regions, enhancing hydrogen evolution and promoting the precipitation of phosphate crystals. A higher concentration of adsorbed nanoparticles increases the number of phosphate crystal nuclei, enhancing nucleation

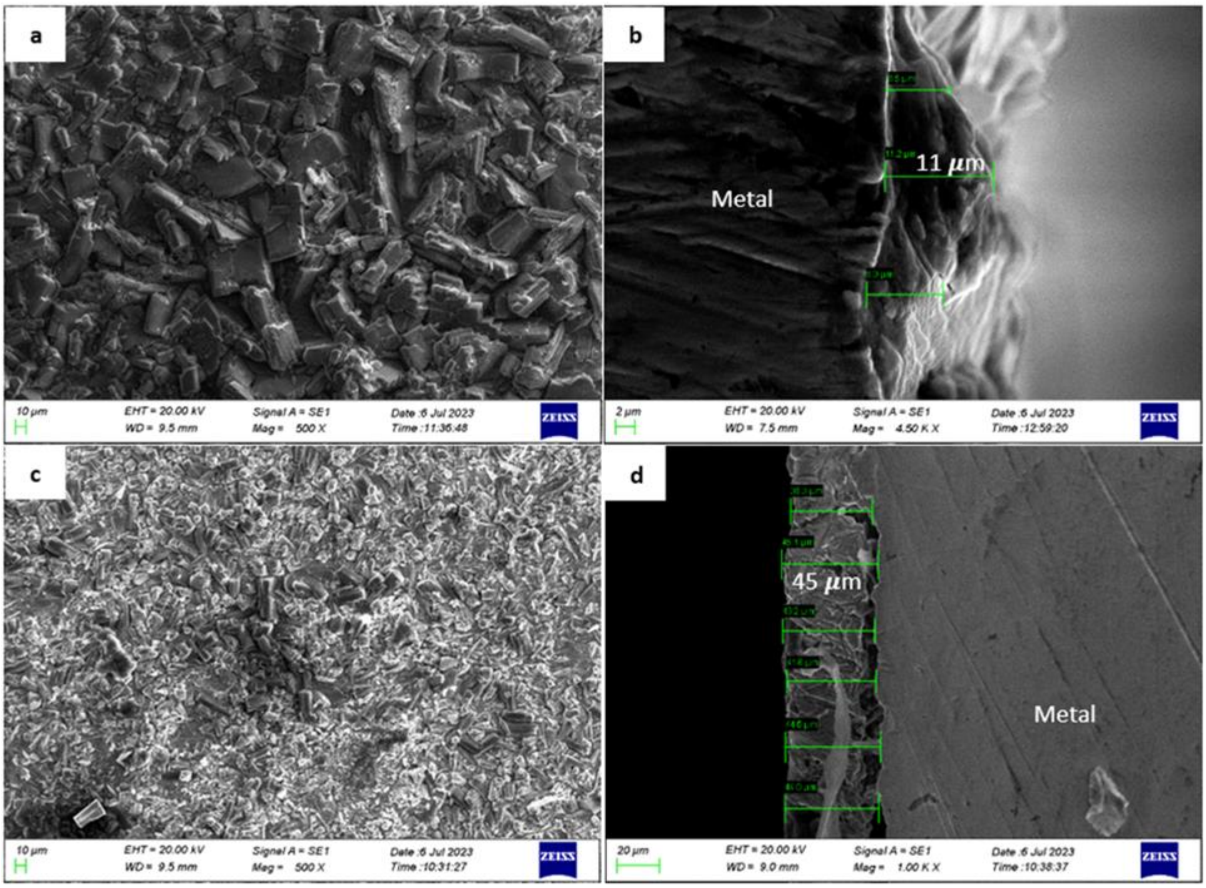

Fig. 2. (a) and (b) exhibits the SEM images of phosphate coating on mild steel without TiO_2, (magnification 500x and 4500x, respectively). (c) and (d) exhibits the SEM images of phosphate coating on mild steel with TiO_2, (magnification 500x and 1000x, respectively). Thicknesses of the coating layers are shown with horizontal bars drawn in cross sectional SEM images of (b) and (d).

density and resulting in smaller crystal sizes in the phosphate coating [13,22,23]. Consequently, large 3D crystal growth is suppressed, while the formation of smaller crystallites is enhanced, as evidenced by SEM images in this and other studies.

