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Effect of ammonium chloride on microstructure, super-hydrophobicity and corrosion resistance of nickel coatings

M. Hashemzadeh, K. Raeissi, F. Ashrafizadeh, S. Khorsand *

Department of Materials Engineering, Isfahan University of Technology, Isfahan 8415683111, Iran

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ABSTRACT

Nickel coatings were prepared at different concentrations of NH_4Cl as a crystal modifier in the electrodeposition bath. Surface morphology, wettability and the preferred orientation of the coatings were characterized by scanning electron microscopy, optical contact angle meter and X-ray diffractometer (XRD), respectively. The results showed that NH_4Cl considerably affected the microstructure of the coatings; NH_4Cl modified surface morphology towards an appropriate micro-nano cones structure. The contact angle of water droplets on the nickel coatings increased over time, eventually approaching a super-hydrophobic surface. Indeed, the super-hydrophobic surface showed a good long-term durability in air. XRD results indicated that NH_4Cl changed the preferred orientation from (220) to (111) by a complex growth mode. The role of NH_4Cl was studied by cyclic voltammetry and electrochemical impedance spectroscopy techniques. It was found that NH_4Cl inhibited the nucleation of nickel deposits by increasing charge transfer resistance. Electrochemical measurements at long-term immersions indicated that the super-hydrophobic nickel coatings greatly enhanced the corrosion resistance of copper substrate in the neutral 3.5 wt.% NaCl solution. The results revealed that super-hydrophobicity considerably increased the polarization resistance from 21 to 272 $k\Omega \cdot cm^2$. After decay of hydrophobic property, the passive oxide layer played the major role to protect the coatings in the corrosive solution.

1. Introduction

Super-hydrophobic surfaces with large water contact angles (WCA ≥ 150°) and such attractive properties as water repellency, anti-corrosion, self-cleaning and anti-fouling may be produced by electrodeposition process [1]. Two necessary parameters for making super-hydrophobic surfaces are high surface roughness and low surface energy [2,3]. According to the literature, coatings morphology is influenced by conditions of electroplating such as current density, deposition time, bath composition and temperature [4–11]. Also, it has been found that the presence of appropriate additives, such as NH_4Cl [12] and ethylenediammonium dichloride (EDA) [13–16], in the plating bath is essential for preparing nickel coatings with rough morphology. Geng et al. [12] achieved micro-nano structures of nickel in the presence of NH_4Cl. They observed that the freshly prepared nickel film was super-hydrophilic, but, after storing the surface in air for 15 days, the nickel film exhibited super-hydrophobic nature. Deng et al. [9] synthesized large-scale copper nano-cones in the presence of Janus Green B as crystal modifier by electrodeposition. The electrodeposited copper film with nano-cones structure exhibited a superhydrophobic property after the chemical modification. Wang et al. [7] fabricated cone-like and mushroom-like cobalt nano-structures in the presence of several organic crystalline modifiers such as methylamine, propylamine, n-butylamine, and ethylenediamine. They found ethylenediamine is optimal for synthesizing mushroom-like nanostructures.

It has established that super-hydrophobic coatings could improve the corrosion resistance of metallic substrates considerably [17–21]. A useful super-hydrophobic surface should resist wetting even after prolonged exposure to water. Stability of different super-hydrophobic coatings has been studied by electrochemical impedance spectroscopy (EIS) and water contact angle meter at different immersion times. Ishizaki et al. [18] reported that the super-hydrophobicity of magnesium alloy coated with nanostructured cerium oxide film and fluoroalkylsilane molecules disappeared after 24 h immersion in the corrosive NaCl aqueous solution. Wu et al. [19] deposited superhydrophobic silica films onto mild steel substrate by one-step electrodeposition of inorganic/organic hybrid sol–gel films from tetraethoxysilane and dodecyltriethoxysilane mixed sol–gel precursors. They reported the super-hydrophobicity of silica films maintained within the initial 48 h immersion in the 3.5 wt.% NaCl solution.

