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Self-assembly of organic acid molecules on the metal oxide surface of a cupronickel alloy

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ABSTRACT

Corrosion of the metal oxide surface of cupronickel (CuNi) alloys is a problem in applications such as household water pipes, industrial pipelines, and marine vessels. On other substrates, thin films have been used as barriers to corrosion. Here, the formation of self-assembled monolayers (SAMs) on the CuNi metal oxide surface has been investigated. Stable, well-ordered SAMs of octadecylphosphonic acid (ODPA) and 16-phosphonohexadecanoic acid (COOH-PA) were formed on the metal oxide surface of CuNi foils (55% Cu/45% Ni) using a solution deposition method. The ODPA modified surfaces could be used to provide a non-reactive barrier that inhibits corrosion of the CuNi metal oxide surface. Meanwhile, COOH-PA films could be used for further surface reactions such as surface initiated polymerization, in which polymer coatings are grown directly from a well-ordered film. Film-modified surfaces were characterized using diffuse reflectance infrared Fourier transform spectroscopy, contact angle analysis, and matrix assisted laser desorption ionization time of flight mass spectrometry. The ability of the films to inhibit corrosion by limiting oxidation of the CuNi surface was assessed using cyclic voltammetry.

1. Introduction

The surface of the cupronickel alloy (CuNi) is readily corroded in the presence of water by the formation of a reactive metal oxide layer [1,2]. This is an issue because CuNi alloys are used in many applications, such as in marine vessels and pipelines, where structural integrity is crucial and the material is exposed to water [3,4]. In these applications, corrosion is facilitated through biofouling, which occurs when bacteria and marine organisms adhere to the surface [5–7]. Previous approaches to limit marine biofouling have consisted of using coatings that actively release biocidal toxins such as cuprous oxide, tributyltin, and diuron [8–10]. This active release strategy is suboptimal for two main reasons. First, the coatings are usually not strongly bound to the surface and can delaminate, exposing the metal oxide surface to corrosive biofouling. Second, the release of toxic biocides has been shown to adversely affect the marine ecosystem [9]. Therefore, an alternate, passive approach is necessary to inhibit biofouling and limit the disruption of the marine ecosystem [4,6,11]. One such strategy consists of controlling the interfacial reactivity of the metal oxide surface using strongly adhered thin films or polymer coatings [6,11]. In a first approach, methyl terminated films of octadecylphosphonic acid (ODPA) were formed on the surface of a CuNi alloy. This method aims to limit corrosive biofouling by forming non-reactive interfaces consisting of self-assembled organic molecules.

In addition, self-assembled monolayers (SAMs) can be used as a platform for surface engineering to control the reactivity of the CuNi metal oxide surface [12,13]. One way to accomplish this is by changing properties such as the functional tail groups of the film molecules [12]. In order to accomplish this, carboxylic acid terminated films of 16-phosphonohexadecanoic acid (COOH-PA) were formed on the surface of CuNi. The COOH-PA films could be used to provide a uniform, reactive surface for further organic reactions such as generating polymer coatings grown directly from the surface [14]. In this approach, the tail group of a well-ordered thin film provides a network of densely packed initiator sites for polymerization to occur. The self- assembling ODPA and COOH-PA films formed on CuNi were characterized using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, contact angle analysis, and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS). Film stability was further examined after sonication in water and a brine solution and the ability of the films to inhibit oxidation of the CuNi surface was evaluated using cyclic voltammetry.

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2. Experimental section

2.1. Materials

Octadecylphosphonic acid (ODPA) was obtained from Alfa Aesar, 16-phosphonohexadecanoic acid (COOH-PA, 97%) from Sigma Aldrich, and α-cyano-4-hydroxycinnamic acid (CHCA) was purchased from Fluka and were used as received. Tetrahydrofuran (THF) optima grade solvent was obtained from Fisher Scientific and was distilled over sodium and benzophenone before use. Cupronickel alloy (CuNi: 55% Cu/45% Ni), copper (Cu) and nickel (Ni) foils of 0.25 mm thickness were obtained from Goodfellow, Inc. and prepared as follows.

2.2. Preparation of the foils

Foils of CuNi, Cu, and Ni were sanded (150, 320, 400, 600 grit sandpaper) then cut into 1 cm × 1 cm × 0.25 mm coupons. Cleaning consisted of rinsing the CuNi coupons with acetone and sonicating in methanol for 30 minutes followed by immersing coupons in boiling methanol for 10 minutes. This cleaning procedure served to remove organic residue and metal dust from the surface. The clean coupons were placed in a 100 °C oven to dry.

2.3. Preparation of the brine solution

A brine solution was prepared as described by Liu et al. [15]. Briefly, the following salts were added to 500 mL of deionized water: 0.009 g $FeCl_3$, 12.063 g $MgCl_2 \cdot 6H_2O$, 2.245 g KCl, 88.586 g NaCl, 0.005 g $BaCl_2 \cdot 2H_2O$, 3.045 g $SrCl_2$, and 35.839 g $CaCl_2 \cdot 2H_2O$. The brine solution models an environment with high salinity and was used to evaluate the stability of films for use in marine applications that were formed on CuNi as described below.