The SEM image of the sample cross-section in Fig. 2(d) confirms a dense and uniform coating with a thickness of approximately 45 µm in the presence of TiO_2, whereas samples without TiO_2 exhibit an average thickness of about 11 µm. Adding nano- TiO_2 to the phosphating bath enhances the degree of crystalline coverage by reducing the grain size and minimizing the voids of the phosphate coating. Fine surface structures may increase the effective surface area of the metal substrate, which is crucial for improved adhesion of subsequent paint or coating layers and various applications. Notably, the addition of nano-TiO_2 particles has increased the coating thickness by approximately four times compared to samples without TiO_2, aligning with the coating weight data. This is advantageous in commercial applications as it allows to produce high-quality thick layers in a shorter time, resulting in cost reduction and higher profitability.

Table 2
Comparison of XRD peak positions of various phases in phosphate coatings with reference data

Crystalline Phases	**H (Hopeite)**	**P (Phosphophyllite)**	**Zn (Zinc)**	**ZPH (Zinc phosphate Hydrate)**	**T (TiO_2)**
Without TiO_2	24.75, 30.50, 43.75, 59.85, 81.50,	33.05, 49.10	38.60	8.75, 15.80, 18.50	-
WithTiO_2	31.05, 46.60, 60.30, 81.95	34.05	39.10	9.40, 19.10, 64.75, 81.95	9.40, 19.10, 26.00, 34.05, 44.40, 64.75, 81.95
Reference data [8,11]	22.60, 24.80, 30.50, 44.20, 46.20, 59.80, 65.20	20.2, 34.4, 45.5, 60.9		9.40, 16.40, 18.60, 19.60, 46.20	25.90, 47.10, 37.10, 62.20, 69.70

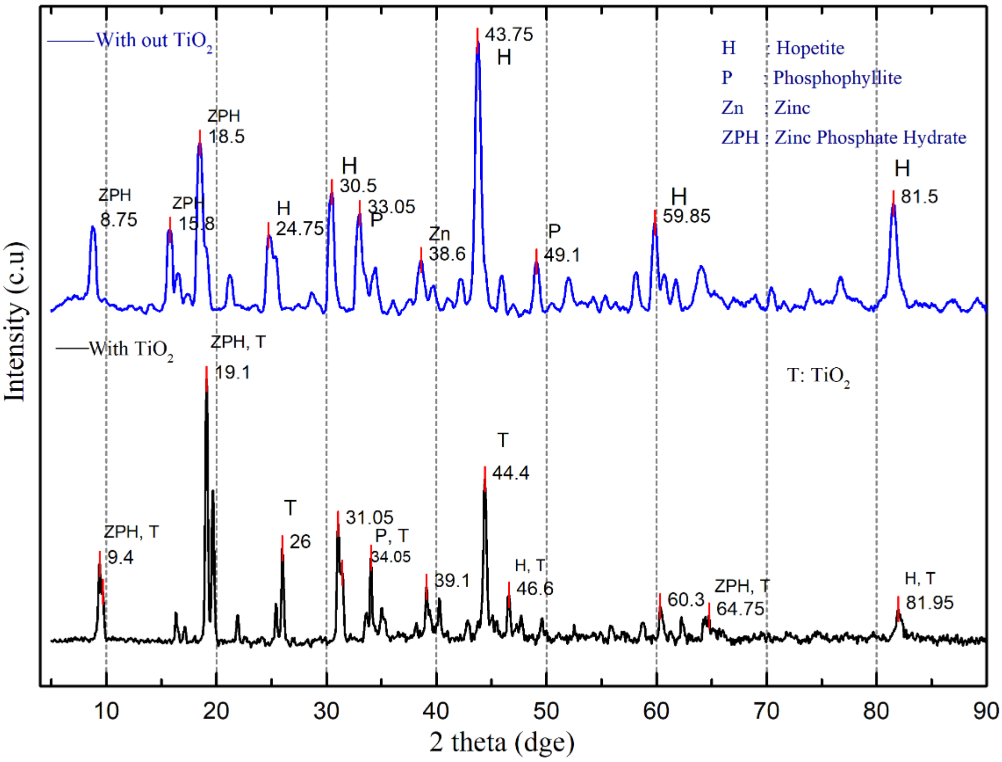

Fig. 3. XRD patterns of the phosphate coating on mild steel substrate, (a) without TiO_2, and (b) with TiO_2.

