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ORIGINAL PAPER

The formation of hydrophobic and corrosion resistant surfaces on copper and bronze by treatment in myristic acid

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Abstract The surface of freshly etched copper and bronze samples was modified by immersion in ethanol solutions of myristic (tetradecanoic) acid. Modification resulted in the formation of hydrophobic layers with contact angles up to 141°. Two kinds of surface structure were observed. The modified surface of copper was covered by a uniform layer containing nano-grains or knitted-like structure, whereas the modified surface of bronze was covered by a layer with lamellate patterns and nano-grains. The corrosion properties of bare and modified copper and bronze surfaces were tested by potentiodynamic polarization experiments in 0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$ solution. The deduced effectiveness of corrosion inhibition by the modified layers on copper and bronze was up to 97 and 68%, respectively. Modification of the surface by immersion in an ethanol solution of myristic acid appears to be a promising treatment for improving the corrosion resistance of copper. The same treatment was not very effective when used on bronze.

Keywords Copper · Bronze · Myristic acid · Hydrophobicity · Inhibition

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1 Introduction

A hydrophobic surface is one that exhibits the physical property of repelling bulk water. Water on hydrophobic and superhydrophobic surfaces exhibits high contact angles greater than 90° and 150°, respectively [1, 2]. This effect can produce interesting phenomena. Due to superhydrophobicity, lotus plant leaves exhibit self-cleaning properties; droplets of water roll off the surface, taking mud and undesirable particulate contaminants with them [1]. This effect is known as the Lotus effect. The microscopic structure and surface chemistry of the leaves result in a contact angle greater than 90° and a sliding angle less than 10°, preventing them from being wetted by liquids [2]. Structures ascribed to superhydrophobicity have also been observed in other plants like rice, faro and India canna [2]. Nanometre sized protuberances on insect wings were also studied in order to relate the nano-structure of their surface to their very high mechanical strength under load [3].

Inspired by these exceptional properties of natural plant leaves, superhydrophobicity was successfully mimicked on various substrates such as aluminium and copper alloys [2]. In the last decade several studies aimed at transferring these properties to important engineering processes were published [4–7]. Various surface modifications designed to form hydrophobic surfaces on copper, include the formation of $Cu_2(OH)_3NO_3$ [8], immersion in oxalic acid followed by chemical modification with a siloxane compound [9] and combined chemical etching and polymer plating [10]. The preparation of superhydrophobic metal surfaces can be achieved by surface roughening [11]. Surface modification was also achieved by applying stearic acid to a surface [12].

Corrosion protection of copper [13–16], galvanized steel [16], aluminium [17] and zinc [18] is reported to result from modification of the surface to achieve superhydrophobicity. Another application was related to the modification of native oxide surfaces of Ti and Ti-6Al-4V by self-assembly of α,ω-diphosphonic acid, resulting in the surface being more effective for osteoblast binding and proliferation [19].

Myristic acid (IUPAC name tetradecanoic acid), a saturated fatty acid $CH_3(CH_2)_{12}COOH$, formed superhydrophobic self assembled monolayers on copper, leading to a significant decrease of corrosion rate in seawater [13–16]. In the present work we investigated the possibility of using myristic acid to modify the surfaces of copper (Cu) and bronze (Cu-6Sn) in order to increase their hydrophobicity and corrosion resistance. The aim behind the study is to investigate the possibility of modifying the surface of natural heritage copper and bronze monuments and thus increase their corrosion resistance during long-term outdoor exposure. In this preliminary study the corrosion resistance of modified surfaces was tested in an aerated solution of sodium sulphate and sodium hydrogencarbonate (0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$).

2 Experimental

2.1 Materials and chemicals

Copper (99.95%) and phosphor bronze (Cu 94/Sn 6) sheets were purchased from Goodfellow Cambridge Ltd., UK. Samples were sectioned from 2 to 3.2 mm sheets, in the form of discs of 14 mm diameter, and served as working electrodes. Prior to measurement, specimens were abraded with 1,000- and 2,400-grid SiC emery papers, ultrasonically cleaned in ethanol for 2 min and then well dried. The samples then underwent different pre-treatment procedures, as described below (Sect. 2.2).

Myristic acid (tetradecanoic acid, $C_{14}H_{28}O_2$, ($CH_3(CH_2)_{12}$ COOH)), of >98.5% purity, was obtained as white flakes from Fluka, Sigma–Aldrich Chemie GmbH, Germany. It was dissolved in absolute ethanol (Carlo Erba, Milan, Italy) to give 0.005, 0.01, 0.04, 0.06 and 0.1 M solutions.

