Polystyrene films as barrier layers for corrosion protection of copper and copper alloys

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Abstract

Dip-coated polystyrene layers of sub-micrometre thickness (85–500 nm) have been applied on copper and copper alloys (aluminium brass, copper-nickel 70/30), as well as on stainless steel 304, and produced an effective barrier against corrosion and adhesion of corrosion-relevant microorganisms. According to the dynamic wettability measurements, the coatings exhibited high advancing (103°), receding (79°) and equilibrium (87°) contact angles, low contact angle hysteresis (6°) and surface free energy (31 mJ/m^2). The corrosion rate of copper-nickel 70/30 alloy samples in 3.5% NaCl was as low as 3.2 μm/a (44% of that of the uncoated samples), and in artificial seawater was only 0.9 μm/a (29% of that of the uncoated samples). Cell adhesion was studied by fluorescence microscopy, using monoculture of *Desulfovibrio alaskensis*. The coatings not only decreased the corrosion rate but markedly reduced the number of bacterial cells adhered to the coated surfaces. The PS-coating on copper gave the best result, 2×10^3 cells/cm^2 (1% of that of the uncoated control).

Keywords

1 Introduction

Corrosion causes severe damage worldwide. The presence of corrosion-relevant microorganisms initiates biofilm formation; under these layers the metal surface starts to corrode. This is referred to as microbial corrosion or microbially influenced corrosion (MIC). Since MIC usually starts up under a developed biofilm, the strategies to control it are strongly related to the inhibition of microbial adhesion. Two different approaches are in application: 1) use of inhibitors and biocides; and 2) modification of surfaces by coatings.

A typical occurrence of MIC in the energy sector is the fouling and corrosion of condenser tubes of the cooling circuits of power plants. Most commonly, MIC is mitigated by chlorination, ferrous iron treatment and mechanical cleaning by circulating sponge balls. These are more or less effective methods, but even so, periodic shut-downs are unavoidable due to the need of maintenance and cleaning by hand [1–3].

Nanocoatings offer a new alternative solution of equal or better efficiency, being more cost-effective and implying less environmental load [4]. Self-assembled monolayers (SAM), Langmuir–Blodgett (LB) films and other organic thin films with the thickness of a few nanometres have been investigated and used for a long time in corrosion protection and against biofouling. The first SAMs were thiols on gold surfaces [5]. Since then, many different substances on different metals and alloys have been proven to be effective against corrosion. The list includes thiols [6–19], amines [12], phosphates [20], sulfates [21], thiosulfates [22], carboxylic acids [23–29], hydroxamic acids [29–31], amino acids [32–34], phosphonic acids [29, 35], sulfonic acids [29], silane derivatives [36], as well as heterocyclic and other compounds [16, 37–44].

Our previous results with carboxylic-, hydroxamic- and phosphonic acids applied in SAM nanocoatings proved the usefulness of these molecular layers as barriers against corrosion and microbial cell adhesion [45–51]. Recently, the focus of our research moved towards thicker polymer coatings. Out of the several possibilities, polystyrene (PS) was chosen as a model polymer in our experiments. The reasons for this choice are that:

a. PS is ubiquitous, available in large quantities as unprocessed waste;
b. it is non-toxic;
c. it is non-biodegradable;
d. it is inexpensive;
e. it is a simple, non-exotic polymer;
f. it can be further functionalised;
g. it is well soluble in some common, inexpensive, non-toxic solvents;
h. its surface free energy [52] is close to the minimum biofouling value on the Baier-curve [53], predicting low cell adhesion.

As part of our overall endeavour to screen out potential candidates for efficient protective nanolayers, in this study we demonstrate a quick-test for monitoring the efficiency of PS nanocoating barrier layers against corrosion of copper and copper alloys as well as stainless steel 304, used as the materials of heat exchangers of power plants. Since in heat exchangers operating partly with seawater biofouling is a phenomenon occurring in parallel to, inseparable from corrosion, cell adhesion tests with *Desulfovibrio alaskensis* monoculture – as model microorganisms - were also conducted.