3.4. Crystal phases in the phosphate coatings – XRD

Fig. 3 (a) and (b) shows the XRD profile of the top surface of the zinc phosphate coating with and without incorporation of nano- TiO_2. It is shown that the phosphate coating mainly consists of Hopeite $[Zn_3(PO_4)_2.4H_2O]$, phosphophyllite $[Zn_2\ Fe\ (PO_4)_2.4H_2O]$, and zinc phosphate hydrate $[Zn_3(PO_4)_2.H_2O]$ [3,8,14]. Fig. 3(b) clearly depicts additional phases (represented by 'T') that are likely associated with the incorporation of TiO_2 into the layer. Peaks related to TiO_2 representing mixed phases of both rutile and anatase. Table 2 shows the XRD crystal phases position compared with some literature data available for zinc phosphate coatings with and without incorporation of nano- TiO_2 [8,11]. The observed phases of the phosphate coating align well with the available literature data. Moreover, the presence of nano- TiO_2 particles has led to an increase in the intensity of these phases.

3.5. Surface porosity of the coatings - Ferroxyl reagent test

Fig. 4 displays the results of the Ferroxyl test, which is employed to identify surface porosity in coatings. This method was based on formation of blue spots on an agar medium dipped in potassium ferricyanide, hydrochloric acid, distilled water and phenolphthalein mixture when applied over the phosphate coated specimen for one day. Fe^{2+} reacts with ferricyanide ions $(Fe(CN)_6{}^{3-})$ to form Prussian Blue $(Fe_4[Fe(CN)_6]_3)$ and blue spots indicate the presence of Fe^{2+}. The porosity is quantified by the number of blue spots per square centimetres [15]. In this study, the analysed top-side area of the phosphate-coated samples with and without TiO_2 was measured as 3.4 cm² and 4.0 cm², respectively. The uncoated areas of the two specimens are 2.2 cm² and 1.8 cm² for the samples with and without TiO_2, respectively. No color change was observed around the coated area even after one day, indicating the absence of

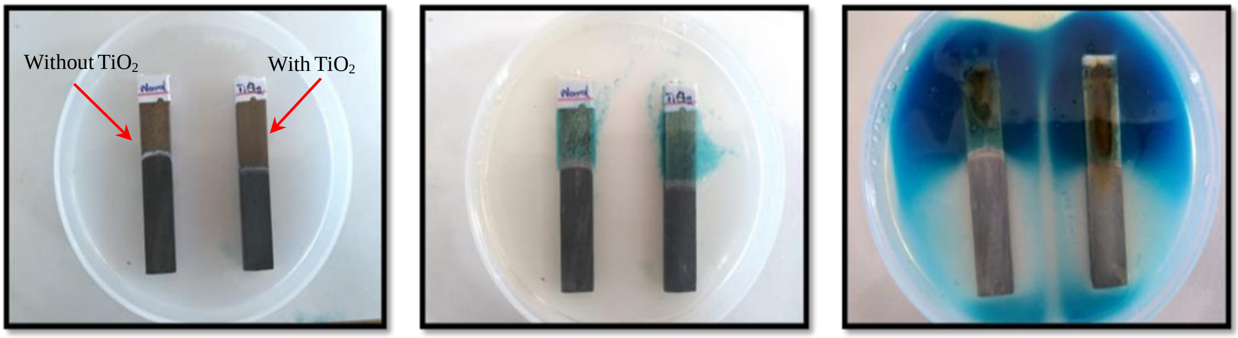

Fig. 4. Progression of the corrosion with the Ferroxyl regent test. (a) Before the test, (b) after five minutes, and (c) after 24 hours of starting the test.

significant porosity in both types of zinc phosphate layers, with and without TiO_2. However, color changes were noticed around the uncoated area due to the presence of Fe^{+2} ions generated through oxidation. The findings of this study suggest that, under preliminary testing conditions, both coatings with and without nano-TiO_2 exhibit minimal porosity and are adequately suitable as pre-coating layers. However, coating weight analysis and SEM analysis indicates that the nano-TiO_2 incorporated layers have greater thickness, improved crystallite structure, and possibly a higher effective surface area, along with an enhanced growth rate. This increased growth rate is particularly beneficial for industrial applications, offering improved efficiency and cost-effectiveness in large-scale coating processes.