The applications of the electrodeposited coatings with micro-nano cone structures are commonly in microelectronics, optoelectronics, magnetic storages, and sensors because of their novel physical and chemical properties [22]. In addition, superhydrophobicity capability

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* Corresponding author.
E-mail address: s.khorsand@ma.iut.ac.ir (S. Khorsand).

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of these coatings can provide them a good protection during transportation. However, the micro-nano cone structures can easily be destroyed if subjected to mechanical or wear attacks, and thus, they should be avoided to contact with other surfaces during their service.

Up to now a few papers have been published regarding the effect of additives concentration on the properties of electrodeposited coatings. The role of additives in electrodeposition process usually is unclear [9,10,13,22]. The objectives of the present work are to introduce a super-hydrophobic nickel coating by a facile electrodeposition method without further modification, and study the effect of different amounts of NH_4Cl on microstructure and wettability of nickel coatings with micro-nano cones structure. In addition, the precise role of crystal modifier in the electrodeposition bath was clarified. The corrosion behavior, long term stability and durability of super-hydrophobic nickel coatings prepared in the presence of NH_4Cl were also investigated.

2. Experimental procedure

Commercial pure copper plates in disk shape with a surface area of 1.54 cm^2 were used as the substrates. The substrates were mechanically polished down to 2400 grit size using abrasive SiC papers and polished to a mirror finish using Buehler alumina powder (0.05 μm). Then, the specimens were cleaned in ethanol by ultrasonic methods. After that, the substrates were electro-polished in a solution composed of 70 $g \cdot L^{-1}$ Na_2CO_3, 10 $g \cdot L^{-1}$ KOH and 10 $g \cdot L^{-1}$ sodium dodecyl sulfate at 2 $A \cdot dm^{-2}$ for 1 min; then it was activated in 10 wt.% HCl for 20 s, rinsed in deionized water and immediately placed in an electrodeposition bath. The composition of the electrodeposition bath was $NiCl_2 \cdot 6H_2O$ (238 $g \cdot L^{-1}$), H_3BO_3 (40 $g \cdot L^{-1}$) and different amounts of NH_4Cl (0, 150, 200, 250 and 300 $g \cdot L^{-1}$) as the crystal modifier. As has been mentioned previously [23], only chloride baths can provide primary micro-cone structures, which facilitate reaching to a regular rough morphology using crystal modifier. The bath temperature was kept constant at 60 °C and pH 4. The nickel coatings were produced by applying two successive current densities. At first, the current density of 2 $A \cdot dm^{-2}$ was applied for 10 min [5,14], and then 5 $A \cdot dm^{-2}$ was immediately applied for 3 min. At first stage, a layer of micro-cone array was deposited at lower current density (2 $A \cdot dm^{-2}$ for 10 min). After that nano-cones were produced appropriately on the surface of former micro-cones at the higher current density (5 $A \cdot dm^{-2}$ for 3 min).

The surface morphology of the prepared coatings was observed using the scanning electron microscopy (SEM, Philips XL30). The preferred grain orientation of the coatings was assessed through X-ray diffraction (XRD) patterns measured by a diffractometer (Philips X'pert model). The wettability of the coatings was evaluated by measuring the contact angle of a water droplet of 4 μL placed on the coating surface using Theta Attension optical tensiometer (KSV Instruments) with the automatic multi-liquid dispenser, monochromatic cold light source and the accompanying software. The static water contact angles (WCAs) were measured at five different positions for each sample and the average value was reported as the contact angle value. The average roughness (R_a) of the coatings was acquired using an optical imaging profilometer Plμ 2300 (Sensofar) that operated at 100×. In order to investigate the corrosion behavior of the prepared coatings, the electrochemical impedance spectroscopy (EIS) tests were performed with an EG&G (model 263A) computer controlled potentiostat/galvanostat. The EIS tests were performed in 3.5 wt.% NaCl aqueous solution at room temperature using a three electrode system. A platinum plate and a saturated Ag/AgCl were used as the counter and reference electrodes, respectively. The frequency range studied was from 10^{-2} to 10^5 Hz. The EIS tests were started after 30 min immersion in NaCl solution and continued until substantially reducing the corrosion resistance. Potentiodynamic polarization curves were recorded after 30 min immersion in the test solution. The potential range for these measurements was fixed from −250 mV from the open circuit potential (OCP) value in the cathodic regime to 500 mV from OCP value in the anodic regime, at a scan rate of 1 $mV \cdot s^{-1}$.