2.4. Film deposition procedures

2.4.1. Octadecylphosphonic acid (ODPA) film deposition

Films of ODPA on CuNi were prepared using a solution deposition method. A 1 mM solution of ODPA in distilled THF was prepared and heated to 50 °C. Cleaned coupons were cooled on ice for 60 minutes and then placed in the 50 °C ODPA solution and heated for 30 minutes. After 30 minutes, the coupons were removed and placed in a 100 °C oven for approximately 8–12 hours.

2.4.2. 16-Phosphonohexadecanoic acid (COOH-PA) film deposition

Films of COOH-PA were formed on CuNi coupons using a solution deposition method. A 1 mM solution of COOH-PA in distilled THF was prepared and stored at ambient temperature (20 °C). Cleaned CuNi coupons were immersed in solution for 1 hour, removed, and placed in a 100 °C oven for approximately 8–12 hours.

2.5. Film characterization techniques

2.5.1. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

DRIFT spectroscopy was primarily used to confirm film deposition on CuNi coupons. A Nexus 470 Fourier transform infrared spectrometer with the DRIFT attachment was used to analyze the functional group stretching regions of molecules bound at the surface. Film stability was examined by analyzing substrates after rinse (15 minutes) and sonication (15 minutes) in each THF, water, and a concentrated brine solution. Each sample run consisted of 1024 scans at 4 cm^{-1} resolution.

2.5.2. Contact angle analysis

Contact angle analysis was used to evaluate the wetting properties of ODPA and COOH-PA films formed on CuNi. In contact angle analysis, a 1 μL droplet of test liquid is placed in contact with a surface and the advancing contact angle (θ) the liquid makes with the surface is measured [16]. A Video Contact Angle (VCA) 2000 instrument was used to deposit 1 μL of deionized water on the CuNi coupon surface for analysis. The left and right advancing angles of the test liquid contacting the coupon surface were measured. Contact angles were acquired in four different spots on each of three samples. The mean and standard deviation of each film-modified coupon were calculated and compared to data collected for the control CuNi surface.

2.5.3. Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS) analysis

MALDI-TOF MS was used to differentiate between monolayer films and those with aggregate multilayers [17]. An Agilent Technologies model G3250AA LC/MSD-TOF mass spectrometry system with model G1969A AP MALDI source was used in positive mode. Spectra were collected using a capillary voltage of 3300 V, fragmentor voltage of 330 V, and skimmer voltage of 60 V. Nitrogen drying gas purged the instrument at a rate of 10 L $minute^{-1}$. The film-modified CuNi coupons were attached to the MALDI target with double sided tape. A matrix solution of CHCA (10 mg mL^{-1}) was prepared in distilled THF and spotted in 1 μL droplets on the substrate using a dried droplet method. Three areas on each of three coupons were examined to determine if the films formed on CuNi were monolayers.

2.5.4. Cyclic voltammetry (CV)

Corrosion inhibition was assessed using CV to determine if ODPA and COOH-PA films reduced oxidation of the CuNi surface. Measurements were taken using a VersaSTAT3 system (Princeton Applied Research, Inc.). Voltammograms were recorded with a standard three electrode system consisting of: CuNi coupons with an exposed area of 0.5 cm^2 as the working electrode, a saturated calomel reference electrode, and a platinum wire auxiliary electrode. Measurements were obtained in a quartz cell containing 0.1 M NaOH with a potential scan ranging from -0.6 to $+0.7$ V at a rate of 0.05 V s^{-1}. First, unmodified CuNi coupons and coupons of the constituent metals Cu and Ni were examined to determine the composition of the alloy metal oxide layer. Then, CuNi coupons modified with ODPA and COOH-PA films were evaluated and compared to the control CuNi to determine if the films were effectively inhibiting oxidation.

3. Results

SAMs of ODPA and COOH-PA were formed on the metal oxide surface of CuNi using solution deposition methods described above. Briefly, ODPA films were formed by first cooling CuNi substrates on ice for 1 hour followed by immersion in a 1 mM solution of ODPA in THF heated to 50 °C for 30 minutes. COOH-PA films were formed by placing CuNi substrates in a 1 mM solution of COOH-PA in THF at ambient temperature (20 °C) for 1 hour. After deposition, both ODPA and COOH-PA modified substrates were placed in an oven at 100 °C for 8–12 hours before analysis. DRIFT spectroscopy was used to determine if the film formed initially and if the films persisted through rinse and sonication in THF. This served to remove loosely bound physisorbed molecules and multilayers. Examination of the methylene (CH_2) stretching region of the DRIFT spectrum indicates whether or not an ordered film was present on the surface [12,18]. A well-ordered film has been characterized as having alkyl chains in an all *trans* configuration with characteristic peaks at $\nu_{CH2asymm} \leq 2918\ cm^{-1}$ and $\nu_{CH2symm} \leq 2950\ cm^{-1}$ [18,19]. Shifts of these peaks to higher wavenumbers indicate a disordered film with *gauche* interactions in the alkyl chain [18,19]. The DRIFT spectra of ODPA and COOH-PA films deposited on CuNi substrates contained peaks attributed to $\nu_{CH2asymm}$ at 2916 cm^{-1} and $\nu_{CH2symm}$ at 2848 cm^{-1} (Fig. 1a,b). The peaks were prominent through THF rinse (15 minutes) and sonication (15 minutes), indicating the presence of a stable film with ordered alkyl chains. Additionally, the DRIFT spectra of ODPA films exhibited a peak corresponding to the methyl tail group