4. Conclusion

Zinc phosphate coating is a widely utilized surface pretreatment method in metals prior to top coating. The next generation of phosphating involves the integration of ceramic nanoparticles into the phosphate layers. This study demonstrates that the incorporation of nano- TiO_2 significantly enhances the effective surface area, layer thickness, and homogeneity, crucial factors for secondary coatings. When nano- TiO_2 is added to the phosphating bath, it reduces the size of the nano zinc phosphate crystals, activating the surface of mild steel. Corrosion studies indicate that the prepared layers exhibit minimal porosity, ensuring high-quality coatings. Additionally, the presence of nano- TiO_2 promotes faster growth, making it favourable for industrial applications. In the future, we aim to further reduce the growth time by increasing bath concentrations while maintaining the free acid value at an optimal level to minimize reverse reactions. Additionally, we plan to conduct standard characterizations, such as salt spray testing and crosscut adhesion tests, in collaboration with metal coating industries to ensure the commercial viability of these findings.

Conflict of Interest

No conflicts of interest to declare.

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References

[1] Shibli, S.M.A. and Chacko, F., 2011. Development of nano TiO_2-incorporated phosphate coatings on hot dip zinc surface for good paintability and corrosion resistance. Applied Surface Science, 257(7), pp.3111-3117.

[2] Chen, T.T., Ke, S.T., Liu, Y.M. and Hou, K.H., 2006. The study on optimizing the zinc phosphate conversion coating process and its corrosion resistance. Journal of Chung Cheng Institute of Technology, 34(2), pp.1-11.

[3] Tamilselvi, M., Kamaraj, P., Arthanareeswari, M., Devikala, S. and Selvi, J.A., 2015. Development of nano SiO_2 incorporated nano zinc phosphate coatings on mild steel. Applied Surface Science, 332, pp.12-21.

[4] Samosir, R. and Simanjuntak, S.L., 2017, September. The influence of concentration and pH on corrotion rate in stainless steels–316 solution HNO_3 medium. In IOP Conference Series: Materials Science and Engineering (Vol. 237, No. 1, p. 012047). IOP Publishing.

[5] Subramanyam, K., (2003). Scattering, laws of. Ency of Library and Inform Sci 2e V4 (Print), 4, p.2564.

[6] Tamilselvi, M., Kamaraj, P., Arthanareeswari, M., Devikala, S. and Selvi, J.A., 2015. Progress in zinc phosphate conversion coatings: A review. International Journal of Advanced Chemical Science and Applications (IJACSA), 3(1), pp.25-41.

[7] Abdeen, D.H., El Hachach, M., Koc, M. and Atieh, M.A., 2019. A review on the corrosion behaviour of nanocoating's on metallic substrates. Materials, 12(2), p.210.

[8] Thomas, R. and Umapathy, M.J., 2015. Nano silicon dioxide accelerated zinc phosphate conversion coating on mild steel using decyltriethylammonium bromide as an additive. Silicon, 7, pp.371-381.

[9] Arthanareeswari, M., Kamaraj, P., Tamilselvi, M. and Devikala, S., 2018. A low temperature nano TiO_2 incorporated nano zinc phosphate coating on mild steel with enhanced corrosion resistance. Materials Today: Proceedings, 5(2), pp.9012-9025.

[10] Bagal, N.S., Kathavate, V.S. and Deshpande, P.P., 2018. Nano-TiO_2 phosphate conversion coatings–a chemical approach. Electrochemical Energy Technology, 4(1), pp.47-54.

[11] Su, H.Y. and Lin, C.S., 2014. Effect of additives on the properties of phosphate conversion coating on electrogalvanized steel sheet. Corrosion Science, 83, pp.137-146.

[12] Akbari, M.M., Shayegh Boroujeny, B. and Raeissi, M., 2021. Cerium Oxide Nanoparticles as an Accelerating Agent for Zinc Phosphate Coatings with Enhanced Corrosion Resistance. Journal of Advanced Materials and Processing, 9(2), pp.3-16.