The test solution for electrochemical measurements comprised 0.2 g/L Na_2SO_4 (0.014 M) and 0.2 g/L $NaHCO_3$ (0.024 M), pH = 7.8. Analytical grade chemicals (Merck, Darmstadt, Germany) and deionized water were used.

2.2 Preparation of the modified surfaces

The Cu and Cu-6Sn specimens were first etched in concentrated nitric acid (ca. 14 M) for 20 s to remove surface oxides, rinsed with deionized water and dried with a stream of nitrogen. The specimens were then immediately immersed in non-stirred, aerated ethanol solution of myristic acid at room temperature. Two sets of experiments were performed. In the first, the concentration of myristic acid was constant at 0.06 M, and the immersion time varied from 3 to 15 days (3, 7, 10 and 15 days). In the second set, the immersion time was constant at 10 days, and the concentration of myristic acid was varied from 0.005 to 0.1 M (0.005, 0.01, 0.04, 0.06 and 0.1 M).

2.3 Electrochemical measurements

Electrochemical measurements were conducted at room temperature in aqueous, aerated solutions of sodium sulphate and sodium bicarbonate (0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$).

An Autolab three-electrode corrosion cell was used, with the working electrode embedded in a Teflon holder. The exposed area measured 0.785 cm^2. A Ag/AgCl electrode served as a reference electrode and two stainless steel rods as counter electrodes. All potentials in the text refer to the Ag/AgCl scale. An Autolab PGSTAT 12 potentiostat/galvanostat controlled by GPES software was used for potentiodynamic measurements.

Following a 1-h stabilization at open circuit potential (OCP), potentiodynamic measurements were performed starting from –250 mV vs. OCP up to +1.1 V using a scan rate of 1 mV/s.

2.4 Wetting tests

The contact angles (in deg.) of the modified copper and bronze surfaces were measured with a 3-μL demineralized water droplet at ambient temperature (25 °C) with a home made apparatus equipped with a CCD camera and a PC computer. Contact angles were determined based on high resolution pictures of the water drop on the sample surface. Each value reported is the average of at least six measurements made on different areas of the same surface, the deviations of which were within ±2.0°. The contact angles were determined by software which enables fitting of the water drop on the surface in order to allow a precise determination.

2.5 Surface analysis of the modified surfaces

A field-emission scanning electron microscope (FE-SEM) SUPRA 35 VP (Carl Zeiss, Germany) was used to analyze the products formed on the surface of the copper and bronze in the ethanol solution of myristic acid. An accelerating voltage of 1 kV was used. The composition of the product was analyzed using X-ray diffraction analysis (D4 Endeavor, Bruker AXD).

3 Results and discussion

3.1 Formation of hydrophobic surfaces and wetting tests

The morphology of products formed on copper (Cu) and bronze (Cu-6Sn) samples immersed for 10 days in 0.005, 0.01 and 0.1 M ethanol solutions of myristic acid was recorded by SEM (Figs. 1, 2, 3). Photographs of water droplets on the modified surfaces, given in insets, indicate the hydrophobicity of the surface. The contact angles of the droplets were measured (Table 1). During the SEM measurements, the energy of the beam was kept low, at 1 kV, since at higher beam energies the products, evidently containing organic matter, were seen to start to melt, causing blurring of the image.

