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Corrosion behaviour of electroless high boron-mid phosphorous nickel duplex coatings in the as-plated and heat-treated states in NaCl, H_2SO_4, NaOH and Na_2SO_4 media

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HIGHLIGHTS

- NiP deposits present the best anti-corrosion behaviour in neutral electrolytes.
- Low current densities for electroless nickel coatings are obtained at high pH.
- The heat treatment drastically increases the current density of the nickel coatings.
- The top layer dominates the corrosion behavior of the duplex coatings.

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ABSTRACT

The corrosion behaviour of electroless nickel–boron and nickel-phosphorous coatings, as monolayers and duplex systems was investigated with and without heat-treatment (400 °C - 1 h, non-reactive atmosphere). Monolayer coatings with 20 μm of thickness were compared with duplex coatings composed of two 10 μm layers. Four distinct configurations of duplex coatings were prepared: NiB/NiP; NiP/NiB; NiB/NiB and NiP/NiP. The salt spray test showed that visible differences exist in terms of general corrosion: corrosion starts after 24 h for the NiB samples and after 48 h for the NiP samples. In addition, image analysis was used to quantify the corroded surface after salt spray. The duplex coatings presented intermediate behaviour when compared to the monolayer systems. Furthermore, the corrosion behaviour was evaluated by means of potentiodynamic polarisation technique. Results clearly suggested that monolayer NiP exhibits higher corrosion resistance than monolayer NiB. In all cases, polarisation tests showed that a NiP layer is preferable as the outer part of the coating rather than a NiB layer. Finally, cross-section analysis allowed better understanding of the corrosion properties.

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1. Introduction

Electroless nickel is a useful method to provide protection against corrosion to steel and light alloys substrates. Many deposition processes based on electroless nickel method have known a surge in interest among researchers due to their versatility. Diverse recent applications, on various surfaces, were made possible on behalf of promising corrosion and wear resistance properties of electroless Nickel [1–4].

Electroless plating is a process where aqueous metal ions are chemically reduced on an activated base substrate, forming a coating without the use of external current. This reduction is possible due to the presence of a reducing agent in the plating bath. Autocatalytic solutions generally contains a source of metallic ions, reducing agent, complexing agent, stabilizer and a pH controller. Several reducing agents have been used in the electroless nickel process, including sodium hypophosphite [3,5–8], sodium borohydride [9–11] [12], dimethylamine borane [13–15] and hydrazine [16].

Electroless deposition with hypophosphite (Nickel-phosphorus, NiP) bath is the most used electroless nickel plating method, having some advantages when compared with boron and hydrazine reduced baths. Indeed, nickel-phosphorus baths are generally cheaper and Ni-P provides better corrosion resistances [17]. On the other hand, sodium borohydride is the most powerful reducing

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agent for electroless nickel plating and NiB coatings are particularly employed in the aerospace and automotive industries due to their high hardness and wear resistance [18].

As described above, by modifying the reducing agent, different classes of electroless nickel coatings suitable for specific applications are generated. Summarising, nickel-phosphorous is more convenient for corrosion resistance and nickel-boron for mechanical and wear applications. In addition, electroless nickel coatings can be submitted to heat-treatment in order to enhance their mechanical properties [2,10,19–22]. Vitry et al. showed that NiB coatings can achieve hardness higher than 1100 hk_{50} [23] after heat-treatment - although heat-treatment may have a negative impact on the corrosion properties [24] [25].

Different works based on a system that combines both kinds of coatings (NiB and NiP) have been developed in the last few years [11,23] [26,27]. Using different approaches, all these studies aimed at obtaining coatings combining the mechanical properties of NiB with the anti-corrosion behaviour of NiP.

Hypophospite reduced electroless coatings have been used on metal substrates such as firearms, to enhance corrosion resistance. However, these coatings do not possess high wear resistance and lubrication properties. NiB coatings have been used in firearms to enhance abrasion resistance and lubricaction properties. Duplex systems with the corrosion properties of NiP and the wear properties of NiB coatings would be the ideal coatings for these applications. Another application for these duplex systems is in a marine environment. Items, like propellers and hulls are affected by marine growth and fouling. The nickel boron coating can be applied to reduce friction and increase the hydrodynamic performance. In the same time, NiP coatings can be applied to enhance corrosion properties.

The present research compares two monolayers, NiP and NiB, two bilayers NiB/NiB and NiP/NiP and two duplex NiP/NiB and NiB/NiP coatings. In the as-plated condition, the corrosion behaviour of the coatings were analysed in four different media (NaCl, H_2SO_4, NaOH and Na_2SO_4). After that, the impact of heat-treatment on the corrosion behaviour was analysed in sodium chloride medium.

