



# Corrosion resistance and long-term durability of super-hydrophobic nickel film prepared by electrodeposition process



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## ARTICLE INFO

### Article history:

Received 4 February 2014

Received in revised form 18 March 2014

Accepted 19 March 2014

Available online 27 March 2014

### Keywords:

Nickel  
Electrodeposition  
Super-hydrophobic  
Micro-nano structure  
Corrosion resistance

## ABSTRACT

A super-hydrophobic nickel film with micro-nano structure was successfully fabricated by electrodeposition process. By controlling electrodeposition parameters and considering different storage times for the coatings in air, various nickel films with different wettability were fabricated. Surface morphology of nickel films was examined by means of scanning electron microscopy (SEM). The results showed that the micro-nano nickel film was well-crystallized and exhibited pine cone-like microstructure with nano-cone arrays randomly dispersed on each micro-protrusion. The wettability of the micro-nano nickel film varied from super-hydrophilicity (water contact angle  $5.3^\circ$ ) to super-hydrophobicity (water contact angle  $155.7^\circ$ ) by exposing the surface in air at room temperature. The corrosion resistance of the super-hydrophobic film was estimated by electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. The potentiodynamic curves revealed that the corrosion rate of superhydrophobic surface was only 0.16% of the bare copper substrate. Moreover, EIS measurements and appropriate equivalent circuit models revealed that the corrosion resistance of nickel films considerably improved with an increase in the hydrophobicity. The superhydrophobic surface also exhibited an excellent long-term durability in neutral 3.5 wt.% NaCl solution.

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## 1. Introduction

In recent years, super-hydrophobic surfaces with large water contact angle (CA) greater than  $150^\circ$  and a sliding angle (SA) below  $10^\circ$  have attracted an enormous amount of interest in both fundamental research and potential applications due to their unique properties such as water repellency [1–3], self-cleaning [4], anti-corrosion [5–7] and anti-icing [8–11]. It is demonstrated that super-hydrophobic surface can be fabricated via either creating micro-nanostructured hydrophobic surface or chemically modifying the micro-nanostructured surface with low surface free energy materials, or both [12–15]. Up to now, a number of methods have been successfully developed to produce artificial super-hydrophobic surfaces, including plasma etching [16], anodic oxidization [17], chemical vapor deposition [17,18], sol-gel method [19–21], phase separation [22], and electrodeposition [23,24,6,13]. Most of these methods involve either severe conditions or expensive materials, limiting their practical applications. Furthermore, such processes use organic substance to modify surface for reducing surface energy.

The modified surfaces are not stable and contaminate easily [25]. Therefore, increasing attempts have been made to fabricate super-hydrophobic surface without any low surface energy materials, such as the synthesis of lotus-like super-hydrophobic copper surfaces via electroplating in large current density [25]. Wang et al. [26] fabricated hierarchical nanostructured CuO surface by electrodeposition. The pristine super-hydrophilic CuO surface spontaneously transitioned to be super-hydrophobic after exposed in air at room temperature for about 3 weeks. They attributed the wettability change to the adsorption of oxygen molecules on the top layer. Hang et al. [24] prepared a surface with nickel micro-nano cone array by two electrodeposition steps, exhibited super-hydrophilic nature when freshly prepared. They reported the transition from super-hydrophilicity to super-hydrophobicity after exposing the surface in air for 15 days. This transition is attributed to the change of surface chemical composition and formation of NiO on nickel surface [27]. Several approaches have been proposed to improve the resistance of super-hydrophobic coatings to moderate shear stresses, mechanical abrasion and environmental contamination [10,28,29].

Nickel, as an essential engineering material, possesses good properties such as high hardness, corrosion resistance and magnetism. When deposited on copper surface, Ni can protect Cu surface from corrosion. Combined with super-hydrophobicity, it seems nickel coating could demonstrate its unique advantage,

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**Table 1**  
Operating conditions for electrodeposition of Ni films.

Specimens	Storage	Deposition-step 1		Deposition-step 2		Time of storage (day)
		Current density (mA cm <sup>-2</sup> )	Time (s)	Current density (mA cm <sup>-2</sup> )	Time (s)	
Smooth nickel film	No	40	300	–	–	0
	Yes	40	300	–	–	14
Micro-nickel film	No	20	600	–	–	0
	Yes	20	600	–	–	14
Micro-nano nickel film	No	20	600	50	60	0
	Yes	20	600	50	60	14

which can greatly broaden its applications such as anti-corrosion and anti-contamination materials. However, almost all the above efforts have been made to fabricate metallic super-hydrophobic structures without any low surface energy materials by electrodeposition; little attention has been paid to investigate properties of these super-hydrophobic surfaces such as corrosion resistance and long term stability. Therefore, the aim of this work is to study corrosion behavior of super-hydrophobic Ni coating via polarization and impedance spectroscopy.

