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ULTRATHIN ORGANIC COATINGS ON COPPER, COPPER ALLOYS AND STAINLESS STEEL FOR CONTROLLING THE MICROBIOLOGICALLY INFLUENCED CORROSION

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ABSTRACT. Organic coatings only a few nanometres thick have been prepared on surfaces of pure copper, copper alloys and stainless steel samples by self-assembly, Langmuir–Blodgett technique and dip-coating. The resulted thin films have been characterized by dynamic contact angle measurements as well as by infrared techniques. The stability of the layers in aqueous environment and their protective effect against corrosion in NaCl solution and against bacterial adhesion was investigated.

Keywords: *microbiologically influenced corrosion, self-assembling monolayers, Langmuir–Blodgett-film, copper, stainless steel*

INTRODUCTION

Energy sector is of strategic importance within the industry, where the appearance of microbiologically influenced corrosion (MIC) may have severe consequences. In power plants circulating seawater as cooling agent, the biofouling and corrosion of the condenser tubes is controlled by biocides and corrosion inhibitors [1]. Chlorine and chlorine-related oxidising compounds are the cheapest and most effective chemicals against microorganisms; however, their direct aquatic toxicity and the result of chlorinated organic by-products rigorously limit their dosage [2–3]. In addition, the high amounts of corrosion inhibitors consumed bring on appreciable environmental load. The use of nanocoatings would significantly reduce the consumed chemicals, thus cutting down both expenses and environmental impact.

Nanocoatings are coatings involving primarily organic surfactants, which, by their nature, can readily adsorb to the metal/water interface into compact layers, assuring protection. Although their thickness is only of a few nanometres, these coatings were proved to offer good protection against

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both corrosion and microbial adhesion. Common features of the molecules involved are a hydrophilic functional group, which can make strong bonds with the metal surface, and a hydrophobic hydrocarbon chain of typically 14-22 carbon atoms long, which accounts for the dense packing of the molecules and for the hydrophobicity of the layer.

Such coatings are prepared and tested in several laboratories worldwide by SAM, Langmuir–Blodgett, dip-coating or other techniques. The number of publications on nanocoatings prepared and tested on pure metals (mainly copper and iron, but also nickel and aluminium) is large. The reported layers include amines [4, 5], thiols [6–10], carboxylic acids [11–16], hydroxamic acids [15–20], amino acids [21–23], phosphonic acids [12], sulphonic acids [12], silane derivatives [24–26], and heterocyclic compounds traditionally used as inhibitors (benzotriazole, benzothiazole, imidazole and their homologues and derivatives) [27, 28]. However, the literature on similar works involving alloys, especially others than stainless steels, is much scarcer [29, 30]. On one hand, this is not surprising, since the surface of an alloy is always a more complicated system than a pure metal, with several new variables and unknowns. On the other hand, alloys have larger field of industrial application, thus studying nanocoatings on alloys is strongly justified and of even bigger possible economic impact. Through our experiments, we try to bring our contribution into this international pioneering work.

RESULTS AND DISCUSSION

Surface free energies of coated alloy samples. There are a few widely acknowledged methods for extracting surface free energy values from contact angle data [31–35]. Most of these require measurement of contact angles with 2-3 polar and non-polar liquids, thus making the procedure long and cumbersome, however, offer the incontestable advantage of obtaining the different components of the total surface free energy. From the available methods, we have chosen the one based on Neumann's equation of state (Eqs. 1 and 2), which makes possible to use only one test liquid, however, at the expense of obtaining only the total surface free energy, without its components [35].

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S \gamma_L}\, e^{-\beta_1(\gamma_L - \gamma_S)^2} \tag{1}$$

$$\beta_1 = 1.247 \times 10^{-4} \left(\frac{\mathrm{m}^2}{\mathrm{mJ}}\right)^2 \tag{2}$$

Combining the above expression with Young's equation (Eq. 3), the γ_{SL} solid-liquid interfacial energy term can be eliminated. The resulting transcendental equation in γ_S, the surface free energy of the solid, can be solved numerically, by knowing the γ_L surface tension of the test liquid at a given temperature and the measured value of the θ_Y equilibrium (Young) contact angle. This latter can be calculated from the measured θ_A advancing and θ_R receding contact angles through Tadmor's relation (Eqs. 4–6) [36].

