Relationship between the structure and water repellency of nickel–cobalt alloy coatings prepared by electrodeposition process

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ABSTRACT

The combination of suitable hierarchical structure and low surface energy plays a vital role in fabricating super-hydrophobic coatings on hydrophilic metal substrates. The present study introduces a highly anti-corrosion and self-cleaning super-hydrophobic Ni–Co alloy coating fabricated by electrodeposition process. Based on the structures grown at various process parameters, different morphologies including nano-cones and flower-like were obtained. The relation between surface morphologies and wettability behavior was investigated in detail. The surface of Ni–Co coatings freshly grown on copper substrate was super-hydrophilic with water contact angle below 10°. However, without further processing, the wettability transited from super-hydrophilic nature to a super-hydrophobic one by passing time under ambient condition. The results showed that when the deposition current density falls in the range 20–30 mA cm^{-2} with times longer than 600 s, the water contact angle on the Ni–Co coating was as high as 160°, and sliding angle was ultra-low (below 5°). A detailed XPS analysis indicated that this wettability transition was mainly caused by adsorption of airborne hydrocarbons onto the coating surface. The potentiodynamic polarization curves revealed that the super-hydrophobic film has considerably improved the corrosion performance of the Ni–Co alloy coating. Moreover, the super-hydrophobic surface showed a strong self-cleaning property.

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1. Introduction

Lotus leaf exhibits excellent water repellency due to the synergistic effect of hierarchical rough structure and hydrophobic wax on the surface [1–3]. By mimicking nature, artificial super-hydrophobic surfaces have been fabricated by creating rough structures on intrinsically hydrophobic surface or chemical modification of rough surfaces with low surface energy materials [4]. Up to now, various methods have been explored to fabricate super-hydrophobic surfaces such as chemical etching [5], chemical vapor deposition [6], hydrothermal synthesis [7,8] anodic oxidation [9,10] and electrodeposition [11–15]. However, most of the methods involve severe conditions or expensive materials, limiting their practical applications. Furthermore, the hydrophobicity of chemically modified surfaces is not stable over time, which brings major problems to the artificial super-hydrophobic surfaces [4,16]. There have been numerous reports [17,18] converting intrinsically hydrophilic surfaces to super-hydrophobic by constructing a rough surface structure without artificial modification using organic substances. Due to the inherent roughness provided by micro- and nano-scale multilayers, hierarchical structured surfaces could exhibit super-hydrophobic property. But, to

date, the effect of size and distribution of hierarchical structures on super-hydrophobic property has not been clarified. In addition, it is not very clear why the smooth hydrophilic metal surfaces become super-hydrophobic only by formation of micro/nanostructures without further processing [19].

The objectives of the present work are to introduce a super-hydrophobic Ni–Co alloy coating by a facile method without further modification, to study the relation between size and distribution of hierarchical structures on wettability property and to investigate the possible reason for transition from super-hydrophilicity to super-hydrophobicity.

2. Experimental procedure

2.1. Preparation of Ni–Co alloy coatings

Using direct current, nickel–cobalt alloy coatings were electrodeposited on copper substrates. The substrates were disc shaped, having a surface area of 3.14 cm^2. Specimens were mechanically polished down to 4000-grit size by using abrasive SiC papers followed by polishing with 3 μm alumina. Prior to electrodeposition, the specimens were cleaned ultrasonically in acetone for 20 min, electropolished at 20 mA cm^{-2} in a solution containing 70 g L^{-1} Na$_2$CO$_3$, 10 g L^{-1} KOH and 10 g L^{-1} sodium dodecyl sulfate (C$_{12}$H$_{25}$NaO$_4$S) for 1 min and then activated in 10 wt.% HCl at room temperature for 20 s, washed in

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distilled water, and then immediately placed in the electrodeposition bath. The optimized bath composition and the operating parameters are given in Table 1. In the electrodeposition process, H_3BO_3 was added into bath as a buffer agent and ethylenediammonium dichloride ($C_2H_{10}Cl_2N_2$) as a crystal modifier. The pH of the bath was adjusted at 4 by adding NaOH solution. Using a digital coulometer (model BHP 2050), deposition was performed in a cell with platinum wire as counter electrode. To investigate the effect of deposition current density, electrodeposition was performed at different current densities (20–50 mA cm^{-2}) with corresponding time. After deposition, the coating surfaces were rinsed with twice distilled water and dried at ambient temperature. Then, the nickel–cobalt surfaces were stored in desiccator for further tests.

2.2. Characterization

The surface morphology of the coatings obtained were examined by a field emission gun scanning electron microscope (FEG–SEM) utilizing HITACHI 4800 instrument, operated at 10 keV for secondary electron imaging.

X-ray diffraction (XRD) measurements were carried out using a Bruker AXS D8 diffractometer. The X-ray tube was equipped with a Goebel mirror optic to obtain a parallel and monochromatic X-ray beam. The 2θ scan varied between 30° and 100° with a step size of 0.02° and Co K$_\alpha$ radiation ($\lambda = 0.178897$ nm).

Roughness measurement (R_a) were examined by using an optical imaging profilometer Plµ 2300 (Sensofar) operated at 100×. The cited R_a values were an average of five measurements. The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired with a VG-CLAM analyzer in a high vacuum using a magnesium anode with an acceleration voltage of 5 keV and a sample current of 1.2 µA. Surface contact angles were measured using distilled water using a Theta Attension optical tensiometer (KSV Instruments) with automatic multi-liquid dispenser and monochromatic cold light source. Contact angles were calculated using the Young–Laplace drop profile fitting method. Each contact angle value was cited as an average of three measurements performed at three different locations on the specimen surface. An average of 30 frames has been used to calculate the contact angle for each drop. The water droplet size used for the measurements was 4 µL. The water sliding angle of the superhydrophobic surfaces was measured using a Theta Attension optical tensiometer at ambient temperature.