In order to investigate the role of NH_4Cl in the plating bath, cyclic voltammetry (CV) and EIS tests were performed in two baths consisting of 0 and 200 $g \cdot L^{-1}$ NH_4Cl. Temperature, pH and other parameters were similar to those selected for producing the coatings, but, here, instead of stirring by the magnetic stirrer, rotating disk electrode (RDE, EG&G, model 636) was used and the copper substrates were cylindrical with the exposed area of 4 cm^2. All preparation steps applied for the preparation of copper disk substrates were also used for these samples. The cell used in the experiments consisted of cylindrical copper as the working electrode, platinum electrode as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. CV tests were performed from 0 to −1.5 V vs. OCP and the scan was reversed in −1.5 V vs. OCP (scan rate: 40 $mV \cdot s^{-1}$). EIS tests were performed at the corresponding potentials for 2 $A \cdot dm^{-2}$. These potentials were determined through galvanostatic tests.

3. Results and discussion

3.1. Electrochemical aspects of deposition and the effect of modifier

Fig. 1 shows cyclic voltammograms of nickel deposition onto the copper substrate in the presence (200 $g \cdot L^{-1}$) and the absence of NH_4Cl. It should be noted that during the electrodeposition, the cathodic reaction may be divided into nickel and hydrogen sub-reactions. In the literature, it has been shown that acid boric inhibits the formation of H_2 [24]; thus, the observed changes in electrochemical tests can be mainly ascribed to nickel reduction. In the absence of NH_4Cl, the onset of nickel reduction was E = −670 mV vs. SCE. Adding 200 $g \cdot L^{-1}$ NH_4Cl made a marked effect on the voltammogram. Here, the onset of reduction was shifted cathodically by ~90 mV, suggesting that NH_4Cl inhibited the initiation of nickel reduction. In both voltammograms, it could be seen that by reversing the potential scan, the backward reduction current density was equal to the forward reduction current density, but at the lower over-potentials, it became a little higher than the forward direction. Such a behavior is typical in the electrochemical deposition of metals on a foreign substrate in which an excess overpotential is required for nucleation; after that, growth of the metallic layer occurs at the characteristic redox potential of the metal, thereby leading to a trace crossing

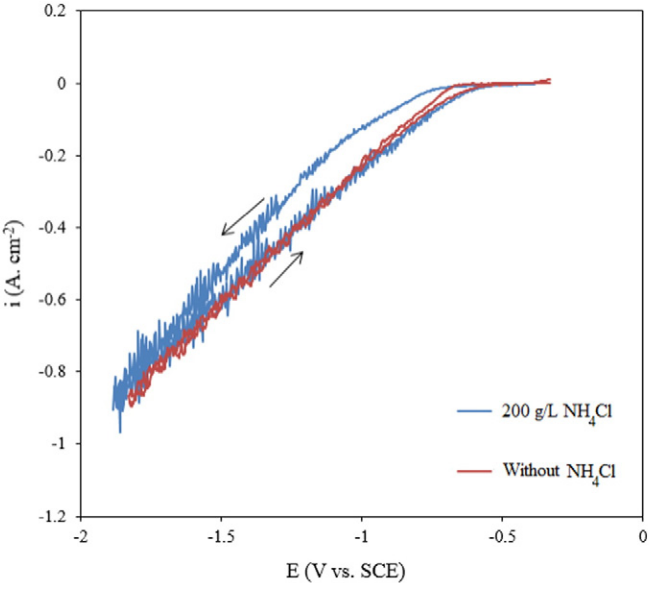

Fig. 1. Cyclic voltammograms obtained at nickel plating bath at 60 °C, 300 rpm at 40 $mV \cdot s^{-1}$ in the presence and absence of NH_4Cl.