2 Materials and methods

Substrates. Pure (99.99%), plane-parallel, polycrystalline Cu samples of 14×9×2 mm^3 dimension were polished by a P220 grit sandpaper. Tube section samples of aluminium brass (Al-b; composition: 76.447% Cu, 21.115% Zn, 2.166% Al, 0.046% Fe, 0.040% V), copper nickel 70/30 (CuNi; composition: 66.660% Cu; 31.411% Ni; 0.829% Mn; 0.692% Fe; 0.053% Cr) [54] and stainless steel type 304 (SS; composition: 68.973% Fe; 18.371% Cr; 9.299% Ni; 1.680% Mn; 0.488% Si; 0.365% Mo; 0.302% Cu; 0.056% V; <0.080% C) [55] were of 12×10×1.3 mm^3 dimension and 11 mm inner, respectively 13 mm outer radii of curvature. These were not polished due to the difficulties arising from their geometry. For thickness measurements, silicon wafers were used as substrates.

Cleaning and pre-treatment. As proven indispensable [56–57], metal samples were degreased with acetone, and oxidized in a two-step pre-treatment consisting of a 5 min ultrasonic bath in 14 mM HNO$_3$, followed by a 5 min ultrasonic bath in 5% H$_2$O$_2$.

SAM coatings. Cleaned and pre-treated copper and alloy substrates were dipped into 2.0 mM solutions of *n*-octadecane 1-derivatives: octadecanoyl hydroxamic acid (C18N) and octadecyl phosphonic acid (C18P) in dichloromethane (DCM), for 1, 5 and 24 h. The coated samples were rinsed with pure solvent to remove the non-specifically bond, excess materials and were dried in air or in a stream of nitrogen.

Dip-coated PS. Cleaned and pre-treated copper and alloy substrates were immersed/withdrawn into/from solutions of atactic PS in DCM, at three different concentrations (10, 30 and 50 g/L) with a rate of 5 mm/s. Two PS sources have been used, H-type and T-type, differing in their average molar mass and dispersity (H-type: M_n = 74800 and Đ = 2.30; T-type: M_n = 88700 and Đ = 2.84)

Contact angle measurements. A Wilhelmy-type [58] digital surface tensiometer (Nima) was used. Samples were automatically dipped into and pulled out from water with a rate of 10 mm/min, while the apparent weight change of the target sample was registered. The contact angles were retrieved by inputting the cross sectional dimensions of the samples and the surface tension of the water. Ultrapure (MilliQ) water was used in the experiments.

Layer thickness measurements by ellipsometry. Thickness measurements were carried out close to the upper edge of the PS coating. The spectroscopic ellipsometer used (MM–16, HORIBA Jobin Yvon) was equipped with a non-rotating, liquid crystal compensator. The parameters of the measurements were: spectral range 430–850 nm; angle of incidence 65°; spot size 1 mm. Fitting the thickness and refractive index to the measurement data was done with the DeltaPsi2^{TM} software of the instrument.

Layer thickness profile determination by AFM. Parallel lines were scratched with a diamond tip in the PS coatings on Si along the dipping direction, perpendicularly to it, and the step heights were measured by a NanoScope® Dimension™ 3100 AFM apparatus (Digital Instruments/Veeco) equipped with a silicon nitride cantilever, operating in contact mode.

Corrosive liquids. Coated and uncoated metal samples were dipped in unstirred, non-deoxygenated solutions of 0.1 M Na$_2$SO$_4$ for 28 h, 3.5% NaCl solution for one week, and artificial seawater (ASW) for one week, respectively. ASW was prepared according to the recipe of Kester et al. [59]. Its composition is presented in Table 1.

Corrosion measurements by ICP-OES. The metal ion concentrations in the aqueous solution dissolved in the course of corrosion could be measured very precisely by inductively coupled plasma atomic emission spectroscopy (ICP-OES). For this, the solutions containing the metal ions were treated with concentrated nitric acid and measured in a simultaneous ICP-OES setup (Spectro Genesis) equipped with a CCD detector system with axial plasma viewing and a special optical-

plasma-interface (OPI) system. Due to OPI, matrix effects were reduced dramatically. The CCD camera systems made possible to cover completely the spectral range of 175–775 nm. The optimized Rowland-circle alignment (ORCA) and the Spectro Smart Vision software allowed the measurement and storage of the whole interval of the spectrum (12000 emission lines). Due to its broad bandwidth (0.362 MHz) and special frequency of operation ($f(op)$ =27.12 MHz), the plasma remained extremely stable during the measurements.