2. Materials and methods

2.1. Sample and bath preparation

Mild steel plates (ST 37-DIN 17100) were cut into square samples (10 cm × 10 cm × 0.1cm) and their surface was polished (emery paper up to 2000 grit). For convenient handling, a hole of 2 mm diameter was drilled close to one edge of the samples. The substrates were degreased by acetone. Prior to plating, the samples were activated by etching in 32 vol % hydrochloric acid for 3 min, rinsed in flowing distilled water and then immersed in the electroless solution.

A thermostable teflonized cell under constant mechanical agitation was used for the electroless plating process. Electroless nickel mid-phosphorous deposition was carried out at $88 \pm 1\,^{\circ}C$ with a commercial bath: Niklad ELV 808A and Niklad ELV 808B from Mc Dermid (7–9 wt. % P). The average composition of the NiP coatings is 7 wt.% P and 93 wt.% Ni.

Electroless nickel high-boron bath operated at $96.5 \pm 0.5\,^{\circ}C$. The bath parameters and composition were developed by our group and are presented in Table 1, with sodium borohydride ($NaBH_4$) employed as a reducer, nickel chloride hexahydrate ($NiCl_2.6H_2O$) as a nickel source, ethylenediamine ($NH_2-CH_2-CH_2-NH_2$) as a complexing agent and lead tungstate ($PbWO_4$) as a stabilizer. The precise composition and parameters of the bath were presented in previous works [11,28]. The average composition of the NiB coatings is 8 wt.% B, 0.5 wt.% Pb and 91.5 wt.% Ni.

In the case of the bi-layers (NiB/NiB, NiP/NiP) and duplex samples (NiB/NiP, NiP/NiB), freshly prepared baths were used for each layer. The two layers of duplex systems were always deposited on the same day. After the deposition of the first layer, the samples were stored in a desiccator. The time gap before depositing the second layer was kept between 1 and 6 h. The second layer was directly deposited on the sample without any surface preparation or cleaning process.

The nomenclature employed in this work is NiB 20 and NiP 20 for the two monolayers, NiB 2 × 10 and NiP 2 × 10 for the bilayer coatings and finally, NiB/NiP for the duplex sample with NiP on the top layer and NiP/NiB for the duplex sample with NiB on the top layer.

2.2. Heat-treatment

Part of the samples were heat-treated under controlled atmosphere (95% Ar and 5% H_2). The heat-treatment was carried out at 400 °C for 1 h and samples were cooled in turned off furnace, also under controlled atmosphere.

2.3. Characterization methods

The cross-section morphology of each sample was observed using a JEOL-SEM 6400 scanning electron microscope. Samples were mounted in resin, polished with silicon carbide paper followed by diamond paste up to mirror finish and etched with Nital 10%. X-rays diffraction (XRD) patterns of the samples in as-deposited condition and after heat treatments are recorded at room temperature, using a Siemens D500 X-rays $\theta - 2\theta$ apparatus applying Cu Ka (15.406 A).

Corrosion characterization was performed by potentiodynamic polarisation curves in four different media (0.1 M Na_2SO_4, 0.1 M NaCl, 0.1 M NaOH, 0.1 M H_2SO_4) through the use of a Bio-logic SP-50 potentiostat. Before polarisation analysis, a waiting time of 20 min at OCP (Open Circuit Potential) was respected. A platinum plate and an Ag/AgCl (KCl saturated) electrode were used as counter and reference electrodes, respectively. A potential range of −600 to 250 mV from OCP, with 0.167 mV/s as scan rate, was applied to the working electrode under aerated conditions.

Additionally, salt spray tests were performed in a Q-FOG Cyclic corrosion tester which simulates marine environments. Such tests are commonly used to evaluate the corrosion resistance of nickel coatings on ferrous and nonferrous substrates. Neutral salt spray test was carried out as one type of accelerated test according to ASTM B117-07. The samples were suspended in a cabinet and exposed to 50 g/l ± 5 g/l NaCl solution. The air pressure of the atomized saline solution was maintained in the range of 6–8 Bar. The tests were conducted for a variety of time periods ranging from 0.5 h to 14 days with intermediate periods of 1 h, 4 h, 8 h and 1, 2, 3, 4, 5, 7 days.

Salt spray corroded surfaces were quantified by image analysis, with the open source image processing software ImageJ. In order to extract and analyse features of a digital image, it is first necessary to identify and separate the different regions. Image segmentation involves dividing an image based on features such as brightness or morphology. For this work, the analysis was based on semi-automatic and automatic procedures. The original image (Fig. 1(a)) was first transformed into a grey level image, and the thresholding method was then applied to segment the pixels darker than the threshold value. The ImageJ algorithm was used along with the semi-automatic thresholding option. This process resulted in a binary file (Fig. 1(b)) containing only black and white pixels, where the black pixels corresponded to the regions above the threshold value (in this case, corroded areas). Sequentially, the

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