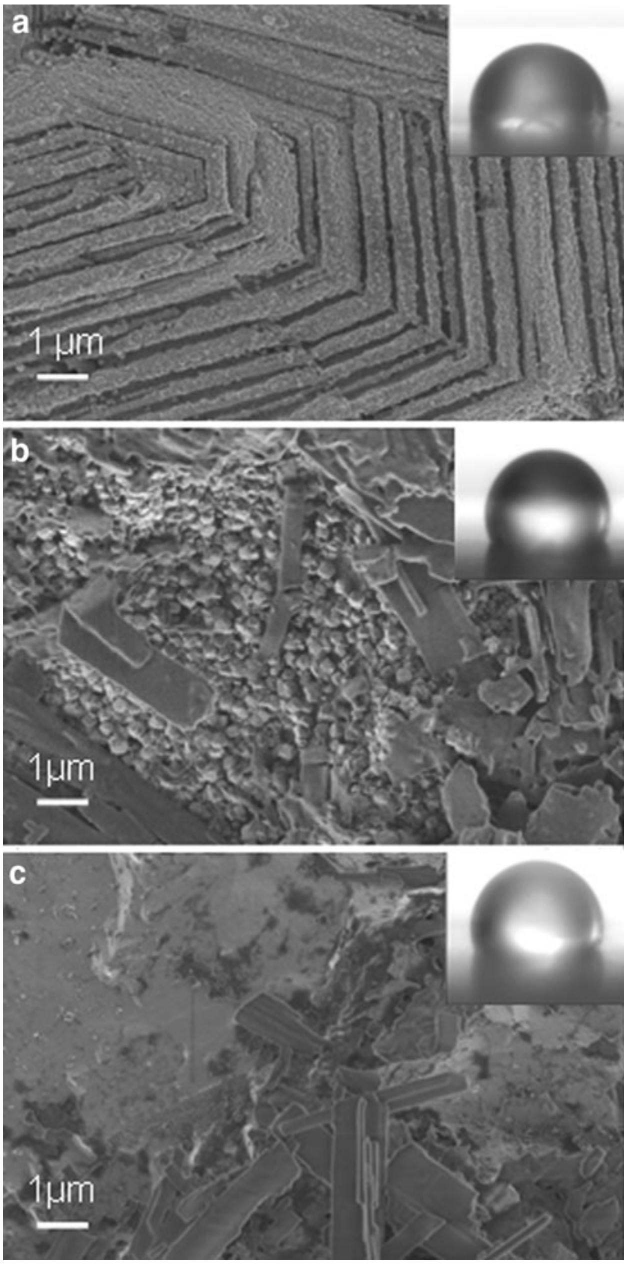


Fig. 1 SEM images of Cu surface after immersion for 10 days in ethanol solutions of myristic acid: **a** 0.005 M, **b** 0.01 M and **c** 0.1 M. Photographs of water droplets are given in insets and the resulting contact angles presented in Table 1

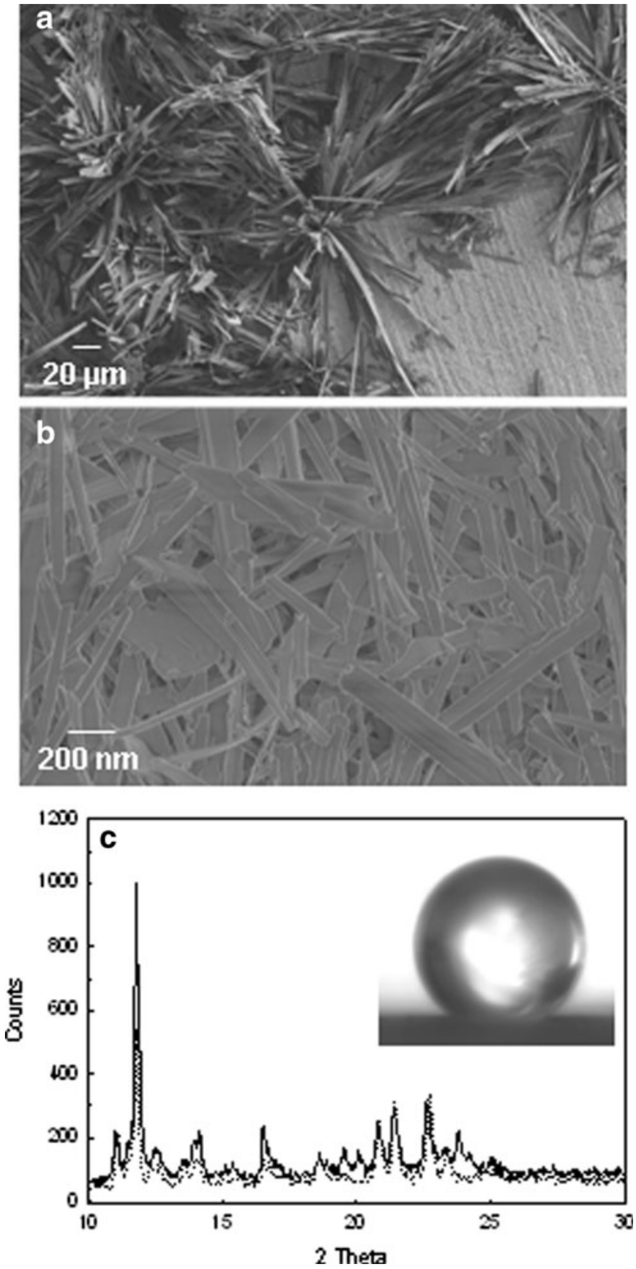


Fig. 2 SEM images recorded at the Cu surface containing bluish products with nano-plates. Samples were immersed in 0.06 M myristic acid in ethanol for **a** 3 days and **b** 10 days. **c** XRD spectra of the bluish product before (—) and after (····) heating at 105 °C and a photograph of water a droplet showing a contact angle of 141°

