Development of nano SiO$_2$ incorporated nano zinc phosphate coatings on mild steel

M. Tamilselvi [a], P. Kamaraj [b], M. Arthanareeswari [b,*], S. Devikala [b], J. Arockia Selvi [b]

[a] Department of Chemistry, Thiru Kolanjiappar Government Arts College, Virudhachalam 606001, India
[b] Department of Chemistry, SRM University, Kattankulathur 603203, India

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ABSTRACT

This paper reports the development of nano SiO$_2$ incorporated nano zinc phosphate coatings on mild steel at low temperature for achieving better corrosion protection. A new formulation of phosphating bath at low temperature with nano SiO$_2$ was attempted to explore the possibilities of development of nano zinc phosphate coatings on mild steel with improved corrosion resistance. The coatings developed were studied by Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Electrochemical measurements. Significant variation in the coating weight, morphology and corrosion resistance was observed as nano SiO$_2$ concentrations varied from 0.5–4 g/L. The results showed that, the nano SiO$_2$ in the phosphating solution changed the initial potential of the interface between mild steel substrate and phosphating solution and reduce the activation energy of the phosphating process, increase the nucleation sites and yielded zinc phosphate coatings of higher coating weight, greater surface coverage and enhanced corrosion resistance. Better corrosion resistance was observed for coatings derived from phosphating bath containing 1.5 g/L nano SiO$_2$. The new formulation reported in the present study was free from Ni or Mn salts and had very low concentration of sodium nitrite (0.4 g/L) as accelerator.

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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]. 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 [2]. One possible way of meeting the energy demand and eliminating the difficulties encountered due to scaling of heating coils and, over heating of the bath, is through the use of low temperature phosphating baths. Though known to be in use since the 1940s [3], 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. The use of nitrites as the accelerator is most common in low temperature operated phosphating baths. However, a higher concentration of nitrite is required to increase the rate of deposition of phosphate coatings at low temperatures. The environmental protection agency (EPA) has classified nitrite as toxic in nature and hence use of nitrite as accelerator could cause disposal problems [4]. Recent efforts to enhance the corrosion resistance of phosphate coatings have mainly been focused on the pre-treatment methods before phosphating and the process technologies for phosphating [5,6]. Zinc phosphating is one of the promising method for enhancing the corrosion resistance of iron and steel [7]. It has been shown that addition of metal salts in the phosphating bath can greatly influence the microstructure of zinc phosphate coating and make the coatings denser and finer [8–10]. The utility of the galvanic coupling for accelerating low temperature zinc phosphating processes was established recently [11,12]. Nowadays, nanostructure materials have attracted considerable interest due to their importance in fundamental research and potential wide ranging applications. In the coating industry, the quality of the coatings might be enhanced using nano particles [13–17]. Development of nano zinc phosphate coatings for enhanced corrosion resistance of mild steel was reported recently [18]. Nickel plays a major role in achieving an acceptable corrosion resistance of the coating as

* Corresponding author. Tel.: +91 044 27455855.
  E-mail address: arthanareeswari@gmail.com (M. Arthanareeswari).

well as accelerating the process chemistry. More recent developments have created nickel-free processes that can compete with the nickel containing processes [7,17–19]. In the present study, it was aimed to develop a phosphating bath at low temperature and with low concentration of accelerator, to explore the formation of nano zinc phosphate coatings with improved corrosion resistance using nano SiO_2 and nano ZnO. Phosphate coatings of enhanced corrosion resistance was developed, characterized and evaluated.

2. Experimental details

Mildsteel specimens of dimensions $8.0\,cm \times 6.0\,cm \times 0.2\,cm$ having 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, and balance iron (all in wt.%) were used as the substrate materials for the deposition of zinc phosphate coating. The specimens were abraded with a series of emery papers up to 400 grits and degreased with alkaline solution and rinsed in deionised water. The chemical composition of the zinc phosphating bath and its operating conditions are given in Table 1.

The nano ZnO and nano SiO_2 were purchased from Aldrich. The particles of the nano ZnO and nano SiO_2 has an average grain size between 30 and 40 nm. All the other chemicals used for the study were of analytical grade. Nano zinc oxide was dissolved in water in the presence of phosphoric acid. Nano SiO_2 was added to the phosphating solution with vigorous stirring and $NaNO_2$ was added just before the phosphating process. The pH of the bath was adjusted to 3 by adding NaOH. Phosphating was done by immersion process at room temperature ($27\,°C$) for 30 min. Then the phosphated specimens were rinsed with deionised water to remove the acid and the soluble salts left after phosphating. After rinsing, the specimens were subjected to drying by using compressed air. The amount of iron dissolved during phosphating and coating weight were determined in accordance with the standard procedures [7].