For the electrochemical characterization, potentiodynamic polarization curves were performed in a three electrode cell using an Ag/AgCl reference electrode and a platinum wire as the counter electrode. All corrosion tests were carried out in 3.5 wt.% NaCl solution at room temperature. The potential range for these measurements was similar from −250 mV for the open circuit value (OCP) in the cathodic regime, to 500 mV from OCP value in the anodic regime, at a scan rate of 0.166 mV s^{-1}. The corrosion current density (i_{corr}) for the specimens was determined by extrapolating the anodic and cathodic Tafel slopes.

3. Results and discussion

3.1. Microstructure

The influence of current density and deposition time on surface morphology was investigated where the other operating parameters were

Table 1
Bath composition and operating conditions for electrodeposition of Ni–Co coating.

Bath composition	Concentration (g L^{-1})	Condition
NiCl$_2$·6H$_2$O	240	Current densities (20–50 mA cm^{-2})
CoCl$_2$·6H$_2$O	40	Temperature 60 °C
H$_3$BO$_3$	30	Time of deposition (240–900 s)
C$_2$H$_{10}$Cl$_2$N$_2$	200	pH 4, under stirring

kept constant. In order to obtain films with the same thickness (4 and 6 µm for lower and higher deposition time, respectively), the time was tuned regarding the deposition current density according to Faraday's law. The cross-section morphology of the electrodeposited Ni–Co alloy coatings was analyzed by SEM as shown in Fig. 1a and b. It can be seen from Fig. 1a and b that the thickness of Ni–Co alloy coatings was approximately 4 and 6 µm, respectively. In addition, there was no crack on the coating and can also be found that the adhesion between the Ni–Co alloy coating and copper substrate was good. The electric charge during electrodeposition was kept constant at 37 C for coatings in (Fig. 2a, c and e) and at 56 C for coatings in (Fig. 2b, d and f). Fig. 2a shows surface morphology of Ni–Co alloy coating deposited at current density of 20 mA cm^{-2} for 600 s. Clearly, micro-flowerlike structures are distributed on the coating surface. The micro-flowers are featured with nano-cones of diameters ranging 100–500 nm and spiral steps on their side faces. With further prolonging the time of deposition to 900 s (Fig. 2b), both coating thickness and size of micro-flowers have increased. Based on the theoretical point, various crystal growth parameters including the current density, concentration of electrolyte, deposition time and temperature act as effective parameters to impact the metallic crystal growth rate and the resultant morphology [20,21]. The surface morphology of the Ni–Co alloy coating deposited at current density of 30 mA cm^{-2} and 400 s is shown in Fig. 2c. Comparison of Fig. 2a and c reveals that by increasing the current density, the Ni–Co structure becomes finer and turns into a pyramid one. This phenomenon relates to the variation of nucleation and growth rates of deposits. The effect of over-potential enhances with the increase of current density [22]. As a result, the nucleation rate of deposits becomes higher than the growth rate leading to a finer structure. However, with further deposition time (600 s), the pyramid cones have turn to the microflower like features and distribution of the flower-like pattern became more uniform (Fig. 2d). It seems that by increasing the time of the deposition process, a uniform hierarchical structure is achieved. At higher current density of 50 mA cm^{-2} and 240 s (Fig. 2e), surface morphology is composed of very small and compact nano-cones. Also, small flowerlike structures can be seen. Then, by increasing the current density to 50 mA cm^{-2}, a large number of nucleates with a small average growth rate of each nucleus is formed. However, there is some non-uniformity in the structure. The surface morphology of the Ni–Co alloy coating deposited at current density of 50 mA cm^{-2} at 360 s is shown in Fig. 2f. The micrograph exhibits that the flower size has become bigger with the increase of deposition time. Prolonging the deposition time at this current density resulted in some large micro-flower structures appeared at some local areas of the nickel-cobalt coating.

3.2. Wettability

3.2.1. Hydrophilicity of the freshly Ni–Co coatings

The copper surface was hydrophilic and its contact angle was around 85° (Fig. 3a). Water droplets on all of the freshly prepared Ni–Co coatings spread quickly over the surface with a contact angle below 10° (Fig. 3b). Thereby, the freshly coatings exhibited super-hydrophilicity character. The freshly Ni–Co coatings can be modeled by the Wenzel theory [23,24], $\cos \theta = r \cos \theta_0$, where θ represents the apparent contact angle of water on the actual surface, θ_0 is the equilibrium contact angle on a smooth surface and r is the surface roughness ratio defined as the actual area divided by the projected area. From the Wenzel's equation, it can be seen that the roughness decreases water contact angle of surfaces with $\theta < 90°$ and increases water contact angle of surfaces with $\theta > 90°$ [25]. Metals having high surface energy show water contact angles less than 90° on a smooth surface [21]. Increasing the surface roughness of these materials further decreases the contact angle of water droplets on the surface [26]. Evidently, increasing the surface roughness with deposition of Ni–Co coating on copper substrate (Table 2), increases r factor of the Wenzel model and hence the water contact angle reduces on the freshly Ni–Co coating. When a water