

## Contact Angle Measurement is an Efficient Tool for the Characterization of Corrosion Protection Nanolayers on Copper Alloys and Stainless Steel

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With the advent of the nano-era, a pronounced interest in the nanolayers has emerged. The development of more and more sophisticated measurement devices and techniques made possible the visualization, characterization and investigation of nanolayers. However, there exists a variety of simple, old means which should not be despised either. In this work, the use of contact angle measurement as a simple, fast, inexpensive and accessible tool for the study of surfaces with and without nanolayers is demonstrated. Furthermore, it is evidenced that in contrast to its simplicity, contact angle measurement can address surprisingly complex questions and give proper answers to these.

**Keywords:** Nanolayer, Microbiologically Influenced Corrosion, Contact Angle, Aluminium Brass, Copper-Nickel, Stainless Steel, Self-assembled Monolayers.

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### 1. INTRODUCTION

Aluminium brass (Al-brass), copper nickel 70/30 (CuNi) [1] and stainless steel 304 (SS) [2] are important alloys in the energy sector. Due to their good heat conductivity and corrosion resistance, the former two are often used as materials of the cooling circuits of power plants operating with seawater as a cooling agent, while SS is a common material of fresh water tubings.

In the presence of microorganisms, all these alloys suffer, to some extent, from biofouling and the consequent microbiologically influenced corrosion. Means to protect these alloys include dosage of biocides to control the growth of microorganisms and inhibitors for the corrosion protection. However, none of these are always successful. In severe cases, the developed thick biofilm can only be removed by manual cleaning, and during the maintenance shutdown of complete power plant blocks may become unavoidable [3–5].

Ultrathin organic protection layers, such as self-assembled monolayers (SAMs) and Langmuir–Blodgett films have been proven efficient in laboratory experiments against both the corrosion itself and the adhesion of microorganisms [6–9]. However, their reduced stability in aqueous environment set a limit to their industrial applicability [10]. In the coating industry, a proper pretreatment of the respective surface to be protected is the prerequisite of the success of the coating procedure and the performance of the protection layer. However, thorough cleaning is often time consuming and costly.

Similarly, in laboratory experiments with SAMs, surface pretreatment may be an important, but circui-

tous process step. It is therefore desirable to investigate the necessity of it.

Contact angle (CA) measurement is a basic tool to characterize surfaces. In spite of that it offers much useful information to be extracted from, generally it is applied to serve rather modest purposes only, such as differentiation between a hydrophobic and a hydrophilic surface.

Through our experiments, we attempted to answer the question whether CA measurements could be used in a more efficient way in order to obtain information about the success of the nanocoating procedure and the stability of the prepared layer, especially in conjunction with the pretreatment of the substrate surface.

### 2. EXPERIMENTAL

Aluminium brass, copper-nickel and stainless steel alloy specimens were of 10×12 mm<sup>2</sup> dimension, and cut from standardized tubes [1–3], therefore being curved, with approx. 12.7 mm (0.5 in) radius of curvature.

Octadecanoyl hydroxamic acid (C18N) was synthesized from hydroxylamine and the appropriate acyl chloride. Octadecyl phosphonic acid (C18P) was synthesized in a Michaelis–Arbusov reaction. The products were re-crystallized and characterized by melting points, elemental analysis, infrared spectroscopy and thin layer chromatography.

As substrate cleaning, 10 min. sonication in spectroscopic grade acetone was applied, occasionally completed by 20 min. cleaning in ozone generated under an UV lamp.

SAM coatings were prepared by dipping the pretreated metal samples into 2.0 mM solutions of the film forming compounds (C18N, respectively C18P) in chlo-

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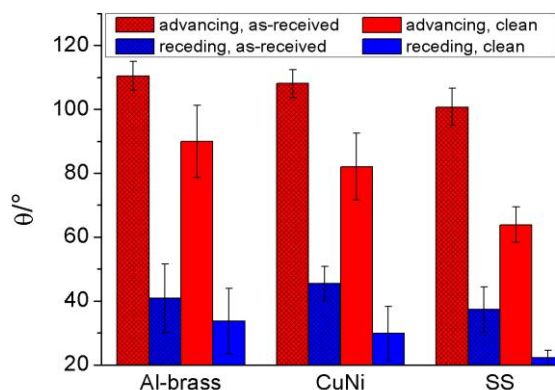
roform, dichloromethane, or tetrahydrofurane. Dipping times were 1, 5 and 24 h in the case of the alloys. The coated samples were rinsed with the respective solvent in order to remove non-specifically bond excess material and were dried in air or in a stream of nitrogen.