Bacterial attachment. Coated and uncoated samples were introduced into a 10-fold diluted, slightly modified VM medium I [60] (ρ_{NaCl}=20 g/L, no thioglycolic acid) inoculated with a 10^8 cells/mL bacterial suspension of *Desulfovibrio alaskensis* AL1, a representative species of corrosion-relevant physiological group of sulfate-reducing bacteria. After 24 h of incubation under anaerobic conditions, at 28°C, the samples were removed, rinsed with sterile, deionised water and stained with 0.36 mM 4',6-diamidino-2-phenylindole (DAPI) in 1.3 M formaldehyde for 20 min. Care was taken to ensure anaerobic conditions and to avoid contamination of the monoculture, as well as direct sunlight during staining, transportation and storage.

Cell counting. Fixed and stained cells were counted under an Axio-Imager A1m epifluorescence microscope (Zeiss, Germany) on 1/8 × 1/8 mm^2 areas. Data collected on six locations per sample, three parallel samples of each type, were averaged.

{Here Table 1}

3   Theory

3.1   Contact angles, surface free energies and surface coverages

The θ_Y equilibrium (Young) contact angles [61] were calculated as a weighted trigonometric average of the measured advancing and receding contact angles (θ_A and θ_R) based on Tadmor's equations (Eq. 1–3) [62].

$$\theta_Y = \arccos\left(\frac{\Gamma_A \cos\theta_A + \Gamma_R \cos\theta_R}{\Gamma_A + \Gamma_R}\right) \tag{1}$$

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

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

To extract surface free energy values from contact angle data, the method based on Neumann's equation of states was chosen (Eq. 4–7) [63]. Although disputed [64], the main arguments for this choice are that only one test liquid is enough, thus considerable time can be saved; and that this liquid can be water, thus avoiding the dissolution of the PS by different organic solvents. However, the obvious disadvantage of the method, compared to other, equally well-established ones [64–65] is

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that only the total surface free energy can be obtained, without its dispersive and non-dispersive components. Combining these equations with the Young equation (Eq. 8), the solid/liquid interfacial tension γ_{SL} can be eliminated and, knowing the measured equilibrium contact angle θ_Y and the liquid's surface tension γ_L, the γ_S free surface energy of the solid surface can be calculated.

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S \gamma_L} \exp[-\beta_1 (\gamma_L - \gamma_S)^2] \tag{4}$$

$$\beta_1 = 1.247 \times 10^{-4} (m^2/mJ)^2 \tag{5}$$

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S \gamma_L} \left[1 - \beta_2 (\gamma_L - \gamma_S)^2 \right] \tag{6}$$

$$\beta_2 = 1.057 \times 10^{-4} (m^2/mJ)^2 \tag{7}$$

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta_Y \tag{8}$$

Surface coverage values of PS (denoted here by f instead of the standard θ, in order to avoid confusion with the symbol of the contact angle) were calculated from the respective θ_Y values, based on the Cassie–Baxter theory [66], assuming a two-component surface consisting of domains of the uncoated substrate with θ_s equilibrium contact angle and the PS chains of θ_{PS} equilibrium contact angle (Eq. 9). Porosity, roughness and chemical heterogeneity of the two model constituents were not taken into account.

$$\cos\theta_{film} = f\cos\theta_{PS} + (1-f)\cos\theta_s \tag{9}$$

4   Results and discussion

4.1   Thickness measurements

The thickness of the polystyrene films deposited from solutions of three different concentrations ($\rho_{PS} =$10, 30 and 50 g/L) was first measured by ellipsometry, in each case close to the upper edge of the coating. The results were 45, 220 and 460 nm, respectively, being in very good agreement with those obtained from AFM measurements at the same spots.

In order to gain information on the thickness variation of the coatings, the measurements were continued in several points along the dipping direction, thus constructing the thickness profiles shown in Figure 1. It was found that

1. the thickness generally increased from the top towards the bottom of the coating;
2. the average thickness increased with increasing ρ_{PS};
3. the non-uniformity increased with increasing ρ_{PS};

but interestingly

4. the thickness was always 45 nm at the very top edge, irrespective of ρ_{PS}.

