Electrochemical synthesis and characterization of bioinspired copper hydrophobic coatings

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Electrochemical synthesis and characterization of bioinspired copper hydrophobic coatings

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Abstract. A copper hydrophobic coating on API 5L steel was synthesized by three consecutive steps: electrodeposition of copper in 1.25M CuSO4+0.85M H2SO4 electrolyte, chemical oxidation in 2.5M KOH+0.1M (NH4)2S2O8 solution, and modification in 0.015M stearic acid solution. The morphology and wettability of the obtained coatings were evaluated by the measurement of the optical contact angle (OCA) and scanning electron microscopy (SEM). The electrochemical response of the coated steel NaCl 3.5wt% was evaluated by the measure of the open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). OCA results show a variation in the contact angle from values lower than 10° to 129.5° for the modified coating, showing a transition between the hydrophilic and hydrophobic response in function of the treatments time. The relation between the wettability and the surface morphology was confirmed by analyzing the SEM images. Furthermore, the electrochemical evaluation in NaCl 3.5wt% shows a reduction of one order magnitude in the corrosion current in comparison with the bare steel, therefore these results open the possibility of its application in pipe steel to reduce its corrosion rate.

1. Introduction

Bioinspired materials are those materials developed thinking on nature, taking the function principles of animals and plants parts as a reference. One of the most interesting structures existing in nature are the hydrophobic surfaces which form the external layer of the wings of birds and the leaves of various plants [1-2]. Lotus leaves are the main reference for the bioinspired coating fabrication, these leaves are known for its self-cleaning property, where the surface can repel contaminants by the action of rolling-off liquid drops [3], this characteristic is known as a “Lotus effect”. The surface of the Lotus and other hydrophobic plants (i.e.: Salvinia and Euphorbia myrsinites) [4] has an especial micro and nanoarchitecture, that promote the entrapment of air bubbles under the drops, reducing the water-surface contact, hence the wettability of the leaves. This phenomenon is described by the Cassie-Baxter equation, where the apparent contact angle depends on the fractions of solid and air that are in contact with the water drops [5]. This behavior has aroused the interest of materials and corrosion researchers, who are looking for the development of protective coatings against electrochemical corrosion in aqueous media [6]. In parallel, is well known that the copper coatings show an antibacterial activity promoted by the liberation of Cu2+ ions and could reduce the formation of biofilms that are related with the microbiologically induced corrosion. In this work, a hydrophobic copper coating with hierarchical surface morphology was synthesized by the electrochemical-chemical method, evaluating the influence of the synthesis parameters variation on the surface wettability and morphology. Furthermore, its
possible application as a protective coating on API 5L steel against the corrosion in saline solutions was evaluated.

2. Experimental procedure

2.1. Synthesis of the coating
The hydrophobic coatings were obtained by three consecutive steps: copper electrodeposition, chemical oxidation, and stearic acid modification. The electrodeposition of the copper coatings was made in a three-electrode cell, using a graphite rod as a counter electrode, a Cu/CuSO\(_4\) pseudo-reference electrode and API 5L steel as the working electrode. The reduction of the copper ions was studied by cyclic voltammetry in 1.25M CuSO\(_4\) and 0.85M H\(_2\)SO\(_4\). Once the reduction potentials zone was established, the deposit synthesis was performed under potentiostatic deposition varying the applied potential, bath temperature and deposition time. Obtaining the best adhesion and coverage applying -100mV vs Cu/CuSO\(_4\) for one hour at ambient temperature. The chemical oxidation of the copper coating was performed in 2.5M KOH and 0.1M (NH\(_4\))\(_2\)S\(_2\)O\(_8\) solution at 60°C for 30, 60 and 90 minutes. Finally, the stearic acid modification was made immersing the coated steel in a 0.015M stearic acid solution in ethanol for 30 and 60 minutes.

2.2. Morphological and electrochemical evaluation
The coatings were evaluated by the measurement of the open circuit potential (OCP) variation for one hour, the electrochemical impedance spectroscopy (EIS) response varying the applied frequency since 100kHz to 0.01Hz and by linear sweep voltammetry (LSV), in 3.5wt\% NaCl solution. All electrochemical tests were made using a GAMRY 750 potentiostat/galvanostat. The morphology and composition evaluation of the coatings were determined using a Scanning Electron Microscopy (SEM) Quanta 650 FEG (Field Emission Gun) varying the magnification between 5000 and 20000X, coupled with semiquantitative microchemical analysis (EDS). The wettability of the coated steel was studied using 1\(\mu\)l water drops with a Dataphysics Optical Contact Angle (OCA) 15 EC equipment.

3. Results

3.1. Synthesis of the coatings
The variation of the wettability of the surface with coating application and modification was measured by OCA, the results are shown in Figure 1.