The morphology of products formed on copper in the presence of myristic acid was dependent on its concentration

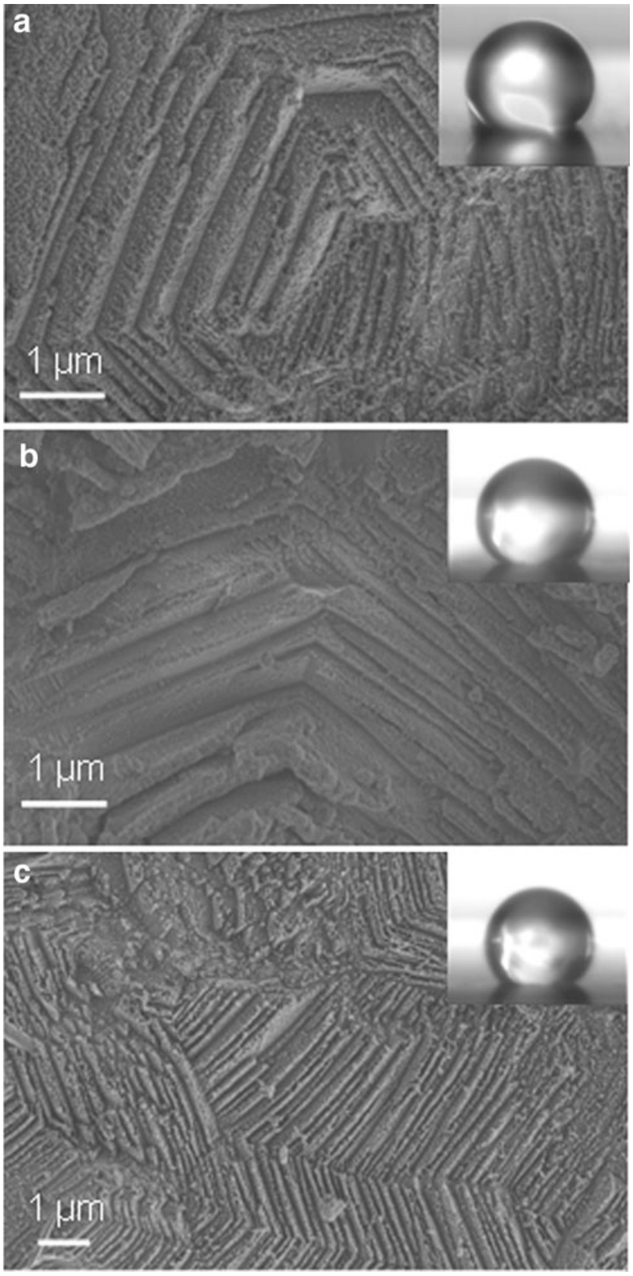


Fig. 3 SEM images of Cu-6Sn (bronze) surface after immersion for 10 days in solutions of myristic acid in ethanol **a** 0.005 M, **b** 0.01 M and **c** 0.1 M. Photographs of water droplets are given in insets and the resulting contact angles presented in Table 1

