



Preparation of silver-cuprous oxide/stearic acid composite coating with superhydrophobicity on copper substrate and evaluation of its friction-reducing and anticorrosion abilities



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ABSTRACT

A simple two-step solution immersion process was combined with surface-modification by stearic acid to prepare superhydrophobic coatings on copper substrates so as to reduce friction coefficient, increase wear resistance and improve the anticorrosion ability of copper. Briefly, cuprous oxide (Cu_2O) crystal coating with uniform and compact tetrahedron structure was firstly created by immersing copper substrate in 2 mol L^{-1} NaOH solution. As-obtained Cu_2O coating was then immersed in 0.33 mmol L^{-1} AgNO_3 solution to incorporate silver nanoparticles, followed by modification with stearic acid (denoted as SA) coating to achieve hydrophobicity. The surface morphology and chemical composition of silver-cuprous oxide/stearic acid (denoted as Ag- Cu_2O /SA) composite coating were investigated using a scanning electron microscope and an X-ray photoelectron spectroscope (XPS); and its phase structure was examined with an X-ray diffractometer (XRD). Moreover, the contact angle of water on as-prepared Ag- Cu_2O /SA composite coating was measured, and its friction-reducing and anticorrosion abilities were evaluated. It was found that as-prepared Ag- Cu_2O /SA composite coating has a water contact angle of as high as 152.4° and can provide effective friction-reducing, wear protection and anticorrosion protection for copper substrate, showing great potential for surface-modification of copper.

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1. Introduction

Inspired by the water-repellent natural surfaces such as the lotus leaf and the rose petals which show a micro-nano hierarchically rough structure together with a waxy coating [1–4], researchers are keeping a watchful eye on superhydrophobic surfaces with a water contact angle (WCA) higher than 150° [5]. Due to the excellent property of superhydrophobic surfaces, they can potentially be used in anti-corrosion [6], no loss transport of micro-droplets [7], oil-water separation [8,9], and friction reduction [10].

Metals are often selected as structural materials in engineering, because of their desired electrical, thermal, and mechanical properties. However, various metals are usually liable to oxidation, corrosion and wear, which greatly hinders their practical applications in industry [11,12]. To overcome this drawback, researchers often apply various surface-modification techniques to fabricate coating and/or film on metal surfaces.

Among various metals, copper is widely used in industry due to its excellent electrical and thermal conductivity, good mechanical workability, and relatively noble properties [13–15]. Nevertheless, copper is liable to corrosion upon contact with air, water or other substances, and it possesses fair friction and wear behavior [16,17]. This is why many studies have been conducted to prepare superhydrophobic surfaces on copper plate by solution-immersion process [18–20], electrochemical process [21,22], etching [23], electrical deposition [24], in-situ method [25], and surface oxidation [26,27]. It has been found that superhydrophobic surfaces could provide effective corrosion resistance to copper plate [13,16,28–30]. Therefore, in the present research, we adopt a facile solution immersion method to fabricate stable superhydrophobic coatings with low friction and good anticorrosion and antiwear abilities on copper substrates so as to retard its corrosion and wear in engineering applications [10,31–34]. Silver is incorporated into the composite coating, since it is a good solid lubricant and also possesses good electrical and thermal conductivity. Stearic acid (denoted as SA) is adopted to endow the composite coating with superhydrophobicity, because it is readily available and well applicable to lowering surface free energy [35,36]. This paper reports the preparation of superhydrophobic silver-cuprous oxide/stearic acid composite coating (denoted as Ag- Cu_2O /SA) on copper substrate and

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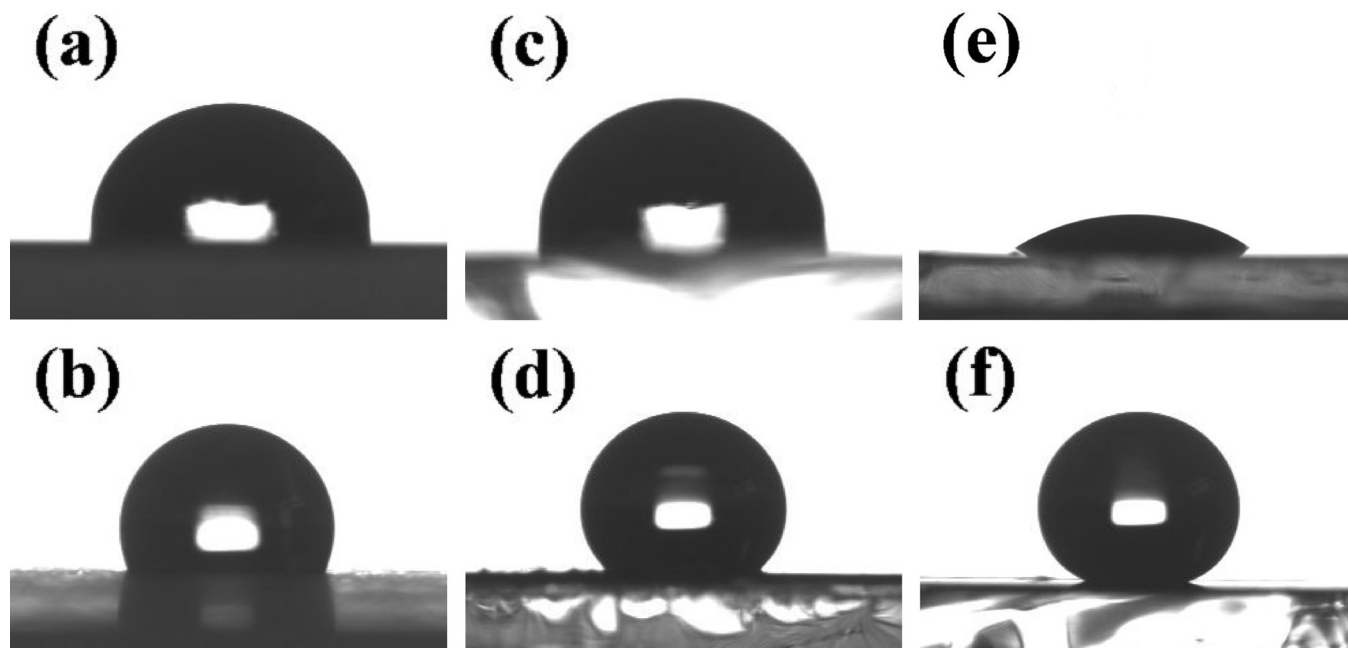


