

Anticorrosion activity of phosphonic acid amphiphile in self-assembled molecular layer

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Abstract

The aim of our experiments was to demonstrate the increase in the corrosion resistance of two stainless steels after nanolayer deposition. The questions we wanted to answer were: how the self-assembled deposition time influences the compactness of the nanolayers and how the steel composition influences the nanofilms deposition, its compactness and the anticorrosion efficiency. To answer these questions self-assembled molecular layers were prepared by dipping technique; the nanolayers were characterized by water wettability values and the two different stainless steel samples with and without nanofilms were subjected to corrosive media (sodium chloride solution). The effect of the chloride ions on the solid surfaces were visualized by atomic force microscopy and characterized by roughness parameters. The anticorrosion efficiency caused by the steel surface compositions as well as by the different self-assembled adsorption time was explained by the experimental data.

Keywords: *undecenyl phosphonic acid, self-assembled molecular layers, wettability, atomic force microscopy, roughness, anticorrosion self-assembled nanolayers.*

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1. Introduction

Corrosion is a well-known, natural, undesired, degradation process when metals – of higher energy – react with the environment in the presence of moisture, aggressive chemicals and corrosion relevant microorganisms; it induces the structural decay which is the consequence of reaction when metals turn into lower energy form, *i.e.* in oxides, salts; then the durability and strength of the metal decreases, its lifespan shortens. The speed of corrosion reactions could be reduced (but never stopped!) in different ways. When metals are immersed into (aqueous or oily) liquids, the rate of metal dissolution can be controlled by addition of inhibitors that in small quantity can decrease the corrosion at very low concentration. These molecules could be of inorganic, organic or biological origin; most of them contain hetero

atoms (nitrogen, oxygen, sulfur, phosphor) that with their special characters (*e.g.* lone electron pair, free acidic groups, unsaturated bonds, *etc.*) improve the anticorrosion effectiveness. Inhibitors with phosphono groups can adhere to a metal oxide layer forming a --P--O--Me bond (Me= metal ion) [1–10].

Other possibility is the application of anticorrosion surface coatings in thin (mono- and multi-molecular) or in thicker layers that can increase the lifespan of metals [11, 12].

There are different methods to produce molecular films: Langmuir–Blodgett (LB) technique (which needs special equipment and the size of the metal to be covered is limited) [13–17], self-assembling [18–22], or layer-by-layer molecular deposition [23, 24].

The formation of self-assembling molecular layers (SAMs) is an adsorption process when the components spontaneously form layer of ordered static structure with a thermodynamic equilibrium. The SAM former molecules that are organic molecules with functional groups, which interact with surfaces, can produce thin films. During layer formation the so-called amphiphilic molecules can spontaneously adsorb onto the metal surface via their head groups by physical or chemical adsorption and by intermolecular interactions among the hydrophobic molecular parts that helps the formation of well-ordered, compact layer. The SAM-coated solid surfaces can effectively attenuate the surface energy of metals and regulate the wettability, protect metals against corrosion and biodeposition. With other words the SAMs protect metals against corrosion effectively inhibiting and slowing down the corrosion processes. The effectiveness of a SAM film against corrosion depends on several factors (structure of the amphiphilic molecule, composition of metal and the passive surface layer, corrosive environment, compactness of the SAM films). The most important is that this type of nanolayers can save the metals against corrosion and, at the same time, increase the lifespan of structural metals.

The SAM layers offer several advantageous application possibilities in the corrosion field as they can form barrier between the metal and the aggressive environment or form a stable oxide layer on the solid surface. It is important to achieve a SAM with highly compact structure, with other words to achieve a balance between packing density, structural integrity and uniformity. The factors that affect the compactness of self-assembled nanolayers are the follows: defects and ordering, surface coverage, molecular packing and mobility, stability to mention only some of them. In special cases the damaged SAM layer can rearrange itself and restore the barrier property.

Applications of SAM layers on different areas are the follows: oil and gas-, aerospace-, marine and chemical industry. The SAMs could be tailored for specific environment and applications.

The quality of SAMs can be characterized by some techniques such as measuring the change in wettability by contact angle values [15, 25, 26], visualizing the surface morphology by atomic force microscopy (AFM) [27, 28], analyzing the chemical composition, structure and thickness of the thin films by surface sensitive techniques as X-ray diffraction, FTIR, ellipsometry, sum frequential vibrational spectroscopy [29–34].