(Fig. 1). At 0.005 M, a regular, lamella-like structure covered with small, nano-sized particles was formed. Lamellae were not formed in the presence of higher concentrations of myristic acid, but the surface was covered by a mixture of nano-sized grains and plates (Fig. 1b, c). The formation of nano-plates was related to the formation of a bluish product at the surface. The latter could usually be rinsed away easily; however, at higher concentrations of myristic acid and/or longer immersion time it became attached more firmly to the surface. SEM images and XRD spectra were recorded at the spots where larger amounts of bluish product containing nano-plates were observed (Fig. 2). The width of the nano-plates ranged from less than 100 nm to 1 µm, and the length from a few to more than 10 µm. Similar structures have been observed by Liu et al. [14]. Based on the peak positions at low values of 2Θ in XRD spectra, we can assume that this product contains at least one large cell of crystalline, presumably organic, compound or a crystallohydrate compound (Fig. 2c). To test the latter suggestion, the product was heated at 105 °C for 3 h and the XRD spectrum recorded again. No significant difference was observed, indicating that the compound was not crystallohydrate. No compound of copper with tetradecanoic acid could be found in the data-bases for XRD spectra [20], so its formation could not be confirmed unambiguously. However, it is supported by reports that, in the presence of *n*-tetradecanoic acid, a spontaneous oxidation of copper leads to continuous release of Cu^{2+} ions, which are immediately captured by coordination with *n*-tetradecanoic acid, forming copper carboxylate [14, 15]. The latter compound would account for the observed bluish product. The XRD spectra prove without doubt that the formation of copper nitrate and nitrite hydride is excluded [20].

Table 1 Contact angles of water droplets measured on Cu and Cu-6Sn surfaces modified by immersion for 10 days in solutions containing various molar concentrations of myristic acid (*c*/M) in ethanol

Contact angle, Θ		
c/M	Cu	Cu-6Sn
0.005	97°	131°
0.01	113°	133°
0.04	104°	104°
0.06	96°	110°
0.1	112°	119°

In contrast to copper, on which the lamella-like pattern was observed only at the lowest concentration of myristic acid (Fig. 1a), repeating lamellate patterns were observed on bronze at all concentrations tested (Fig. 3). No bluish product (Fig. 2) was observed for bronze. Whereas the Cu product was probably formed by chemical reaction [14, 15], in the case of bronze the prevailing mechanism is probably a physisorption of organic acid.

The values of contact angles of the water droplets were not much greater than 90° (Table 1) confirming that the treatment of copper and bronze in myristic acid solutions resulted in the formation of hydrophobic rather than superhydrophobic surfaces (contact angles greater than 150°). Increasing the concentration of myristic acid had no observable effect on the contact angle (Table 1). Contact angles measured for the bluish product containing nano-plates, were as high as 141° (inset in Fig. 2c), higher than for other surface patterns.

The effect of immersion time on the morphology of surface products was investigated for copper and bronze samples immersed in 0.06 M myristic acid in ethanol. SEM images were taken after various immersion times (Figs. 4, 5). The modified surfaces were hydrophobic for all immersion times tested (contact angles between 90° and 109°). The image of the Cu surface after 7 days of immersion shows the formation of a uniform layer containing nanometre-sized grains (Fig. 4a). Similar structures were observed by Guo and Liu and termed nano-flowers [2]. After 10 days, a knitted-like pattern was observed, which became more pronounced as the time of immersion increased (Fig. 4b, c).