The alloy samples, with and without coatings, were characterized by their advancing and receding CAs. Static sessile drop measurements were carried out using a home-built measurement device equipped with a Hamilton micropipette and a CCD camera. For the dynamic Wilhelmy-type CA measurements a digital surface tensiometer (Nima) was used. Samples were automatically dipped into and pulled out from water with a rate of 10 mm/s, while the apparent weight change of the target sample was registered. The CAs were retrieved by inputting the cross sectional dimensions of the samples and the surface tension of the water. Ultrapure water (MilliQ) was used as a measurement liquid in both cases.

A stability test of the SAMs in flowing water was conducted for 2 weeks. Dynamic CAs were measured before and after the test. In this latter case the samples were first thoroughly dried.

### 3. RESULTS AND DISCUSSION

Dynamic CA measurements of as-received and cleaned samples showed the effect of the cleaning procedure (Fig. 1). Al-brass samples exhibited higher advancing and receding CAs than CuNi samples, which exhibited higher values than SS samples, both in as-received and in cleaned state. In this same order, the effect of cleaning became more and more pronounced, from about 20° advancing CA difference in the case of Al-brass, 30° in the case of CuNi and 35° in the case of SS. Similarly, the receding CA differences were 5, 15 and 16° for the three alloy types, respectively.



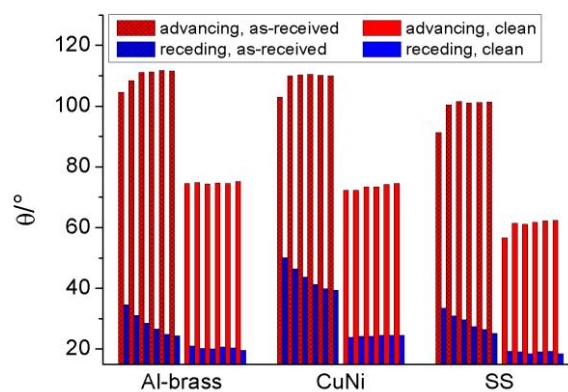
**Fig. 1** – Advancing and receding CAs of as-received vs. cleaned alloy samples, averaged for 4 parallel sample of each type, measured in 6 consecutive dipping cycles in a Wilhelmy-type dynamic measurement

The change in the CAs during the consecutive dipping cycles was spectacular (Fig. 2). In the case of the as-received samples, advancing CAs initially increased, while receding CAs monotonously decreased in each new cycle. Contrarily, cleaned samples showed not only lower CAs, but also much more stable ones.

When the effect of the cleaning on the C18N-SAM formation was studied, it was found that after the com-

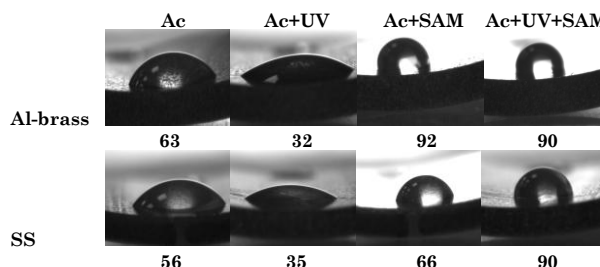
plementary UV cleaning step the static CA of all alloy types decreased approx. to the same value (32-35°), as an indication of a more pronounced hydrophilicity. When SAM preparation was carried out after this UV step, the high CAs on Al-brass and SS (90°) indicated the formation of a SAM. However, in the case of Al-brass, SAM preparation proved to be successful also when performed after a simple acetone-cleaning (CA = 92°), apparently not effective in the case of SS (CA = 66°).

Wilhelmy-type CA measurement can be used in order to learn about the short-term stability of such nano-coatings, as suggested by our results (Fig. 4). When subtracting the values of advancing CAs of the same samples obtained in two consecutive immersion cycles, a few degrees differences can be noticed, as already shown in Fig. 2. The difference depends on the alloy type and has a large statistical spread, but it is generally negative, i.e. the surfaces become slightly more hydrophilic after each new immersion step, as an indication that the structure of SAM layers is slightly altered in water.