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta_Y \tag{3}$$

$$\theta_Y = \arccos\left(\frac{\Gamma_A \cos\theta_A + \Gamma_R \cos\theta_R}{\Gamma_A + \Gamma_R}\right) \tag{4}$$

$$\Gamma_A \equiv \sqrt[3]{\frac{\sin^3\theta_A}{2 - 3\cos\theta_A + \cos^3\theta_A}} \tag{5}$$

$$\Gamma_R \equiv \sqrt[3]{\frac{\sin^3\theta_R}{2 - 3\cos\theta_R + \cos^3\theta_R}} \tag{6}$$

The surface free energies of SAM-coated aluminium brass (Al-b), copper/nickel 70/30 (CuNi) and stainless steel 304 (SS) samples are presented in Table 1. The following observations can be made:

1) The surface free energies decrease after applying a SAM-coating. This is an indication of the presence of the hydrophobic alkyl chains on the surface.
2) The extent of this decrease depends strongly on the applied compound. Among the four compounds studied, hydroxamic and phosphonic acid coatings exhibited the lowest surface energies. This fact can be explained by the different bond strengths between the functional group of the surface-active compound and the oxidic/hydroxidic surface of the substrate.
3) On the surface free energy, the duration of SAM preparation
    a. has evidently a strong influence in the case of C18-carboxylic acid (lower values measured when preparation time is longer);
    b. has apparently no influence in the case of C18-amine (no clear trend of the surface free energy with preparation time);
    and
    c. has certain influence in the case of the other compounds.

Table 1. The influence of duration of layer preparation on surface free energies of SAM-coated alloy samples

		Surface free energy (mJ/m^2)		
SAM-coating	**preparation time (h)**	**Al-b**	**CuNi**	**SS**
control (uncoated)	N/A	58.2	61.3	59.6
C18-hydroxamic acid	1	–	44.8	–
	5	44.5	46.0	47.7
	24	44.8	39.5	47.5
C18-phosphonic acid	1	44.3	45.2	45.2
	5	–	44.4	45.4
	24	41.4	43.9	43.5
C18-amine	1	46.1	55.0	57.2
	5	53.8	54.2	58.0
	24	51.6	–	58.7
C18-carboxylic acid	1	50.8	51.5	58.5
	5	47.0	43.5	56.9
	24	41.2	45.0	54.3

Stability of the coatings in aqueous environment. A frequently encountered, justified concern is whether these nanocoatings can withstand flowing water in a possible real application. A simple experiment was conducted in order to get an answer to this question. Samples coated with nanolayers were immersed in gently flowing water (volumetric flux: 1.8 m/h) for 2 weeks. The samples were analysed before and after by reflection absorption infrared spectroscopy (RAIRS) and sum frequency generation spectroscopy (SFS).

In the RAIRS spectra (Figure 1, left), besides the apparent increase of the r^- peak at 2962 cm^{-1} (corresponding to the antisymmetrical stretching mode of the methyl groups), which is an artefact connected to the baseline definition, the intensity of all other characteristic peaks (d^+ symmetrical stretching mode and d_{FR}^+ Fermi resonance of the methylene groups; r^+ symmetrical and r^- antisymmetrical stretching modes of the methyl groups) decreases after the water immersion test; however, the peaks are still traceable, indicating that the nanolayers withstand the aqueous environment.

SFS is a powerful technique to give information about the molecular-level order of the hydrocarbon chains. Due to the nature of the nonlinear optical phenomenon, a strong signal appears only generated by anisotropic moieties. Therefore, in a well-ordered monolayer, with the hydrocarbon chains all aligned and fully extended in all-*trans* conformation, only the characteristic peaks of the terminating methyl groups are present. Methylene groups become visible in the spectrum only when parts of the chains are distorted in gauche conformations. Therefore, the intensity ratios of the methyl/methylene peaks provide information about the conformation of the chains [37]. We found that the methyl peaks appear also after testing in aqueous environment (Figure 1, right). Moreover, the intensity ratios are almost unchanged, which is an unquestionable proof of the layer stability.