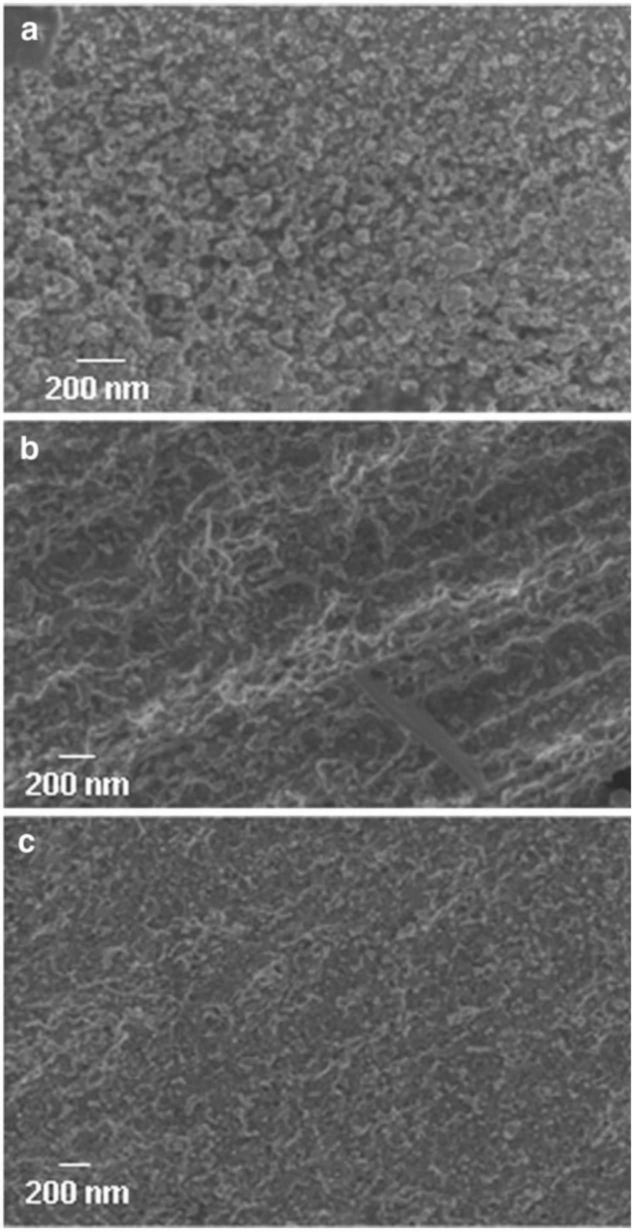


Fig. 4 SEM images of a Cu surface after immersion in 0.06 M myristic acid in ethanol for **a** 7 days, **b** 10 days and **c** 15 days. Magnification ×100.000

With bronze, a more porous, voluminous layer was formed (left-hand side of Fig. 5). Under lower magnification (right-hand side of Fig. 5), it becomes evident that this product forms regular, lamella-like patterns covered with nano-grains (e.g., Fig. 5e). It appears that the shape of the lamellae became more regular as the immersion time increased and formed a hexagonal structure (Fig. 5f).

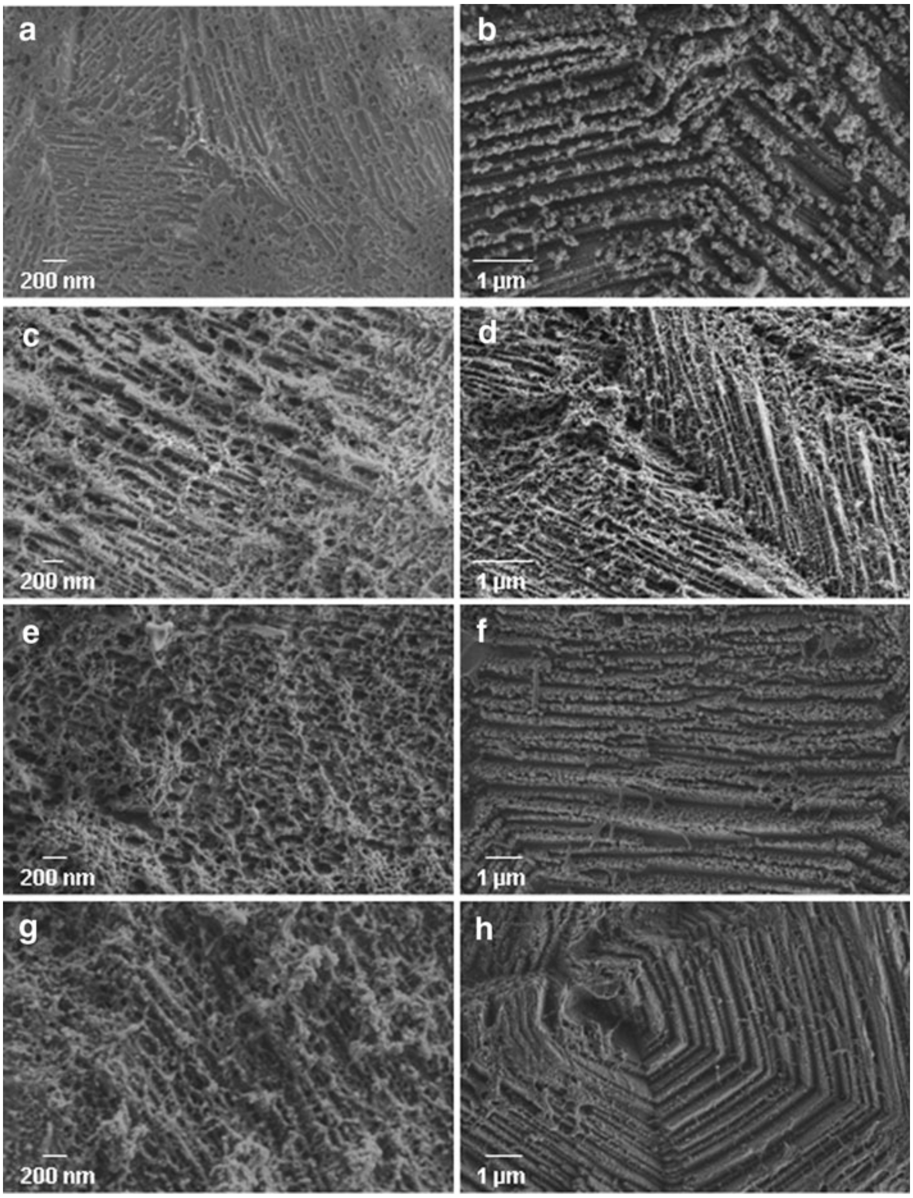
Summarizing, the modification of copper and bronze surfaces by myristic acid produced two kinds of structures. The surface formed on copper (Fig. 4) contained numerous nano-grains (or nano-flowers) uniformly distributed on the surface. The surface formed on bronze (Fig. 5) comprised lamella-like patterns and nano-grains. Additionally, the formation of a bluish, surface product containing nano-plates was observed on copper (Fig. 2).

