Electrochimica Acta 54 (2009) 6718–6724

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Investigation of a transparent chromate (III) passive film on electroless Ni–P coating by XPS and electrochemical methods

Songlin Mu, Ning Li*, Deyu Li, Zhongli Zou

Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, PR China

ARTICLE INFO

Article history:
Received 28 March 2009
Received in revised form 16 May 2009
Accepted 25 June 2009
Available online 4 July 2009

Keywords:
Transparent passive film
Electroless Ni–P coating
XPS
EIS
Composition analysis

ABSTRACT

A transparent passive film on electroless nickel phosphorus coating (ENPC) was obtained in a chromate (Cr^{3+}) bath. An ENPC sample passivated in a Cr^{6+}-containing bath was used for comparison. The corrosion properties were tested by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). SEM, XPS, and EDX were employed to analyze the chemical composition and surface morphology of the films. SEM results indicate that the passive film is too thin to be observed by SEM. The potentiodynamic polarization tests show that the corrosion currents of the two passivated samples are only about 1/25 of the un-passivated coating. The XPS analysis illustrate that the Cr^{6+}-treated film comprises Cr, Ni and O, while the Cr^{3+}-treated film is made up of Cr, C, O, Ni, P and N. High-resolution XPS analysis show that, both in Cr^{6+}-treated and Cr^{3+}-treated films, element Cr is only in the form of trivalent compounds, no hexavalent chromium existing. By XPSpeak analyzing, trivalent chromium compounds on the two treated surfaces were fitted as $Cr(OH)_3$ and Cr_2O_3. However, for the Cr^{3+} and Cr^{6+} passivation routes, the $Cr(OH)_3$ and Cr_2O_3 contents in passive films are widely divergent.

1. Introduction

Electroless nickel method can coat a Ni–P alloy layer on many substrates such as metal, plastic, glass and ceramic through an autocatalytic process in which complex nickel ions are chemically reduced and deposited on substrates [1–11]. This alloy layer owns many advantages such as uniform deposition, good corrosion and wear resistance, perfect electrical and thermal conductivity, and solderability [12–15]. Therefore, ENPC has found widespread applications as printed circuit boards, metallization of plastic, magnetic storage media, microelectronics, computer engineering, textiles, petroleum and aerospace [16–20].

Despite its excellent properties, the Ni–P coating is easily oxidized in air and form an oxide film on the surface, which will make the surface lose its brightness, discolor and finally turn into light yellow. Moreover, it will decrease the solderability of the Ni–P coating seriously, which is a fatal defect to many electronic components. An effective method to solve this problem is to coat a thin passive film on the surface. In industrial fields, manufacturers usually use Cr^{6+}-containing bath to treat the Ni–P coated components to get passive films.

The formation and anticorrosion mechanisms of chromate (VI) passive films on zinc, aluminum, stainless steel etc. have been extensively investigated, and several models have been proposed [21–23]. The forming process generally involves two steps: dissolution of metal atoms from metallic matrixes, and precipitation of insoluble metallic compounds back on the matrixes. When metals or their alloys immersed in passive baths containing $Cr_2O_7{}^{2-}$, a redox reaction will be induced:

$$Cr_2O_7{}^{2-} + 14H^+ + \tfrac{6}{n}M \rightarrow 2Cr^{3+} + 7H_2O + \tfrac{6}{n}M^{n+} \qquad (1)$$

where M = Mg, Al, Zn etc., $n = 2, 3$

The Eq. (1) leads to increase in concentration of M^{n+} and Cr^{3+}. The pH value in the solution layer very close to the surface of matrixes will also increase because of consumption of $H^{+\cdot}$ As the pH value rising, metal ions cannot stay stably in solution and consequently form insoluble hydroxides to precipitate on matrixes, as described in Eqs. (2) and (3).

$$M^{n+} + nOH^- \rightarrow M(OH)_n \qquad (2)$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \qquad (3)$$

With the process of Eqs. (2) and (3), surface of the matrixes will be gradually covered by insoluble compounds, Eq. (1) slows down, which in turn decelerates Eqs. (2) and (3). The deposition rate slows down, passivation process completes. During the following drying period, part of the hydroxides transforms into according oxides [24].

The reason why chromate (VI) passive films own excellent anticorrosion properties lies in at least two aspects. First, the films of a certain thickness act as a barrier, which protect the matrix metals from the corrosive mediums. Second, the hexavalent chromium

---

* Corresponding author. Tel.: +86 451 86413721; fax: +86 451 86221048.
E-mail address: lining@hit.edu.cn (N. Li).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.06.076

contained in films can re-passivate the exposed matrix metals when the passive films are scratched or mechanically damaged [25,26].

As for chromate (III) methods, the reaction mechanism is scarcely researched, only some literatures reported the anticorrosive properties of Cr^{3+}-based passive films [27–29].

Although the Cr^{6+}-produced film can meet the industrial needs, the toxicity of hexavalent chromium has limited its usage scope. Naturally, new passivation approach should be developed to replace those Cr^{6+}-involved methods. In this paper, we have studied the performance of passive film obtained in a new treatment bath, which mainly contains chromium nitrate, nitric acid, ethylenediamine and an aromatic compound. Electrochemical methods have been used to study the corrosion performance of this Cr^{3+}-treated coating. The XPS method was employed to analyze the composition of the passive film. For comparison, similar passive film obtained in $K_2Cr_2O_7$ bath was also examined.

