

The effects of niobium and nickel on the corrosion resistance of the zinc phosphate layers

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Abstract

In this investigation the viability of nickel substitution by niobium in zinc phosphate (PZn) baths has been studied. Samples of carbon steel (SAE 1010) were phosphated in two baths, one containing nickel (PZn+Ni) and the other with niobium substituting nickel (PZn+Nb). Potentiodynamic polarization curves (anodic and cathodic, separately) and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion resistance of the phosphated carbon steels in a 0.5 mol L⁻¹ NaCl electrolyte. The phosphate layers obtained were analysed by X-ray diffraction and it was found that they are composed of Zn₃(PO₄)₂·4H₂O (hopeite) and Zn₂Fe(PO₄)₂·4H₂O (phosphophyllite). Surface observation by scanning electron microscopy (SEM) showed that the PZn+Ni layer is deposited as needle-like crystals, whereas the PZn+Nb layer shows a granular morphology. The electrochemical results showed that the PZn+Nb coating was more effective in the corrosion protection of the carbon steel substrate than the PZn+Ni layer. The results also suggested that nickel can be replaced by niobium in zinc phosphate baths with advantageous corrosion properties of the layer formed.

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1. Introduction

Phosphating is one of the most used surface treatments for metallic surfaces [1–10]. It is known as a conversion coating that leads to the formation of insoluble phosphate salts, mainly zinc phosphate [11,12] and is employed in many industries either for corrosion protection, surface preparation for painting, or for decoration [11,12] in a variety of metallic materials. This type of coating can be applied on steels [1–5,7], galvanized steel [4,10,13], iron [6], magnesium [8,14,15], aluminium [9,16] and zinc [17].

There are many types of phosphating baths such as, zinc based [1,17–20], manganese based [4,21–23], tricationic [24], organic phosphate [6,25,26] or even a combination of them. The type of coating used depends on the phosphated material application.

Studies on the phosphating reactions resulted in decreased temperature of the phosphating bath and also in the time of immersion time. This was possible due to variations in the electrical current and phosphating bath composition with the addition of some components to accelerate the phosphating process and also obtaining phosphate layer with better properties [11].

As mentioned above, the electrical current was among the phosphating accelerator agent investigated [2,5,7,17,18] but also the chemical compounds were used. The chemical compounds that act as accelerators might be oxidant compounds or salts of metals nobler than the metal to be phosphated. The use of chemical additives as phosphating accelerator has the advantage of being less costly in comparison to modifications in the current density.

The accelerators act as: (i) depolarizers of the surface reactions, mainly those of high electronic density (microcathodes), and (ii) oxidant of the metal cations on the microanodes leading to the precipitation of insoluble phosphate salts [11].

Various types of chemical accelerators for phosphating can be used such as sodium nitrite [1,7,14,27–29], nitrates [3,7,8,14,15,27,28,30,31] and chlorates [30,32]. Besides the chemical accelerator other additives are used to afford other

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specific properties. Various additives are used such as calcium ions [7,32–35], manganese ions [19,21,23,30,35–37], tartaric acid [8,15], fluoride ions [8,14–16,27,29], nickel ions [1,16,19,28,30,32,38], copper ions [39] molybdenum ions [15,37] and, more recently, niobium [39].

The present work aims to evaluate the viability of nickel substitution by niobium in zinc phosphate baths, as an environmental friendly alternative to the commercial phosphating processes usually adopted.

2. Experimental

2.1. Sample preparation

The material used as substrate was a carbon steel (SAE 1010) (composition in Table 1) from which samples with $10 \times 15 \times 2$ mm were cut and then phosphated.