3.2 Potentiodynamic measurements of bare and modified copper and bronze in $Na_2SO_4 + NaHCO_3$ solution

Potentiodynamic curves were recorded in 0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$ solution for bare copper and copper modified by immersion in myristic acid for various immersion times (Fig. 6), and the corrosion parameters, i.e., corrosion potential, E_{corr}, and corrosion current density, j_{corr}, were evaluated (Table 2). All the curves are similar, showing a cathodic Tafel region related to reduction of oxygen, a corrosion potential between −0.046 and 0.022 V, and an anodic Tafel region related to dissolution of copper as Cu^+ [21]. At approximately 0.3 V, the increase in the current density changed its slope. In this region cuprous complexes can either diffuse to bulk solution, or oxidize to cupric ions. Compared to bare copper, the modified surfaces showed decrease in cathodic current densities by up to two decades, and decrease in anodic current densities up to one decade. The corrosion potentials are shifted in the negative direction by up to 60 mV, and the values of corrosion current density are decreased by one decade (Table 2).

In contrast to copper, the potentiodynamic curve recorded for bronze shows a narrow passive region extending from −0.08 V to potentials between 0.1 and 0.2 V, depending on the time of immersion in myristic acid (Fig. 7). The modified surfaces on bronze showed curves similar to those recorded for the bare bronze surface. Changes of corrosion parameters and the decrease in cathodic and anodic current densities were rather modest, within one decade, compared to bare bronze surface (Table 2). The passive region is limited by an abrupt increase in current density at potentials between 0.1 and 0.2 V. At more positive potentials, current densities recorded for modified surfaces increased faster than those for the bare surface.

Fig. 5 SEM images of Cu-6Sn surface after immersion 0.06 M myristic acid in ethanol for **a**, **b** 3 days, **c**, **d** 7 days, **e**, **f** 10 days and **g**, **h** 15 days. Magnification: **a**, **c**, **e**, **g** ×100.000; **b**, **d** ×50.000; **g**, **h** ×30.000



The corrosion current density was used to calculate the inhibition effectiveness, IE, of the modified surfaces, according to the equation [22]

$$\mathrm{IE}(\%) = \frac{j_{\mathrm{corr(bare)}} - j_{\mathrm{corr(mod)}}}{j_{\mathrm{corr(bare)}}} \times 100 \qquad (1)$$

where $j_{\mathrm{corr(bare)}}$ and $j_{\mathrm{corr(mod)}}$ are corrosion current densities for bare and modified surfaces (Table 2). For copper, IE increases with increasing time of immersion, reaching 97.3% after 10 days. It then decreases slightly after 15 days of immersion, however, still remaining high (90%). For bronze, IE was highest (67.7%) after 3 days of immersion. It then decreased to only 30% after 15 days of immersion.

No data have been reported for self-assembled monolayers of *n*-alkanoic acid on bronze. Comparable studies of layers formed on silver, copper and aluminium surfaces proved that the structure of the adsorbate films depends strongly on the metal [23]. It is reasonable to assume therefore that the presence of tin in bronze would affect the properties of the layer formed, which would thus differ from that formed on copper, as demonstrated experimentally in the present study.