![Figure 1. Variation of the contact angle in function of the oxidation time, with and without modification in stearic acid solution.](image-url)
Bare steel and coated steel without additional treatment show a hydrophilic surface, the measured contact angle (θ) for both materials was less than 10°. This high wettability allows a homogeneous ion exchange over the entire surface, which is related to the corrosion of the materials. The variation of the measured contact angle with the chemical oxidation treatment in 2.5M KOH+0.1M (NH₄)₂S₂O₈ solution is represented with the red line in Figure 1. Through the chemical oxidation treatment, the OCA values of the surfaces change from less than 10° to more than 75° for all the evaluated times, showing a maximum angle at one hour of treatment. This variation in the OCA values is related to the surface morphology modification during the treatment, where the thermodynamic equilibrium of the species in the surface change promoting the formation of stable oxides. Green and blue lines show the OCA values obtained after the modification treatment in stearic acid solution during 30 and 60 minutes respectively. In all evaluated conditions the OCA values show an increment above 100° with a maximum value of 129.5° for the coating chemically oxidized for one hour and modified in stearic acid solution during the same time. This transition between the hydrophilic and hydrophobic response is related to the chemical attack of the stable oxides in the acid media, generating the expected hierarchical morphology.

Figure 2 compares the OCA images of the coatings with and without modification in stearic acid solution. With consecutive treatments (oxidation and modification), it is evident the transition between the hydrophilic regime described by the Young equation [7] for smooth surfaces to the hydrophobic regime characteristic of hierarchical surfaces. The variation between the untreated copper coating (θ<10°) to the oxidized copper coatings (75°<θ<90°), could be related to the transition between the smooth surface, described by the Young-Laplace equation to the rough surface described by the Wenzel model [8], where the value of the contact angle depends on the actual-area/geometric-area relationship. Therefore, considering that the system is composed by the same materials and the surface tension is constant, the increment of the contact angle implies an increment in the surface area with the oxidation treatment [9].

Finally, the increment in the contact angle with the stearic acid modification (121°<θ<130°) could be related to the transition to the heterogeneous regime described by the Cassie-Baxter model [5], where the measured value includes the solid-water and air-water interfacial energy [9,10]. In this case, the formation of air pockets under the water drops reduce the wettability of the surface [11].

![Figure 2](image-url)
Figure 3(a) and 3(b) show a homogeneous coverage of the copper coating on the API 5L steel surface, characterized by an array of epitaxial micrometric crystals. After the chemical oxidation treatment, the surface shows the formation of secondary polygonal crystals of 800nm approximately (Figure 3(c) and 3(d)), confirming the expected increment in the surface rugosity [9, 10]. The stearic acid modification is confirmed by the variation of the surface of the polygonal crystal, which has a nanometric porous homogeneously distributed (Figure 3(e) and 3(f)). Furthermore, it can be observed a full coverage of the steel with the modified copper coating, which is necessary for its possible application as an anticorrosive coating.

Figure 3. (a) and (b) SEM images of the copper coating, (c) and (d) oxidized copper coating, (e) and (f) oxidized-modified copper coating.
3.2. Electrochemical evaluation

To analyze the protective properties of the modified copper coating on the API 5L steel corrosion, the coated steel was evaluated in NaCl 3.5wt% comparing the response with the bare steel. The OCP value for both surfaces can be seen in Table 1. With the application of the coating the OCP shift 67mV to more positive values that can be interpreted as a stabilization of the surface. The Nyquist plot (Figure 4(a)) shows the electrochemical response of the bare and coated steel in the EIS evaluation. The response of API 5L steel (blue dots) shows the expected behavior with one semicircle related to the iron oxidation with a charge transfer resistance (Rct) of 280Ω.cm². The impedance spectra of the coated steel (red dots) show a depressed capacitive semicircle with a projected total resistance of 965Ω.cm², this increment in the resistance verify the stability of the coating and its protective function. The blue line in Figure 4(b) represents the polarization curve obtained for the bare steel, with an anodic Tafel slope of 79mV.dec⁻¹ related to the iron oxidation to Fe²⁺ ions, confirming the transference of two electrons according to the Butler-Volmer equation [12]. Red line represents the response of the coated steel, in this case, the anodic branch corresponds to the copper oxidation and the obtained anodic Tafel slope of 104mV.dec⁻¹ implies a mixed control when the charge transference is retarded by the resistance of the stable copper oxide products generated in the treatments. Through the application of the modified coating, the corrosion current shows a decrease in one order of magnitude, confirming its possible application as a protective coating. The electrochemical characteristic values for both materials are summarized in Table 1.

![Figure 4. (a) Nyquist and (b) potentiodynamic polarization plots for the bare steel and the coated steel in NaCl 3.5wt%](image)

| Sample         | OCP (V vs Ag/AgCl) | i_corr (μA cm⁻²) | E_corr (V vs Ag/AgCl) | βa (mV dec⁻¹) | R_tot (Ω cm²) |
|----------------|---------------------|-----------------|----------------------|---------------|--------------|
| Bare steel     | -0.591              | 228.9           | -0.600               | 79            | 280          |
| Coated steel   | -0.524              | 22.5            | -0.517               | 104           | 965          |

4. Conclusion

A bioinspired copper coating was chemically oxidized in 2.5M KOH 0.1M (NH₄)₂S₂O₈ solution and modified in stearic acid solution. The measured optical contact angle shift with treatments until obtaining a hydrophobic response. The electrochemical response of the coated steel was evaluated in NaCl 3.5wt%, showing a reduction of one order magnitude in the corrosion current in comparison with the bare steel, therefore these results open the possibility of its application in pipe steel to reduce its corrosion rate.
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