The coatings' surface morphology was examined by a Hitachi Scanning Electron Microscope SU1510 and the chemical composition was investigated by EDX. The phases in the phosphate coating were analyzed by XRD using Philips X'Pert pro diffractometer with Cu Kα ($\lambda = 1.54060\,$Å) incident radiation. The XRD peaks were recorded in the 2θ range of $0°$–$100°$.

Potentiodynamic polarization and electrochemical impedance measurements were carried out using Biologic Electrochemical Analyser (model SP 300) at the open circuit potential. The phosphated mild steel substrate formed the working electrode, whereas a saturated calomel electrode and a platinum electrode served as the reference and counter electrodes respectively. EC Lab software was used for data acquisition and analysis. Polarization technique was carried out from a cathodic potential of $-250\,mV_{(SCE)}$ to an anodic potential of $+250\,mV_{(SCE)}$ with respect to corrosion potential at a sweep rate 1 mV/s. Electrochemical impedance studies were

carried out in the frequency range between 10,000 and 0.01 Hz The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using Tafel extrapolation method. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from Nyquist plot by fitting the data using EC Lab software. All the experiments were repeated with multiple samples for confirming the reproducibility of the coatings.

3. Results and discussion

3.1. Effect of concentration of nano SiO_2 on the phosphate coating weight

The effect of amount of nano SiO_2 on the coating weight was studied by varying its concentrations (0.5–4 g/L) in the phosphating bath with an immersion time of 30 min at room temperature is shown in Fig. 1.

At concentrations less than 0.1 g/L of nano SiO_2, there is no significant effect on the coating weight. It was observed that the phosphate coating weight increases linearly from 0.5–1.5 g/L of nano SiO_2 in the phosphating bath. The phosphate coatings obtained from bath containing 1.5 g/Lof nano SiO_2 is the heaviest. There is no substantial increase in the coating weight beyond 1.5 g/L of nano SiO_2. From the Fig. 1, it was observed that the increase in coating weight with increase in the concentration of nano SiO_2 in the phosphating bath exhibits linearity only from 0.5 to 1.5 g/L while it followed a Boltzmann fit for the entire range. The adj. R-square value given in the fitting parameter gives an estimate of goodness of fit of the function to the data [20]. This is 0.997 for the coating weight, which means that 99.7% of the variation of the 'independent' variable (concentration of SiO_2 in g/L) can be explained by the variation of the 'dependent' variable (coating weight obtained). The iron dissolved during phosphating had followed the LogNormal fit, which is the best fit for entire range. The adj. R-square value for this fit is 0.995.

Presence of nano SiO_2 reduces the crystal size of nano zinc phosphate, increases the compactness of the coating which results in higher coating weight than compared to nano zinc phosphate coatings developed in the absence of nano SiO_2 [18]. Presence of nano SiO_2 at optimum concentration (1.5 g/L), confirmed by further analysis, accelerate the formation of new phosphate crystal nucleation and thereby increasing the phosphate coating weight. But further increase in the concentrations of nano SiO_2 reduce

Table 1
Chemical composition, control parameters and operating conditions of the bath used for zinc phosphating.

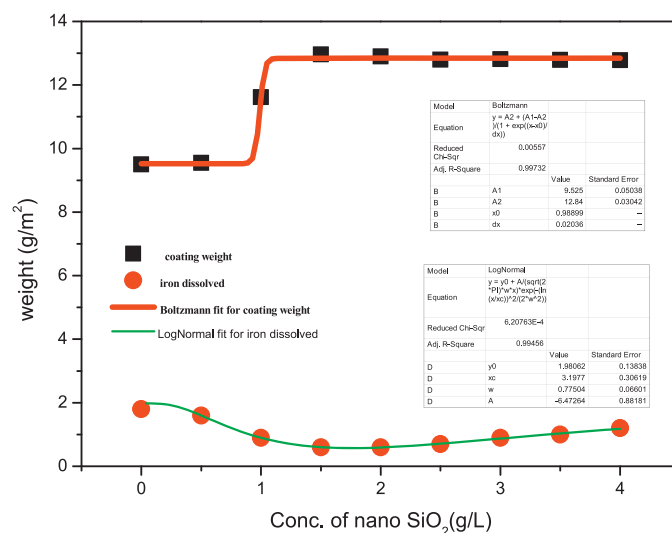| Chemical composition	
Nano ZnO	1.5 g/L
Nano SiO_2	0–4 g/L
H_3PO_4	2.3 ml/L
$NaNO_2$	0.4 g/L
Control parameters	
pH	3 ± 0.1
Free acid value (FA)	3 pointage
Total acid value (TA)	25 pointage
FA:TA	1: 8.33
Temperature	$27\,°C \pm 3\,°C$
Time	30 min

Fig. 1. The weight of phosphate coatings obtained and iron dissolved during phosphating of mild steel using baths containing different contents of nano SiO_2.