This stability depends on the preparation time of the coating. When the immersion time is enough for self-assembled film formation, the result is a properly packed layer of good quality, which can survive the immersion test, as revealed by the stronger IR peaks (Figure 2). Above a threshold time, however, lengthening further the preparation time does not improve further the stability of these layers. According to our results, 5 h preparation time is enough to obtain stable SAM layers.

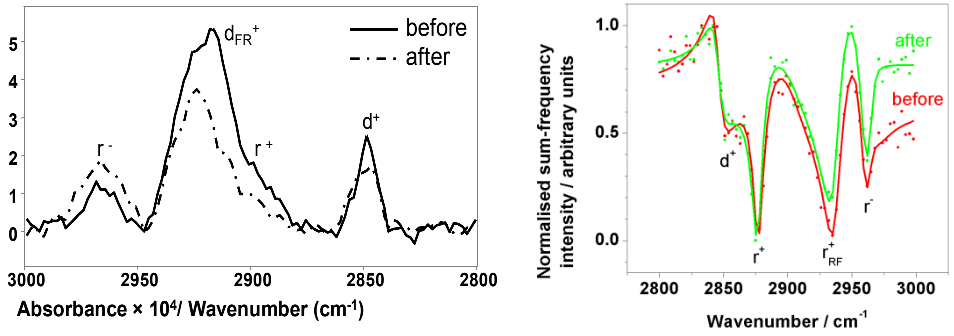

Figure 1. Stability of nanolayers in aqueous environment. Left: RAIRS spectra of C18-hydroxamic acid SAM layer on SS reveals the presence of the layer after the two weeks test in flowing water. Right: SFS spectra of LB-layers of the same hydroxamic acid on copper indicate no alteration of the molecular-level order.

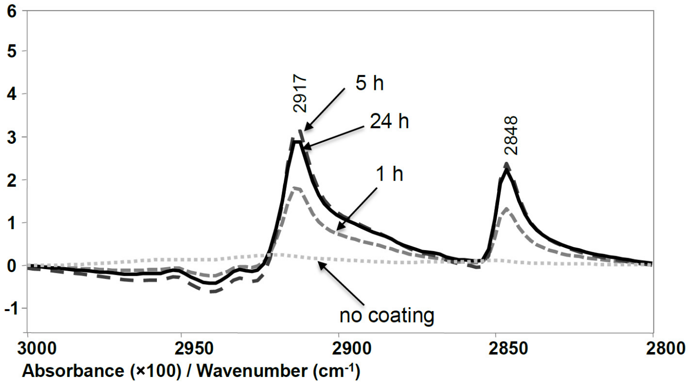

Figure 2. Stability of the nanolayers in aqueous environment: RAIRS spectra of C18-phosphonic acid SAM layers formed in 1, 5, and 24 h on Al-b substrates after the two weeks test in flowing water, as compared to the uncoated reference.

Bacterial adhesion. Samples with different SAM and Langmuir–Blodgett coatings were tested in aqueous environment containing mixed population of microorganisms. The adhesion of cells and formation of biofilm on the coated samples after 48 h immersion time was investigated and visualised by AFM and epifluorescent microscopy. These two techniques revealed that our coatings hamper the adhesion of cells and/or the formation of the biofilm (Figures 3 and 4). The mechanism of action is not completely understood, but we propose the following hypothesis: Bacterial cells are known to adhere to surfaces with the aid of a mixture of secreted macromolecules (proteins, carbohydrates, lipids, uronic acids, nucleic acids etc.), called extracellular polymeric substance (EPS). These macromolecules are mainly hydrophilic by nature. A densely packed hydrophobic nanolayer would not favour the attachment of these macromolecules. In conclusion, the adhesion of the cell is inhibited.

