Corrosion Science 94 (2015) 190–196

Contents lists available at ScienceDirect

Corrosion Science

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

Corrosion inhibition of biomimetic super-hydrophobic electrodeposition coatings on copper substrate

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ARTICLE INFO

Article history:
Received 10 November 2014
Accepted 2 February 2015
Available online 21 February 2015

Keywords:
A. Copper
B. EIS
B. XPS
C. Electrodeposited films
C. Interfaces

ABSTRACT

Inspired by the special microstructure of plant leaves such as lotus leaves, we prepared super-hydrophobic surfaces by a fast, facile, and one-step electrodeposition on copper substrates. The prepared surface revealed super-hydrophobicity with a contact angle value of 161.5° ± 2°. Meanwhile, corrosion resistance of obtained coatings was evaluated by electrochemical measurement in detail. These results indicated that electrodeposition coatings provided greater protection against corrosion behavior. Moreover, the super-hydrophobicity improved corrosion resistance of the coating. This method can be easily extended to other conductive materials and time-saving, having a great potential for future application in industrial fields.

1. Introduction

Copper is an important material because of its high electrical and thermal conductivity, mechanical workability, fine appearance and low chemical reactivity [1–3]. Copper is widely used in many applications such as conductors in electrical power lines, pipelines for domestic and industrial water utilities including seawater, and heat conductors and heat exchangers [4,5]. However, hydroxides and toxic complexes form on copper in wet environments [6]. Thus, the issue of corrosion prevention of copper has attracted the attention of a number of investigators [7–9]. The corrosion resistance of copper can be significantly improved by reducing the contact area between water and copper surfaces [10–12], thereby suggesting that transforming bare copper surfaces into super-hydrophobic surfaces would improve the corrosion resistance of these surfaces.

In nature, a great number of biological materials possess special surface wettability [13–15]. For example, lotus leaves exhibit super-hydrophobicity and possess self-cleaning property, which is called "lotus effect" [16]. Due to the high adhesion to water, the rose petal becomes another relatively typical biological prototype in the super-hydrophobic research [17]. In addition, anisotropic rice leaves, desert beetles and spider silks with water collecting effects, butterfly wings, mosquito eyes, moth eyes, cicada wings, etc., also have their own special wetting behavior. Studies on these organisms' microscopic structure texture reveal the presence of the micro/nano hierarchical structure on the surface, and this structure is the main cause for the observed different wettability [18,19]. Moreover, other special chemical components are also important factors in creating the binary structure with self-cleaning effects. Inspired by these creatures, two elements are needed to realize special wettability on functional surfaces: a surface chemical composition and a rough surface with special hierarchical micro/nano structures [20,21]. However, a super-hydrophobic surface with low surface energy and micro/nano binary structure is difficult to create.

In recent years, various methods have been proposed for the fabrication of bio-inspired super-hydrophobic surfaces and corrosion resistance properties on the metal materials; these methods include electrochemical modification [12], sol–gel methods [22,23], graft polymerization [24], immersion method [25–27], and self-assembled monolayers (SAMs) [28], etc. However, compared with most of these methods, electrodeposition does not require such severe conditions as tedious chemical treatments, expensive materials, complex multi-step processing procedures, or expensive equipment, which limit practical applications [29–32]. Electrodeposition technology is cheap, simple, and highly effective. Beyond that, by setting different parameter values, the surface microtopography will also change correspondingly.

To improve the super-hydrophobicity and corrosion resistance of copper substrate, we tested the capability of coatings obtained via rapid one-step electrodeposition. The relationships among the electrodeposition voltage, microstructure, and wettability of the

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http://dx.doi.org/10.1016/j.corsci.2015.02.009
0010-938X/

deposited Ce coating are discussed in detail. We found that the obtained coatings were effective in preventing corrosion of copper substrate.

2. Experimental

2.1. Materials

Anhydrous ethanol, myristic acid, and sodium chloride ($\geqslant$96%) of analytical grade were used as received. Cerium chloride ($CeCl_3{\cdot}6H_2O$) was used without further purification.

2.2. Sample preparation

All of the prepared surfaces were produced by the same process. The detailed process is shown as follows. First, two cleaned copper plates with dimensions of 60 mm $\times$ 25 mm $\times$ 3 mm were abraded with silicon carbide papers (from 400 to 800 grades), ultrasonically washed with distilled water, and dried under atmosphere condition. Second, 0.038 M cerium chloride and 0.1 M myristic acid were immersed in ethanol under constantly stirring until a uniform electrolyte solution (150 ml) was obtained. Third, the two copper plates were used as cathode and anode in an electrolyte cell, and a direct current (DC) voltage of 20 V was applied to the electrodes with a distance of 2 cm. After being subjected to electrolysis for 30 min, the working electrode was rinsed thoroughly several times with distilled water and ethanol and was then dried under atmosphere condition. As a result, a cathodic surface was obtained. Samples with various deposition voltages were produced at the same time.