**Fig. 2** – Advancing and receding CAs of as-received vs. cleaned alloy samples in the consecutive dipping cycles of the Wilhelmy-type dynamic measurement

When these differences are plotted as a function of the preparation time of the SAM, a reasonable trend becomes obvious: the longer the initial SAM preparation time was (the time allowed the molecules to adopt the best possible arrangement on the surface), the lower this difference is during the immersions. The larger differences are usually measured for the uncoated control samples, as obviously the wetting of these ones progresses with the fastest rate.



**Fig. 3** – The effect of surface cleaning on the C18N-SAM formation, as revealed by static CAs (°) of different alloy surfaces. Ac: cleaned in acetone; Ac+UV: cleaned in acetone, followed by an UV-cleaning step; Ac+SAM: SAM formation after acetone-cleaning; Ac+UV+SAM: SAM formation after acetone- and UV-cleaning

In accord with these above facts, CA measurement proved to be effective also in the correct estimation of the long-term stability of these nanolayers. Layers prepared for 1, 5 and 24 h respectively were measured in three consecutive cycles both before and after a two week long stability test in flowing water. Taking the after/before advancing CA differences in any measurement cycle, we found very drastic CA decrease after the test, indicating a pronounced hydrophilicity originating from a pronounced layer alteration in the water (Fig. 5).

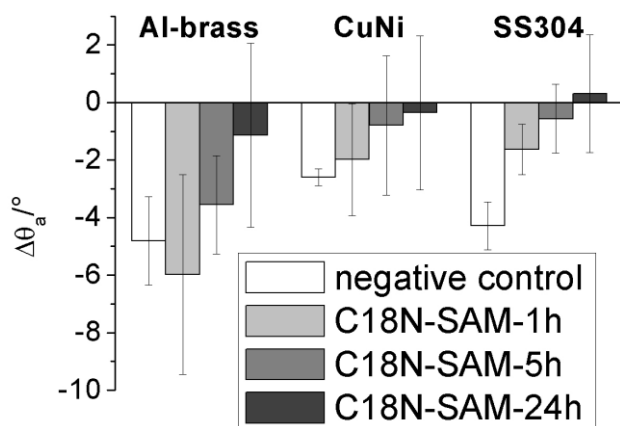


Fig. 4 – Short-term stability of C18N-SAM coatings: wetting during Wilhelmy CA measurement cycles (advancing CA differences between the second and the first immersion cycles) in function of allowed self-assembly time

However, this lowering of the CA showed very strong dependence on the SAM preparation time. The layers allowed to build up for 1 h only showed the largest CA fall (about 45-50°), the ones prepared for 5 h showed only 40°, while the ones assembled for 24 h showed only 25-30°. We found it particularly spectacular that these simple CA measurements could lead to the same conclusion as our previous, more sophisticated reflection absorption infrared spectroscopy (RAIRS) and sum frequency generation spectroscopy (SFG) investiga-

tions [10]. This fact points out the hidden possibilities laying in the CA measurements.

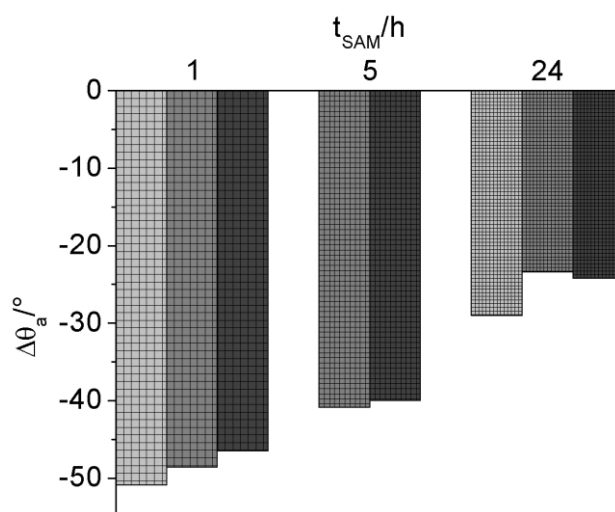


Fig. 5 – Long-term stability of C18P-SAM coated Al-brass samples for 2 weeks in flowing water. After-before advancing CA differences in the 1st (light grey), 2nd (grey) and 3rd immersion cycles (dark grey) as function of self-assembly time

#### 4. CONCLUSIONS

The main conclusion of this work is that, as demonstrated above, simple, fast, inexpensive and accessible CA measurements can provide answers to surprisingly deep questions.

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