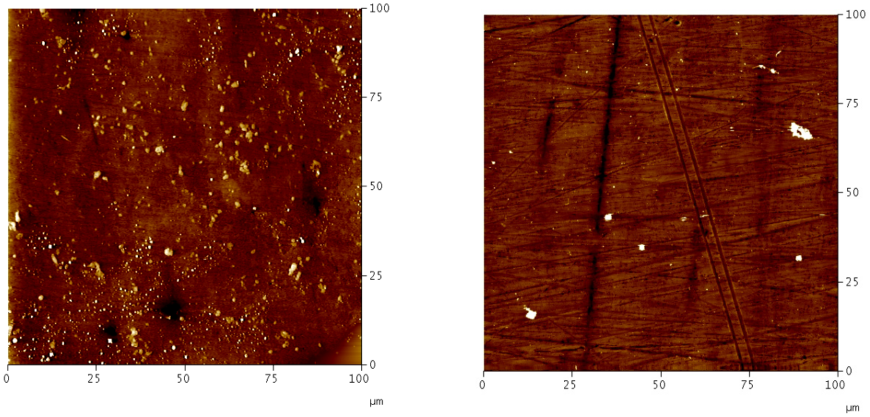

Figure 3. AFM images of copper samples after 48 h immersion in water, containing mixed population of microorganisms. Left: uncoated, right: with stearoyl hydroxamic acid LB1-coating. Scanned area 100×100 μm^2, height range 500 nm.

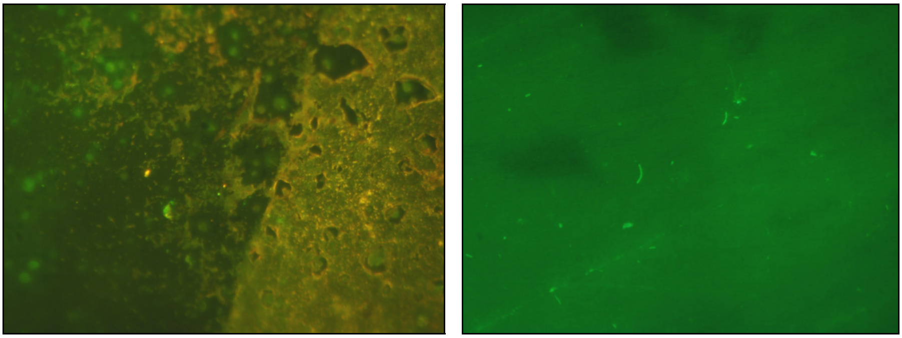

Figure 4. Fluorescent microscope images of an uncoated copper sample (left), respectively a copper sample coated with C18-carboxylic acid LB1 film (right) after being immersed in bacterial environment for 48 h.

CONCLUSIONS

Organic layers already in a few nanometres thickness are able to protect metals against corrosion and to prevent the adhesion of microorganisms. The properties and the efficiency of the protective layers significantly depend on the: type of metal substrate, surface preparation, film forming compound, type of solvent, number of layers.

EXPERIMENTAL SECTION

Metals. The alloys of interest were: aluminium brass (Al-b), copper-nickel 70/30 (CuNi) and stainless steel 304 (SS). Samples cut from standardised condenser tubes of these alloys were used [38, 39]. In addition, pure, polycrystalline copper has been used as model metal.

Preparation and pre-treatment of the substrates. The 10×12 mm^2 Al-b and CuNi condenser tube samples were used without polishing. Conversely, rectangular copper samples with dimensions of 10×15×1.6 mm^3 were consecutively polished in several steps: First, samples underwent consecutive coarse polishing with seven emery papers (220 to 4000 grains/in). After the last, 4000 grains/in paper a fine-polishing procedure followed. In the case of the samples used in corrosion experiments, as well as in AFM and SFS analyses, fine-polishing was done with diamond suspensions of consecutively decreasing grain sizes of 6, 3, 1 and ¼ µm, ended with a final step using 300 nm alumina suspension. For bacterial adhesion experiments the fine-polishing involved only the 1 µm diamond paste, followed by the 300 nm alumina suspension. In order to remove any debris, between each consecutive polishing step the samples were thoroughly cleaned in ultrasonic bath in distilled water, acetone and ethanol. Copper alloys and stainless steel samples were pre-treated for 5 min. in 14 mM HNO_3 in ultrasonic bath, followed by a 5 min. sonication in 5% H_2O_2. The diluted acid removed the inorganic contamination and oxide layers of unknown history, while the diluted peroxide reconstructed the surface oxide in a controllable, reproducible manner, as proven by XPS results (not detailed here). In some cases, this two-step pre-treatment process was substituted by a 10 min. sonication in spectroscopic grade acetone completed by 20 min. cleaning in ozone generated under a UV-lamp.