The samples surfaces for phosphating were prepared by SiC grinding with SiC emery paper in the sequence #220, #320, #400 and #600, respectively. After grinding, the samples were degreased in a commercial alkaline solution for 5 min at (70 ± 5) °C and then, rinsed. Subsequently, the samples were immersed in an alkaline solution titanated with a commercial compound, that is, a titanium phosphate salt in the concentration of 3 g/L (pH=7.5–9.0), for 90 s at (25 ± 2) °C for surface activation. Next, the samples were immersed in the phosphating bath either with nickel (PZn+Ni) or niobium (PZn+Nb), for 5 and 3 min respectively, at (25 ± 2) °C, and then dried and weighed, obtaining m_1 . The determination of the deposited phosphate layer weight was carried out by solubilization of the phosphate layer in a 0.5 g/L chromium trioxide for 15 min at (75 ± 5) °C, followed by weighing, obtaining m_2 . The phosphate layer weight ($m_{\text{phosphate}}$) was estimated by Eq. (1):

$$m_{\text{phosphate}} = \frac{m_1 - m_2}{A} \quad (1)$$

where m_1 is the phosphated steel weight, m_2 is the steel weight after phosphate layer solubilization, and A is the surface area exposed to the phosphating bath.

Concentrated solutions for phosphating, either with Ni (PZn+Ni) or with Nb (PZn+Nb) addition, were prepared and their main composition is shown in Table 2. A niobium compound was prepared by alkaline fusion of 1 g of Nb_2O_5 and 5 g KOH, as described in [40]. Nb was added to one of

Table 1
Chemical composition of carbon steel (SAE 1010) used as substrate for phosphating

Element	Composition (wt.%)
C	0.118
Si	0.023
Mn	0.310
P	0.020
S	0.016
Cr	0.024
Ni	0.028
Mo	0.002

Table 2

Chemical composition of concentrated phosphate bath

Component (g/L)	PZn+Ni	PZn+Nb
H_3PO_4	521.4	521.4
HNO_3	363.3	363.3
Zn	185.8	168.9
Ni	4.24	–
Nb	–	0.136
H_2O_2	0.032	0.032
$\text{H}_2\text{O}(\text{mL})$	434.4	440.7

the concentrated phosphate solutions shown in Table 2 by addition of 0.5 g of the alkaline fusion compound obtained. The Zn, Ni and Nb content in the concentrated solutions was determined by Induced Coupled Plasma Optical Emission Spectroscopy (ICP OES). From the concentrated solutions, the phosphating baths were prepared by dilution and addition of sodium hydroxide (NaOH 50%). The phosphating baths were titrated of the diluted phosphating bath with NaOH 0.1 mol L^{-1} . The total and free acidity values were 28 and 1.6 points, respectively.

Sodium nitrite (NaNO_2) was used as an accelerator in the phosphating bath at concentrations of 0.5 g/L, for the PZn+Ni bath, and 2 g/L for the PZn+Nb one.

All the solutions were prepared with analytical grade chemical compounds and deionized water.

2.2. Characterization of the phosphate layers

The morphology of the phosphate layers obtained was evaluated by Scanning Electron Microscopy (SEM) using a Philips XL30 microscope and their thickness was determined by thickness measurements at 10 areas of 3 different samples.

The phases in the phosphate layer were investigated by X-ray diffraction analysis (XDR) with a diffractometer Rigaku DEMAX 2000 using radiation of $\text{CuK}\alpha$ (1.5418 Å).

The coating roughness was determined according to JIS 2001 standard using a roughness meter Mitutoyo SurfTest J-301 series at 10 areas of 3 different samples.

The electrochemical behaviour of the phosphated samples was evaluated by potentiodynamic polarization (anodic and cathodic) measurements and electrochemical impedance spectroscopy (EIS), using a frequency response analyser (Gamry model EIS 300) coupled to a potentiostat PCI4/300. Working electrodes with an area of 1.5 cm^2 were used in the electrochemical tests. A platinum wire and a silver/silver chloride electrode were used as counter and reference electrodes, respectively. A sodium chloride solution (0.5 mol L^{-1} NaCl; pH=6.0) was used for electrochemical characterization of the phosphate layer. The electrolyte was quiescent, naturally aerated and at (20 ± 2) °C.

Potentiodynamic polarization tests were carried out from the corrosion potential E_{CORR} up to an overpotential of ± 400 mV, using a scanning rate of 1 mVs^{-1} .

The EIS measurements were potentiostatically performed at E_{CORR} with a perturbation amplitude of ± 10 mV in the frequency

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