Fig. 1. Optical microscopic images of water droplets on (a) bare copper surface, (b) copper surface treated with SA, (c) Cu_2O on copper plate, (d) SA overcoat on sample (c), (e) Ag- Cu_2O coating, and (f) Ag- Cu_2O /SA composite coating.

evaluation of its friction-reducing and antiwear performances as well as anticorrosion ability.

2. Experimental section

2.1. Materials

Copper plate substrate ($10\text{ mm} \times 20\text{ mm} \times 0.1\text{ mm}$; purity 99.8%) was provided by Sinopharm Chemical Reagent Company Ltd (Shanghai, China). Analytical reagent sodium hydroxide (NaOH; purity 96%) and silver nitrate (AgNO_3 ; purity 99.6%) were commercially obtained from Tianjin Kemiou Chemical Reagent Company Ltd (Tianjin, China). Analytical reagent stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, denoted as SA) was purchased from Zhengzhou Chemical Reagent Factory (Zhengzhou, China).

2.2. Preparation of silver-cuprous oxide/stearic acid composite coatings

Copper plates were polished mechanically with No. 3000 and No. 5000 abrasive paper to remove surface oxides and organic compounds. As-polished copper substrates were promptly cleaned ultrasonically with deionized water, acetone, and pure ethanol, respectively, followed by 1 min of immersing in 1 mol L^{-1} HNO_3 solution to provide fresh and active surfaces. After being washed again with deionized water and dried with N_2 , the copper substrates were sequentially immersed in 2 mol L^{-1} NaOH for 72 h and in 0.33 mmol L^{-1} AgNO_3 for 6 h to afford silver-cuprous oxide (denoted as Ag- Cu_2O) coating. Resultant Ag- Cu_2O coating was rinsed with deionized water and dried, and finally immersed in 2 mmol L^{-1} stearic acid ethanol solution for 12 h to afford silver-cuprous oxide/stearic acid (denoted as Ag- Cu_2O /SA) composite coatings. As-obtained Ag- Cu_2O /SA composite coatings were rinsed with ethanol and dried with nitrogen stream to provide the samples for characterization.

2.3. Characterization of Ag- Cu_2O /SA composite coating

The surface morphology, crystal structure, and chemical composition of as-prepared Ag- Cu_2O /SA composite coatings were investigated using a scanning electron microscope (SEM, JSM-5600LV, JEOL Ltd., Japan), an X-ray diffractometer (XRD, X' Pert Pro MPD, Philips, Netherlands; copper target tube, incident beam monochromator, $\lambda = 1.54056\text{ \AA}$) and an X-ray photoelectron spectroscope (XPS, Kratos Analytical Ltd., UK; monochromatic Al $K\alpha$ source, $h\nu = 1486.6\text{ eV}$).

Contact angle measurement of deionized water (about $4\text{ }\mu\text{L}$) on as-prepared Ag- Cu_2O /SA composite coatings was conducted with a remote computer-controlled goniometer system (Dropmaster 300, Kyowa Interface Science, Japan) under static condition. Repeat measurements were conducted, and the average value of five measurements obtained at different positions of the same as-prepared samples is cited as the final contact angle in this article.

A UMT-2 multi-specimen test system (CETR, USA) was performed to evaluate the friction-reducing and antiwear abilities of as-prepared superhydrophobic coatings on copper substrate sliding against steel (440c steel ball, diameter 4 mm) under reciprocal mode. Before each test, the steel ball was cleaned with acetone in a supersonic bath. The sliding tests were conducted under a temperature of about $16\text{ }^\circ\text{C}$, a relative humidity of about 20%, an applied load of 0.4 N, and a rotary speed of 30 rpm. Friction coefficient-time plots were automatically recorded by the test rig.

Moreover, the anticorrosion ability of Ag- Cu_2O /SA composite coating was evaluated based on immersion tests in saline solutions and litmus pH indicator solutions with different pH values (pH 4 or 12) in association with subsequent measurement of WCA and/or observation of the immersed coating surfaces or liquid droplets thereon by optical microscopy. In addition, the image of the water droplet on Ag- Cu_2O /SA composite coating immersed in 3.5 wt.% sodium chloride solution at room temperature for three days and the images of the droplets with different pH values ranging from 1 to 13 were also observed with optical microscope so as to estimate the anticorrosion ability of the composite coating.

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