Film forming compounds. Analytical grade octadecyl amine and stearic acid were used without further purification. Stearoyl hydroxamic acid and oleoyl hydroxamic acid were synthesised in our laboratory from hydroxylamine and the appropriate acyl chlorides, then re-crystallized and characterized by melting points, elemental analysis, infrared spectroscopy and thin layer chromatography. Octadecyl phosphonic acid was synthesised in a Michaelis–Arbusov reaction.

Coating procedure. SAM coatings were prepared by dipping the pre-treated metal samples into 2.0 mM solutions of the film forming compounds in chloroform, dichloromethane, or tetrahydrofurane. Dipping times were 1, 5 and 24 h in the case of the alloys, 20 h in the case of corrosion experiments with copper samples, and 2 h in the case of bacterial adhesion experiments with copper samples. The coated samples were rinsed with the respective solvent in order to remove non-specifically bond excess material and were dried in air or in a stream of nitrogen.

The Langmuir–Blodgett coatings on copper substrates were prepared in a Langmuir–Blodgett trough (NIMA Technology), working with ultra pure water (Milli-Q, 18 MΩcm) as subphase. The film forming compounds were dissolved in HPLC grade chloroform (Merck) to a concentration of 2.2 mM and spread onto the thermostated subphase. The time allowed for the evaporation of the solvent and the relaxation of the monolayer was 10 min. The organization of the monolayer at the air/water interface was followed by recording the surface pressure vs. molecular area isotherms and also visualised by a Brewster-angle microscope. Stearic acid and stearoyl hydroxamic acid monolayers were transferred at 25 °C temperature, 25 mN/m constant surface pressure, compressing the monolayer with 50 cm^2/min barrier speed before reaching the target pressure and setting 5 mm/min dipping speed after the target pressure has been reached. The surface pressure was monitored by a Wilhelmy-type pressure gauge and controlled by a feed-back loop.

Contact angle measurements. Copper alloys with and without coatings were characterised by their advancing and receding contact angles. These were measured in a digital surface tensiometer (NIMA Technology) based on the Wilhelmy-method. As measuring liquid ultrapure water (Milli-Q) was used in a clean, thermostated vessel.

Reflection absorption infrared spectroscopy. A Nicolet Magna 750 FTIR spectrometer was used, with the following abilities and parameters: MCT detector, 512 scans, 2 cm^{-1} resolution, incidence of the IR beam: 68.3°, Au/KRS-5 polarizer, Specac 19650 grazing angle accessory.

Sum frequency generation spectroscopy. An EKSPLA spectrometer was used (visible wavelength: 532 nm, energy: 40 μJ). The description of the setup and the experimental parameters can be found in [40].

Corrosion in NaCl solution. SAM- and Langmuir–Blodgett-coated copper samples were dipped in 0.5 M NaCl for 15 h, then thoroughly rinsed in pure water, in acetone and finally dried. 100×100, 50×50 and 10×10 μm^2 areas were scanned in three different points of each sample by a Nanoscope IIIa AFM apparatus (Digital Instruments) equipped with 100 and 10 μm scanners and silicon nitride tips, operating in contact mode.

Bacterial adhesion. A cooling water sample from the pharmaceutical industry, containing mixed microbial population was used in the adhesion experiments. Bare and coated copper samples were dipped in for 48 h, then rinsed in distilled water and treated with acridine orange in order to dye the cells. An Axio Imager upright microscope (Carl Zeiss) has been used at 1000× magnification in immersion oil to image the microbial cells and the biofilm. For complementary information, AFM images of 100×100, 50×50, 25×25 and 10×10 μm^2 areas at three different points of each sample were recorded.

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