This paper deals with the application of self-assembled molecular layer formed by undecenyl phosphonic acid on two steels with different composition. The question was how the composition of the steel as well as the preparation condition changes the anticorrosion activity of the SAM layers and how can we characterize the nanofilms by water contact angle values and by AFM and evaluate the anticorrosion effectiveness by surface visualization and via surface roughening parameters.

2. Experimental Work

2.1. Materials

Metals: Two types of steels were used in SAM deposition experiments:

- ARMCO pure iron (AK Steel International B.V): C 0.01%, Mn < 0.06%, P 0.005%, S 0.003%, balance Fe.
- Mild steel (Yili Steel Materials Co): C < 0.1%, Mn 0.3%, P 0.05%, S 0.05%, balance Fe. This type of steel is mainly used in the construction and automotive industries. Its weldability, ductility and machinability are good.
- 1.4841 steel (APERAM, Genk, Belgium): elements: Cr 25%, C 0.2%, Si 2%, Mn 2%, P 0.045%, S 0.045%, balance Fe. This type of steel is used in construction for high temperature, in mechanical engineering, in oil industry.
- 1.4571 steel (APERAM, Genk, Belgium): elements [%]: Cr 17, C 0.08, Si 1, Mn 2, P 0.045, S 0.045, Mo 2, Ni 12, Ti 0.7, balance Fe. This type of steel is used in construction, chemical, medical and pharmaceutical industry.

The metal samples in size $10 \times 10 \times 1$ mm were first handled with emery paper with different grain sizes (200, 400, 800 and 1200 mesh), then polished by diamond pastes (15, 12, 9, 6, 3 μ m grain size). After all polishing steps the coupons were sonicated in water and at last in methanol to remove the leftover polishing particles from the surface.

Amphiphile: In all experiments the undecenyl phosphonic acid amphiphile ($\text{CH}=\text{CH}-[\text{CH}_2]_9-\text{PO}(\text{OH})_2$, MW: 234), (Specific Polymers, Castries, France) was dissolved in methanol at $5 \cdot 10^{-3}$ M concentration.

2.2. SAM layer preparation

The polished and cleaned coupons were immersed into the solution of the amphiphile for different time length, at room temperature. The excess of the solution was removed by dipping the solids into pure solvent (*i.e.* methanol) for a short time; then the metal samples were dried at air.

2.3. Characterization of SAM layers by water wettability values

The wettability of metal coupons with and without SAM coatings was determined by water contact angle, which was measured by sessile drop of MilliQ water placed by motorized syringe on the top of coupons [25].

2.4. Corrosion experiments

The influence of NaCl solution (3% in water; pH 6.8) on metal coupons (with or without SAM coatings) was studied after 4 hours (in case of ARMCO pure iron and mild steel) and after 5 days (on 1.4841 and 1.4571 steels). After dipping the metal samples into the chloride solution at room temperature, the coupons were pulled out and rinsed by MilliQ water and then dried at air.

2.5. Visualization of the metal surfaces before and after corrosion tests

The metal samples (with and without nanolayers) and before and after corrosion tests were visualized by AFM (NanoScope III, Digital Instrument; tip: Si₃N₄) in contact height mode, on air. The morphology of the solid surface before and after nanolayer deposition as well as after corrosion tests was visualized and presented in 2D and section images. Numerical evaluation of the AFM images allowed the calculation of roughness of the surfaces (measured at least on three different spots).

3. Results and Discussion

The effectiveness of nanocoatings *i.e.* the influence of the SAM layer developed from undecenyl phosphonic acid on two different steels in shorter (4 hours) and longer (24 hours) adsorption time was analyzed in order to show whether the alloying components as well as the nanofilm formation time can influence the layer characteristics and the anticorrosion effectiveness of the films or not. With other words the passive layers formed under normal condition on the steel surface before the SAM preparation can determine the compactness of the nanofilm or not. In order to show the importance of alloying elements in anticorrosion behavior, pure iron and mild steel were also involved into the experiments.

3.1. Evaluation of wettability measurements

The wettability of different metal surfaces measured by water drop is generally assumed to be around 60°; it is important information especially in corrosion processes. We have to remark that it depends on surface oxide layer of unknown composition and thickness that forms during the polishing and cleaning process. The water cannot spread well on an oxide-free metal surface [35, 36]. Table 1 summarizes the contact angle values measured on different metals with and without self-assembled molecular layers.