2.3. Sample characterizations

The surface morphology of the obtained coating was characterized by field emission scanning electron microscopy (FESEM, S4800, Japan Electronic) at 15 kV. The corresponding chemical composition was examined by X-ray photoelectron spectroscopy (XPS, SPECS XR50) attached with the SEM. Contact angles were measured by a contact angle meter (JC2000A Powereach, China) at ambient temperature for each surface. Water droplets (2 μL) were dropped on the super-hydrophobic coatings from a distance of 0.2 cm by vibrating the burette. All of the water contact angles were measured at five different points and then averaged.

Electrochemical corrosion behavior was examined by potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) in a standard three-electrode cell configuration with a saturated calomel electrode (SCE) as the reference electrode, a platinum electrode as the auxiliary electrode, and the bare Cu or coated Cu samples as the working electrode. Measurements were performed by an electrochemical workstation (GAMRY Reference600, America) at room temperature in the 3.5 wt.% NaCl solution. Before electrochemical experiments, these samples were immersed in the NaCl solution for 5 min to get a more stable system. In the electrochemical tests, samples were mounted with a surface area of 1 cm^2 exposed to the corrosive medium. The potentiodynamic polarization curves were acquired at a scan rate of 10 mV/s. EIS measurement was operated in the frequency range of 10^5–10^{-2} Hz at the open circuit potential with the amplitude of the perturbation voltage of 10 mV. EIS results were analyzed by fitting data with the Zsimpwin software. All electrochemical-based experiments were repeated three times, and obtained very good reproducibility.

3. Results and discussion

3.1. Surface morphology

Surface morphology is an important parameter of super-hydrophobic properties, therefore, coatings were characterized by scanning electron microscopy. Fig. 1 shows the SEM images of the obtained surface at different deposition voltages. Fig. 1a shows the SEM image of a cathode surface with electrodeposition DC voltage of 5 V. This surface looks smooth and there are almost no obvious structures on it. As the voltage increased to 10 V, microstructures appeared on the substrate surface, and these irregular micro/nano structures exhibit porous, and are not evenly distribut-

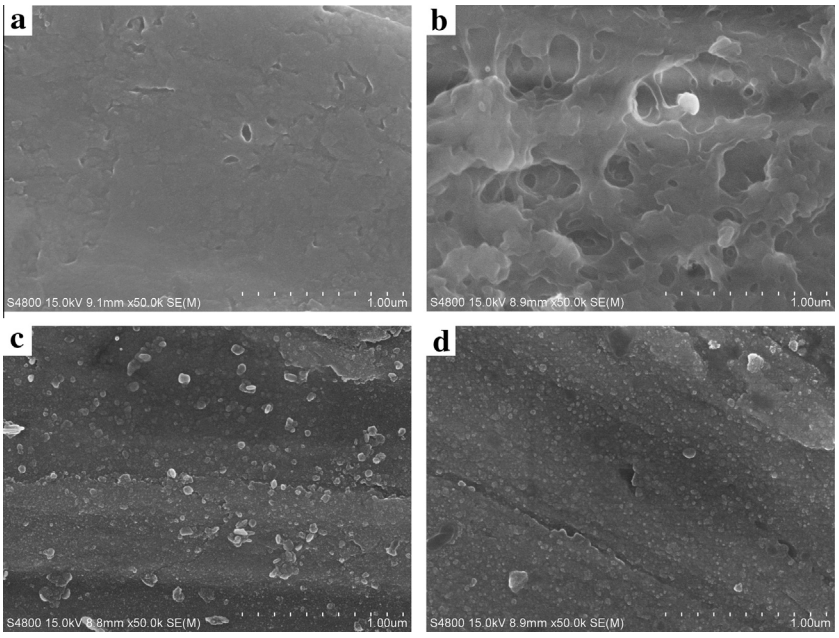

Fig. 1. SEM images of the as-prepared surfaces at different deposition voltages in the electrolyte consisted of 0.038 M cerium chloride and 0.1 M myristic acid 30 min. (a) 5 V; (b) 10 V; (c) 15 V and (d) 20 V.