This latter observation can be explained as follows:

In solution, PS chains adopt a random coil conformation. Their size can be described by their so-called radius of gyration [67]. Knowing the molar mass distribution of the PS, the diameter of the PS coils in solution can be estimated. According to these calculations, the diameter of the PS coils falls between 5–160 nm. When the solid substrate is pulled out from the PS solution, the evaporation of the solvent starts at the upper edge of the immersion line. At this point, the solution becomes more concentrated for the large PS chains, which therefore undergo phase-separation first. Only after that, the smaller chains follow. Upon adsorption, the polymer coils are flattened. Thus, at the upper edge of the coating, the largest, 160 nm PS coils form a 45 nm thick monolayer film on the surface. This is a plausible explanation and is in agreement with the Flory–Huggins theory of polymer solutions [68], therefore the phenomenon was not investigated further.

It is important to emphasise that our nanocoatings are 120 to 1400 times thinner than other reported, PS-based protective coatings [69–70], yet effective, as detailed below.

{Here Fig. 1}

4.2 Contact angles, surface free energies and surface coverages

The measured θ_A and θ_R, as well as the calculated θ_Y and surface free energies agree well with the values reported in the literature for PS [53]. It has been found that surface properties of dip-coated PS layers on Cu, Cu alloys and SS are reflected mainly in their θ_R values. Therefore, contact angle hysteresis and calculated θ_Y values give a better characterization than θ_A. By increasing the PS concentration (ρ_{PS}), the surface coverage (f) (and hence, the surface properties) of PS layers approached a saturation value. θ_Y values increased and surface free energies decreased markedly with increasing PS concentration for all dipping numbers, as an indication of coating improvement, predicting low bacterial cell adhesion, in line with the Baier-curve of biofouling [54]. Results for PS-T coatings on Cu are summarized and presented in Figure 2 to illustrate these trends otherwise found valid for all other types of substrates, too.

Interestingly, as reflected in the contact angle results, the properties of PS layers do not seem to improve unequivocally with increasing dipping number. The reason might be the imperfections of the deposition. During consecutive dippings, parts of the already deposited layers might be re-dissolved or reorganized. This is why the more objective 'dipping number' term was chosen instead of the 'layer number'.

{Here Fig. 2 a–f}

4.3 Protection in Na$_2$SO$_4$ solution

The protective effect of PS layers was tested on copper substrates in 0.1 M Na$_2$SO$_4$. The deposition of a single layer of PS from ρ_{PS}=50 g/L solution influenced markedly the corrosion of the metal. The appearance of black CuO was visible after already a few minutes on the uncoated sample and it developed into a continuous layer (which indicates a general corrosion) in a couple of hours. Contrarily, the PS-coated sample looked intact even after more than one day (Figure 3).

{Here Fig. 3 top and bottom}

4.4 Protection in NaCl, respectively in ASW

The alloys used in our experiments are applied in cooling circuits of power plants operating with seawater, where are exposed to high concentrations of chloride ions. That's why the effectiveness of the PS nanolayers was investigated in pure sodium chloride solution and in artificial seawater.

The first set of experiments was carried out with Al-b, CuNi and SS, in 3.5% NaCl solution. The duration of exposure was 1 week. The concentration of the metal ions found in the NaCl solution, resulting from the corrosion of the alloy samples, was measured by ICP-OES. From the obtained metal ion concentrations, the mass loss of the metals in mg/m^2 units due to corrosion was calculated for each alloying metal type. Then, the concentration data was transformed into the chemical dissolution rate of the respective component metal, v_{cd}, defined in Eq. 10, where m_M denotes the mass of the alloying metal M found in the liquid, A is the area of the alloy sample in contact with the liquid, and t is the time of this contact. The first two graphs (A and B) in Figure 4 show these chemical dissolution rates of the component metals of Al-b and CuNi, respectively, for uncoated control vs. samples coated with 1, 3 and 5 layers of H-type PS, from a 10 g/L PS solution.

$$v_{cd} = \frac{m_M}{At} \tag{10}$$

The chemical dissolution rates of the individual metals, $v_{cd}(M_i)$, can be summed, and, dividing with the ρ density of the respective alloy, the overall corrosion rate of the alloy, v_{cor}, can be expressed in μm/a (Eq. 11). This is shown in Figure 4, C for all three alloy types.