The analysis of the contact angle values measured by water drops clearly show that metals without coatings have smaller contact angles (with other words they are better wetted) than those, that are covered by self-assembled layer. It is also visible that the nanolayer formed in shorter time cannot fully cover the steel surface; there should be some uncovered islands on the basic metal/metal oxide surface. It is also remarkable that the composition of the steel influences the wettability. In case of the 1.4841 steel the Cr content is higher (25%) than in the 1.4571 steel (17% Cr). Additionally, in the 1.4571 steel there are Ni (12%) and Mo (2%) alloying components. The surface composition influences the wettability,

especially the chromium oxides/hydroxides formed on the surface. It is also known that the phosphonic acid groups can better bind to chromium oxide surface than to nickel oxide.

Table 1. Static wettability data measured on ARMCO pure iron, mild steel, 1.4841 and 1.4571 steel surfaces with and without undecenyl phosphonic acid SAM layers (layer preparation: in $5 \cdot 10^{-3}$ M undecenyl phosphonic acid solution at room temperature).

Solid surface	Water contact angle [°]
ARMCO pure iron	68.4
Mild steel	65.3
1.4841 steel	60.2
1.4841 steel + 4 h SAM	70.5
1.4841 steel + 24 h SAM	81.1
1.4841 steel + 48 h SAM	81.3
1.4571 steel	65.6
1.4571 steel + 4 h SAM	66.9
1.4571 steel 24 h SAM	72.4
1.4571 steel 48 h SAM	79.5

3.2. Surface visualization by atomic force microscopy

The atomic force microscopy that was discovered by Binnig, Quate and Gerber in 1985 (they have won Nobel Prize for this invention), is a high resolution, non-optical powerful tool for surface visualization. It can resolve features at small size (μm – nm) in real space.

We applied this technique to show the surface of the original metal, as well as after nanolayer deposition and after the corrosion tests when sodium chloride solution was the aggressive medium. The next figures (Figure 1–3.) summarize the surfaces with and without SAM layers (produced in shorter and longer layer deposition time) and the influence of the chloride ions used in corrosion tests. Please, notice the differences among AFM images taken on pure iron, on mild steel and on the two different steels of different alloying metals in different percentage as well as the influence of the nanolayer formation time.

Important observation is that already FOUR HOUR-LONG immersion in the corrosive solution caused serious roughening of the pure and almost unalloyed mild steel samples unlike in case of alloyed 1.4571 and 1.4841 steels where much less roughening was observed after FIVE DAY-LONG immersion as the visual observation proves. The smoothness of the SAM deposited metal is less visible after shorter time than after longer dipping in the amphiphile solution. It is interesting observation that a longer than 24 h immersion of the 1.4841 steel in the amphiphile solution results in a less smooth surface after the corrosion test. This is the consequence of the formation of second layers and islands on the first monolayer that cannot cover the solid surface fully.