4 Conclusions

The surfaces of copper and bronze were treated by ethanolic solutions of myristic acid. In both cases this treatment modified the surface which became hydrophobic, with contact angles up to 140°. The modified surfaces of copper and bronze differed distinctively. That of copper was covered by a uniform layer containing nano-flowers or

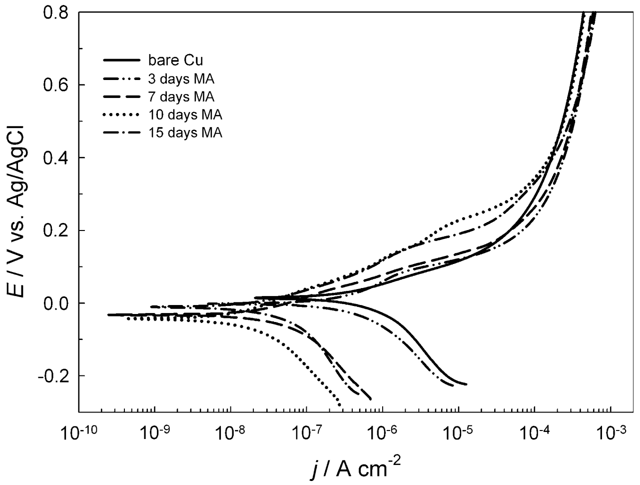


Fig. 6 Anodic polarization curves recorded for bare and modified Cu in 0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$ solution. dE/dt = 1 mV/s. The modified surfaces were prepared by immersion of Cu in 0.06 M myristic acid in ethanol for various days of immersion

Table 2 Corrosion parameters (corrosion potential E_{corr}, corrosion current density, j_{corr}) and inhibition effectiveness (IE) for bare Cu and bare Cu-6Sn samples, and for samples modified by immersion in 0.06 M myristic acid in ethanol for 3, 7, 10 and 15 days

Time of immersion/days	E_{corr}/V	j_{corr}/(A cm^{-2})	IE/%
Cu			
Bare	0.022	7.5×10^{-7}	
3	−0.005	3.1×10^{-7}	58.7
7	0.018	4.5×10^{-8}	94.0
10	−0.046	2.0×10^{-8}	97.3
15	−0.012	7.5×10^{-8}	90.0
Cu-6Sn			
Bare	−0.079	1.3×10^{-6}	
3	−0.057	4.2×10^{-7}	67.7
7	−0.038	4.9×10^{-7}	62.0
10	−0.027	9.1×10^{-7}	34.6
15	−0.089	8.5×10^{-7}	30.0

Corrosion parameters were derived from the Tafel region of the potentiodynamic curves (Figs. 6, 7)

knitted-like pattern. The modified surface of bronze was covered by a more porous layer, with regular, lamellate patterns covered with nano-particles.

The modified layers formed in the presence of myristic acid affect the electrochemical properties of copper and bronze in 0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$ solution. Whereas the inhibition effectiveness for copper reached 97.3%, the values achieved for bronze were significantly smaller (maximum 67.7%). Modification of the metal surface to give a hydrophobic surface is thus demonstrated to be a promising treatment to improve the corrosion resistance of copper during long-term exposure to atmospheric conditions. For bronze, however, this pre-treatment would be expected to be less effective.

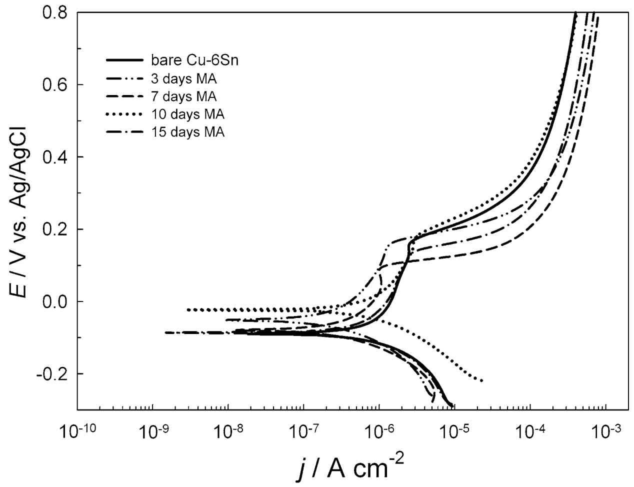


Fig. 7 Anodic polarization curves recorded for bare and modified Cu-6Sn in 0.014 M Na_2SO_4 + 0.024 M $NaHCO_3$ solution. dE/dt = 1 mV/s. The modified surfaces were prepared by immersion of Cu-6Sn in 0.06 M myristic acid in ethanol for various days of immersion

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