2. Experimental

2.1. Preparation of the Ni–P coating

From a commercially operated medium phosphorus content nickel bath supplied by OM Group Inc. of America (OMG), about 14 μm thick Ni–P coating was deposited on substrate of mild steel sheet, 0.5 mm thick, cut into 50 mm × 20 mm. Prior to deposition, the sheets were first mechanically polished with 1000 grade of sandpaper and then degreased in 10% NaOH at room temperature for 5 min, followed by immersion in acetone. After that the sheets were activated in 5% hydrochloric acid solution for 10 s followed by rinsing in de-ionized (DI) water. Then electroless plating was immediately carried out at 88 ± 2 °C for 40 min with pH of the plating bath 4.75 (adjusting at room temperature about 20–25 °C).

2.2. Passivation treatment

After plating, the sheets were firstly rinsed in abundant running tap water then in DI water, and then were passivated immediately. Two kinds of bathes were used to treat the ENPC sheets, one was the Cr^{3+}-containing bath and another was a single reagent bath: 30 g/L $K_2Cr_2O_7$ (pH was not adjusted). Both treatments were conducted in the according passivation bath at 60 °C for 10 min. After passivation, the specimens were rinsed in running tap water then rinsed with DI water, finally were dried in an oven at 120 °C for 20 min.

2.3. SEM and EDX studies

The morphology of untreated Ni–P coating and passivated coating were observed by scanning electron microscopy (SEM, HITACHI S-4700). To examine the content of P in coating, the chemical composition of the Ni–P coating was analyzed by Energy Dispersive X-ray Spectrometry (EDX) attached to the SEM.

2.4. Electrochemical corrosion tests

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were carried out by CHI660B electrochemical workstation (Shanghai Chenhua instrument company, Shanghai, China). The sample was loaded on a conventional three electrode glass cell with a sheet of platinum (about 1.0 cm^2) as counter electrode, a saturated calomel electrode (SCE, +0.242 V versus SHE) as reference electrode connected to the cell by a Luggin capillary, which can minimize the solution resistance. The sample with an exposed area of 0.784 cm^2 was used as working electrode. The measurement was performed in electrolyte of 3.5 wt.% NaCl (0.6 M, pH = 6.8). To minimize the damage to passive film during EIS testing, the AC excitation amplitude of potential was set at 5 mV. The EIS test was conducted prior to the potentiodynamic polarization test, namely both the EIS and potentiodynamic polarization tests were conducted with the same area as working electrode, thus could reduce the error caused by different testing area.

It is believed that the corrosion properties of electroless Ni–P coatings would be affected seriously by not only the phosphorous content, but also the porosity. Hence, porosity test was conducted by a check solution, prepared as: $K_3[Fe(CN)_6]$ 10 g/l; NaCl 20 g/l. A piece of filter paper was dipped in the check solution, then was drawn out and pasted on the tested coating, after 10 min the test paper was taken from the coating and blue spots on this paper were counted to evaluate the porosity. In this test no blue spots was observed on the test paper, which meant there was no porosity in the tested coating.

2.4.1. Electrochemical impedance spectroscopy

Before the electrochemical impedance spectroscopy (EIS) test, the sample was mounted on the three electrode glass cell and the working electrode area was immersed in electrolyte (3.5 wt.% NaCl, pH 6.8) for about 15 min to obtain a steady open circuit potential (OCP) or the steady state potential. The impedance data were collected in the frequency range of 100–0.01 Hz with excitation amplitude of 5 mV under open-circuit conditions. After experiment the impedance data were displayed as Nyquist and Bode plots.

2.4.2. Potentiodynamic polarization

After EIS measurements, the system was settled for 5 min to attain its stable OCP again, then the potentiodynamic polarization measurements were performed by CHI660B electrochemical workstation from −250 mV to +250 mV (with respect to the OCP) at a scan rate of 1 mV/s. The data were recorded as Tafel plots. The corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and polarization resistance (R_{p}) were deduced from the Tafel plot. The corrosion current was obtained using the Stern–Geary equation:

$$I_{\mathrm{corr}} = \left[\frac{b_{\mathrm{a}} b_{\mathrm{c}}}{2.303(b_{\mathrm{a}} + b_{\mathrm{c}})}\right]\left[\frac{1}{R_{\mathrm{p}}}\right]$$

where b_{a} and b_{c} are the Tafel slopes or the Tafel constants, expressed as V/decade (V/dec). R_{p} is the polarization resistance expressed as $\Omega\, cm^2$. The polarization resistance was calculated using the following equation:

$$R_p = \left(\frac{\Delta E}{\Delta i}\right)\bigg|_{\Delta E \to 0}$$

where ΔE is the polarization potential and Δi the polarization current.

2.5. XPS analysis

The outermost surface of the Cr^{6+}-treated passive film was analyzed by X-ray photoelectron spectroscopy (XPS). This XPS analysis was carried out with a PHI 5700 ESCA System equipped with a dual anode X-ray source (Mg/Al) and a spherical capacitor analyzer (SCA). The X-ray source was operated at 15 kV and 400 W. The electrons emitted from the samples were detected at different angles of 15°, 30° and 45° with respect to the sample surface. Overview spectra were recorded in the range of 0–1350 eV with constant analyzer pass energy of 187.85 eV. To analyze the change of elemental contents with the depth of passive film, the surface was sputtered using a 3000 eV Ar^+ ion beam over an area of 4 × 4 mm^2. The overview spectra with 45° detecting angle were recorded after the passivated surface was sputtered by Ar^+ for 0 s, 30 s and 60 s respectively. It should be noted that before sputtering, the sputtering rate of Ar^+ to the surface was calibrated with SiO_2 as 2 nm/min. The intensities of the Cr 2p photoelectron lines were recorded separately with