$$v_{cor} = \frac{\sum_{i=1}^{n} v_{cd}(M_i)}{\rho} \tag{11}$$

The conclusions of these experiments are the followings:

i.   PS layers have clearly a protective effect.
ii. The thicker the layer, the lower the amount of metal ions found in the corrosive liquid.
iii. The corrosion of alloys is non-stoichiometric (selective leaching).
iv. Best result obtained: In the case of CuNi, the calculated corrosion rate decreased by 56%.
     The (general) corrosion rate of SS was immeasurably low, since it follows the pitting mechanism.

{Here Fig. 4 a–c}

The decrease of corrosion with increasing layer thickness was expected. However, two issues need to be clarified. First, the decrease in the corrosion rate caused by the surface coating is not very high (56%). The reason can be understood from Figure 2F. The calculated surface coverage of a PS monolayer deposited from a 10 g/L solution is only 52%, providing thus limited protection. Second, increasing the layer number does not influence the protective effect that much as expected. This is in agreement with the contact angle results and suggests that by multiple dipping, some of the already deposited layer is re-dissolved into the solution or reorganized on the surface, as mentioned previously.

In similar experiments carried out in unstirred ASW for one week, the PS thickness was varied by both dipping number (n=1, 3 and 5) and PS concentration (ρ_{PS}=10, 30 and 50 g/L). Both types of PS (PS-H and PS-T) were used. An uncoated control sample was used as reference. As compared to the simple case of the 3.5% NaCl, the measured metal concentrations and the calculated chemical dissolution rates showed a somewhat more complicated pattern (Figure 5). This can be explained by selective re-precipitations due to the more complex composition of the ASW and the differences in the degree of success of the coating procedure for each sample. Nevertheless, the observed trend is clear and the following conclusions can be formulated:

i.   PS layers clearly show a protective effect.
ii. The trend observed in ASW is qualitatively similar to that measured in 3.5% NaCl.
iii. The corrosion of alloys undergoes non-stoichiometrically.
iv. Best result was observed in the case of CuNi; the calculated corrosion rate decreased by 71%.

{Here Fig. 5 a–c}

As observed also in NaCl solution and explained above, the effectiveness and hence the barrier effect of the PS multilayers is not improved by consecutive dipping, but the concentration is the key parameter.

Figure 5C shows the selective leaching of the constituent metals for the case of CuNi. The k ratio of the calculated chemical dissolution rates of copper to that of iron, from the CuNi samples in the ASW after the one week corrosion test, is defined in Eq. 12. When plotted for the different PS coatings, it becomes evident that this ratio decreases with both increasing ρ_{PS} and n.

$$k = \frac{v_{cd}(Cu)}{v_{cd}(Fe)} \tag{12}$$

4.5   Cell adhesion

Figure 6 shows *D. alaskensis* cells on an uncoated SS sample, adhered preferentially to the grain boundaries of the uncoated alloy.

{Here Fig. 6 a, b}

The results of the adhesion experiments are summarised in Figure 7 as relative cell counts N_{rel} defined as:

$$N_{rel}(\%) = \frac{N}{N_c} \times 100, \tag{13}$$

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where N denotes the cell count on the coated sample for a given area, and N_c is the cell count on the control sample for an area of the same size. For comparison, results obtained on C18N and C18P SAM coatings are also presented.

{Here Fig. 7 a, b}

It is evident that the PS coatings effectively inhibit the cell adhesion. Their efficiency was comparable to or even higher than that of the C18N and C18P SAM coatings. The best achieved result was 99% efficiency on Cu, as compared to the uncoated sample. Error bars were large for the uncoated samples and markedly decreased for the coated ones meaning a more uniform cell adhesion across the surface caused by a more uniform surface energy distribution. The hydrophobicity of the PS must play a key role in the prevention of cell adhesion. Extracellular polymeric substances, mainly of hydrophilic nature, are excreted by the bacterial cells and are responsible for adhesion; therefore corrosion relevant bacteria do not adhere well to hydrophobic surfaces, resulting in low cell counts.