## 2. Experimental procedure

Using direct current, nickel coatings were electrodeposited on copper substrates in disk shape having a surface area of 3.14 cm<sup>2</sup>. Before plating, the substrates were mechanically polished down to 4000 grit size using abrasive SiC papers followed by polishing with 0.3 mm alumina. The specimens were cleaned ultrasonically in acetone for 20 min, electropolished at 20 mA cm<sup>-2</sup> in a solution containing 70 g L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>, 10 g L<sup>-1</sup> KOH and 10 g L<sup>-1</sup> sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S) for 1 min and then activated in 10 wt% HCl at room temperature for 20 s, washed in distilled water, and then, immediately placed in the electrodeposition bath. The bath composition was NiCl<sub>2</sub>·6H<sub>2</sub>O (238 g L<sup>-1</sup>) as ions source, H<sub>3</sub>BO<sub>3</sub> (31 g L<sup>-1</sup>) as pH buffer and ethylenediammonium dichloride; C<sub>2</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub> (200 g L<sup>-1</sup>) as crystal modifier. The electrodeposition solution was kept at 60 °C and pH = 4.0. Using a digital coulometer (model BHP 2050), deposition was performed in a cell with platinum wire as counter electrode. The optimized operating conditions including current density and time are given in Table 1. The electrochemical cell was connected to an EG&G (model 263A) computer-controlled potentiostat/galvanostat. An EG&G ac responder (model 1025) was coupled with the mentioned potentiostat/galvanostat to read the ac impedance data. The counter electrode was a platinum wire and the reference electrode was an Ag/AgCl (Ag/AgCl, +0.197 V vs. SHE). All the potential values were referred to Ag/AgCl. The test solution for the corrosion investigations was 3.5% NaCl electrolyte at room temperature. Potentiodynamic polarization curves were recorded after 30 min of immersion in the test solution. The potential range for these measurements was fixed from –250 mV from the open circuit value (OCP) in the cathodic regime, to 500 mV from OCP value in the anodic regime, at a scan rate of 1 mV s<sup>-1</sup>. The corrosion current density (*i*<sub>corr</sub>) for the specimens was determined by extrapolating the anodic and cathodic Tafel slopes. Electrochemical impedance spectroscopy (EIS) measurements were performed from an initial frequency of 100 kHz to a final frequency of 10 mHz, with an AC sine wave with amplitude of 10 mV. The impedance spectra were collected after different immersion times (30 min, 24 h, 48 h, 72 h, 7 days, and 8 days). All EIS spectra were analyzed in Nyquist representation.

The microstructure and surface morphology of nickel films were studied using a scanning electron microscope (SEM) (model

Philips XL30). Water contact angle of the films was measured by a 4 μL water droplet at ambient temperature using an optical contact angle meter (Data physics OCA15 plus). The initial CA values reported the mean values from three measurements made on different locations of the sample surface. The surface roughness was measured by the Mitutoyo surfest (SJ210) roughness profile meter apparatus.

## 3. Results and discussion

### 3.1. Surface morphology

Fig. 1 shows SEM images of nickel film electrodeposited on Cu substrate in different conditions. Fig. 1a and b demonstrates the micrographs of nickel film fabricated at 40 mA cm<sup>-2</sup> for 300 s in the absence of crystal modifier. It is clear that the nickel film is relatively flat without protuberance. This result is in agreement with other investigations [30,31] that the typical morphology of nickel surface is almost flat. Fig. 1c and d shows the micrographs of microstructure nickel film prepared at 20 mA cm<sup>-2</sup> for 600 s in the presence of crystal modifier. This nickel film is deposited in one stage. According to Fig. 1c and d, nickel film is covered with micro-cone array structures which have an average size of 800 nm in height and 300 nm in width at half of maximum height. According to the literature, the surface morphology of nickel cone arrays is greatly influenced by the crystal modifier (C<sub>2</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>) [32]. The exact role of crystal modifier in electrodeposition process is not clear, but, one possible function of crystal modifier is to kinetically control the growth rates of different crystalline faces of nickel by interacting with these faces through adsorption and desorption [32]. SEM images of the micro-nano nickel film deposited at two stages are shown in Fig. 1e and f. At first stage, a layer of micro-cones array was deposited at lower current density of 20 mA cm<sup>-2</sup> for 600 s (same as micro nickel film). After that nano-cones were deposited onto the surface of former micro-cones at a higher current density of 50 mA cm<sup>-2</sup> for 60 s as second stage. The duration and current density of deposition greatly affect the morphology of nickel film [33], indicating that the size of micro- and nano-cones can easily be controlled. It has been widely reported that increasing the current density leads to a corresponding decrease of the grain size of the deposits [34,35]. This behavior is attributed to the evolution of more hydrogen at the cathode surface at higher current densities. The presence of hydrogen modifies the growth interface on the cathode by influencing the surface energy and growth mechanisms, which finally will facilitate the formation of smaller grains in the deposited layer [34]. From Fig. 1e, it can be seen that the surface was fully and compactly covered with small micro-protrusions. The micro-protrusions were the pinecone-like with average diameter of 1 μm. The enlarged view of the pinecone-like micro protrusions (Fig. 1f) reveals that on the surface of each micro-protrusion, numerous irregular nano-cones structures with diameters ranging from dozens to hundreds of nanometers were dispersed. This

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