[13] Manna, M., Shah, A. and Kulkarni, S.V., 2017. Development of phosphate coating on the surface of TMT rebar: an option to study the effect of n-SiO_2 as an additive. Ironmaking & Steelmaking, 44(9), pp.666-675.

[14] Ahmad, M.M., Mushtaq, S., Al Qahtani, H.S., Mir, A.S. and Alam, W., 2021. Investigation of TiO_2 nanoparticles synthesized by sol–gel method for effectual photo degradation, oxidation and reduction. Reaction. 2021; 11: 1456.

[15] Sankara Narayanan, T.S.N., 2005. Surface pretreatment by phosphate conversion coatings-A review. Reviews in Advanced Materials Science, 9, pp.130-177.

[16] Arthanareeswari, M., Kamaraj, P. and Tamilselvi, M., 2013. Anticorrosive performance of zinc phosphate coatings on mild steel developed using galvanic coupling. Journal of Chemistry, 2013(1), p.673961.

[17] Ayoola, A.A., Durodola, B.M., Babalola, R., Adeniyi, O.D. and Ilobinso, C.E., 2023. Corrosion inhibitive effects of calcium-modified zinc phosphate coating on A36 mild steel. Results in Engineering, 17, p.100880.

[18] Dhawan, S.K., Bhandari, H., Ruhi, G., Bisht, B.M.S. and Sambyal, P., 2020. Corrosion Preventive Materials and Corrosion Testing. CRC Press.

[19] Evans U R 1981 An Introduction to Metallic Corrosion 3rd Edn. (London: Edward Arnold Publishers Ltd)

[20] Ezekiel, S.N., Ayoola, A.A., Durodola, B., Odunlami, O.A. and Olawepo, A.V., 2022. Data on zinc phosphating of mild steel and its behaviour. Chemical Data Collections, 38, p.100838.

[21] Freeman, D.B. 1986. Phosphating and Metal Pretreatment – A Guide to Modern Processes and Practice, Industrial Press, Inc., New York.

[22] Jegannathan, S., Narayanan, T.S., Ravichandran, K. and Rajeswari, S., 2006. Formation of zinc–zinc phosphate composite coatings by cathodic electrochemical treatment. Surface and Coatings Technology, 200(12-13), pp.4117-4126.

[23] Kathavate, V.S. and Deshpande, P.P., 2020. Role of nano TiO_2 and nano ZnO particles on enhancing the electrochemical and mechanical properties of electrochemically deposited phosphate coatings. Surface and Coatings Technology, 394, p.125902.

[24] Abdalla, K., Azmi, R. and Azizan, A., 2013. The influence of deposition temperature on the morphology and corrosion resistance of zinc phosphate coating on mild steel. Advanced Materials Research, 626, pp.183-189.

[25] Kobya, M., Demirbas, E., Dedeli, A. and Sensoy, M.T., 2010. Treatment of rinse water from zinc phosphate coating by batch and continuous electrocoagulation processes. Journal of Hazardous Materials, 173(1-3), pp.326-334.

[26] Sankara Narayanan.T.S.N., 1996. "Performance Evaluation of Phosphating Formulations in Continuous Operation", Metal Finishing., 94(9) pp.40-43.

[27] Sheng, M., Wang, Y., Zhong, Q., Wu, H., Zhou, Q. and Lin, H., 2011. The effects of nano-SiO_2 additive on the zinc phosphating of carbon steel. Surface and Coatings Technology, 205(11), pp.3455-3460.

[28] Zhang, S.L., Chen, H.H., Zhang, X.L. and Zhang, M.M., 2008. The growth of zinc phosphate coatings on 6061-Al alloy. Surface and Coatings Technology, 202(9), pp.1674-1680.

[29] Weng, D., Jokiel, P., Uebleis, A. and Boehni, H., 1997. Corrosion and protection characteristics of zinc and manganese phosphate coatings. Surface and Coatings Technology, 88(1-3), pp.147-156.

[30] Zhang, X., Wang, F. and Du, Y., 2007. Effect of nano-sized titanium powder addition on corrosion performance of epoxy coatings. Surface and Coatings Technology, 201(16-17), pp.7241-7245.