5   Conclusions

Dip-coated PS films can be fabricated easily, quickly, and inexpensively. They serve as good model for dip-coated polymer layers in studies against corrosion and microbial adhesion, i.e. microbiologically influenced corrosion. Moreover, they are non-toxic (important from the point of view of the environment and human health) and non-biodegradable (important from the perspective of microbial attack), representing additional benefits. The most effective thickness of the fabricated PS layers is defined by the appropriate concentration and dipping number. The layers effectively reduce both the corrosion and the microbial cell adhesion on the substrate alloys. Based on the results our future investigations will focus on the development of multifunctional hybrid coatings against general- and pitting corrosion, as well as against MIC, with active compounds embedded in a polymer matrix.

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Figure captions

Figure 1. Thickness profiles of dip-coated PS layers (prepared from PS solutions of ρ_{PS}= 10, 30 and 50 g/L, respectively) along the dipping direction, shown as d/nm thickness, measured at a distance l/mm from the upper edge of the layers. The inset shows the mean layer thickness $\langle d\rangle$/nm in function of $\rho_{PS}/(g/L)$.

Figure 2. $\theta_A/°$ advancing (A), $\theta_R/°$ receding (B) and $\theta_Y/°$ equilibrium (Young) (C) contact angles, as well as $\Delta\theta/°$ contact angle hysteresis (D), $\gamma_s/(mJ/m^2)$ surface free energies (E) and f surface coverage values (F) of PS-coated copper substrates, as function of $\rho_{PS}/(g/L)$ and dipping number *n*. (A) to (E) no colour: uncoated control; light grey: ρ_{PS}=10 g/L; grey: ρ_{PS}=30 g/L; dark grey: ρ_{PS}=50 g/L. (F) uncoated control ($\bigcirc$); *n*=1 ($\bullet$); *n*=2 ($\blacklozenge$); *n*=5 ($\blacksquare$).

Figure 3. Uncoated (top) and PS-coated (bottom) Cu samples after 5, respectively 28 h in Na_2SO_4 solution, $[Na_2SO_4]$= 0.1 M

Figure 4. Chemical dissolution rates and corrosion rates of samples in 3.5% NaCl, calculated from ICP-OES measurement results, for 1 week exposure, shown as function of dipping number n. Alloy samples coated with n=1, 3 and 5 of PS-T of concentration ρ_{PS}=10 g/L. n=0 stands for uncoated negative control samples. (A) Chemical dissolution rates $v_{cd}/(mg/m^2h)$ of individual metal constituents of Al-b. Bars in each cluster: first (orange)-Cu; second (yellow)-Zn; third (grey)-Al. (B) Chemical dissolution rates $v_{cor}/(mg/m^2h)$ of individual metal constituents of CuNi. Bars in each cluster: first (orange)-Cu; second (green)-Ni. (C) Corrosion rates $v_{cor}/(\mu m/a)$ of the alloy samples. Bars in each cluster: first (red)-Al-b; second (green)-CuNi and third (blue)-SS samples.

Figure 5. Chemical dissolution rates and corrosion rates of samples in ASW, calculated from ICP-OES measurement results, for 1 week exposure, shown as function of PS concentration ρ_{PS} and dipping number n. Alloy samples coated with n=1, 3 and 5 of PS-H and PS-T of different concentrations: ρ_1=10, ρ_2=30 and ρ_3=50 g/L. n=0 stands for uncoated negative control samples. (A) Chemical dissolution rates $v_{cor}/(mg/m^2h)$ of individual metal constituents of Al-b. Bars in each cluster: first (orange)-Cu; second (yellow)-Zn; third (grey)-Al. (B) Chemical dissolution rates $v_{cor}/(mg/m^2h)$ of individual metal constituents of CuNi. Bars in each cluster: first (orange)-Cu; second (green)-Ni. (C) k ratio of chemical dissolution of Cu to Fe, from CuNi samples.

Figure 6. (A) Deflection mode AFM image of a 50 × 50 μm^2 area revealing the grain structure of the SS sample. (B) *D. alaskensis* cells preferentially adhere to grain boundaries of the uncoated SS sample.

Figure 7. Relative cell counts N_{rel}/% on SAM- and PS-coated copper (A), respectively SS (B) samples