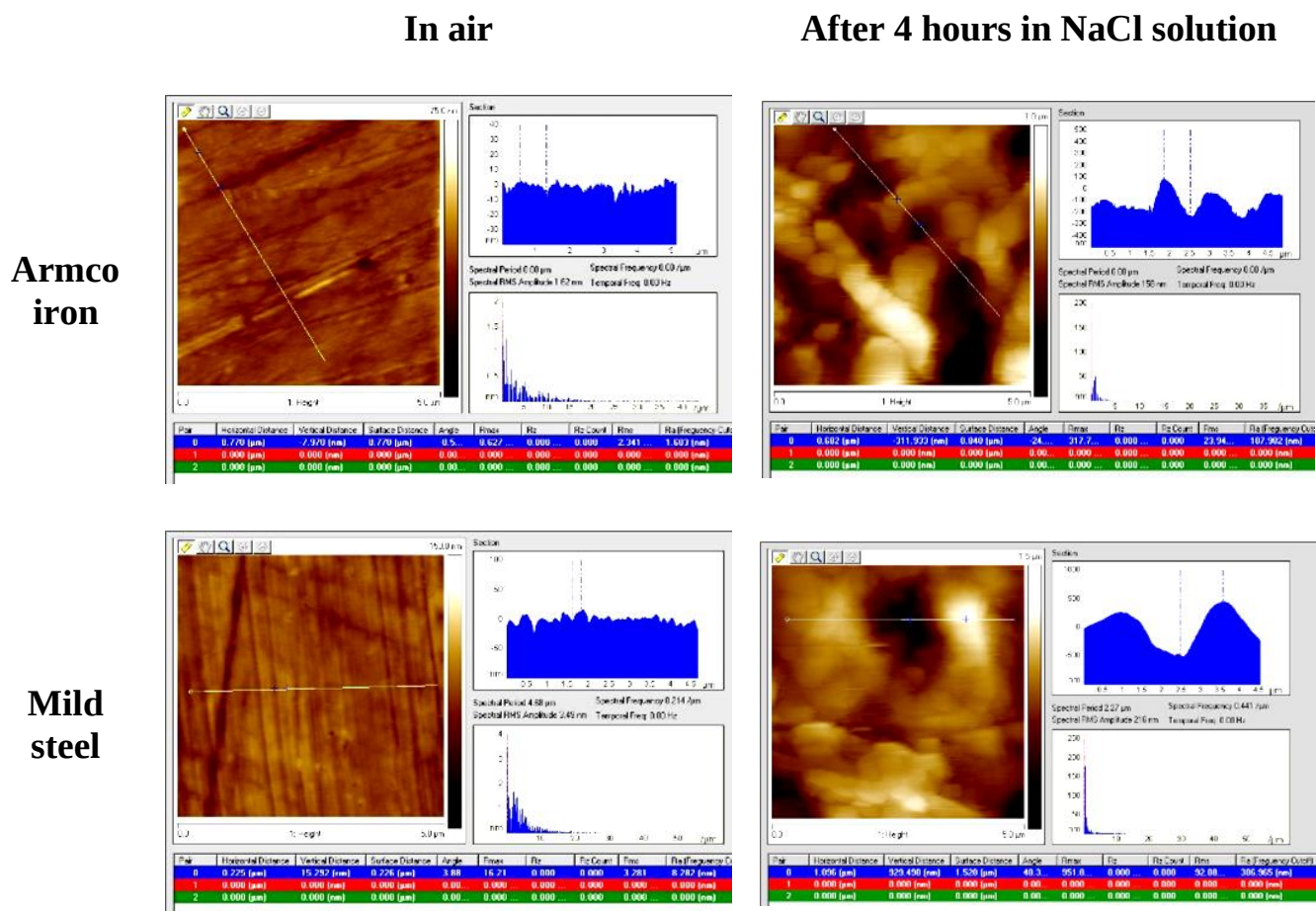


Figure 1. Surface of ARMCO pure iron and mild steel before and after corrosion experiment. AFM images were taken in contact mode, demonstrated in 2D and in section analysis.

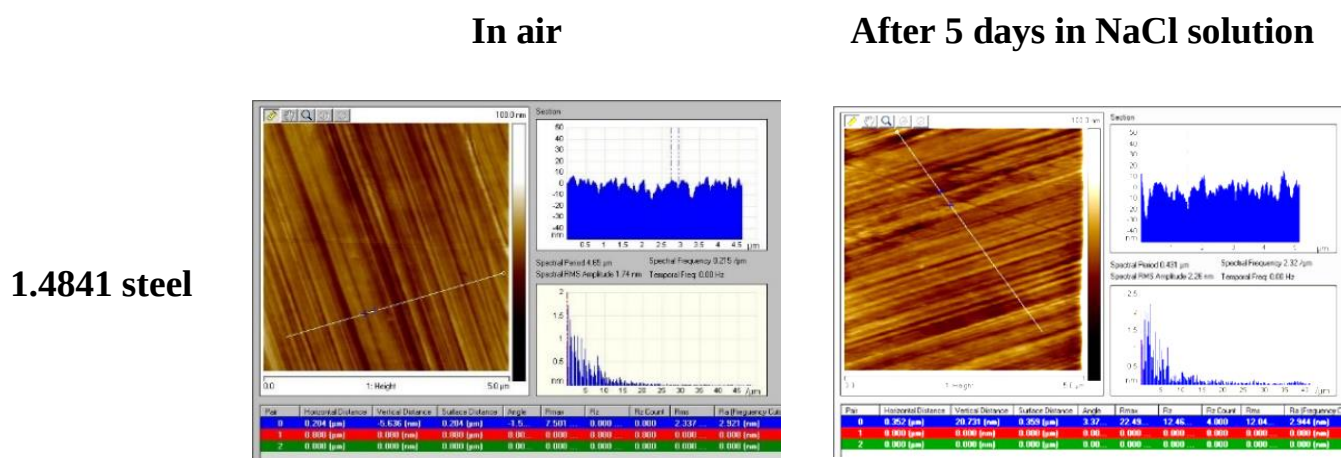


Figure 2a. Surfaces of 1.4841 steel in uncovered form. AFM images were taken in contact mode, demonstrated in 2D and in section analysis.

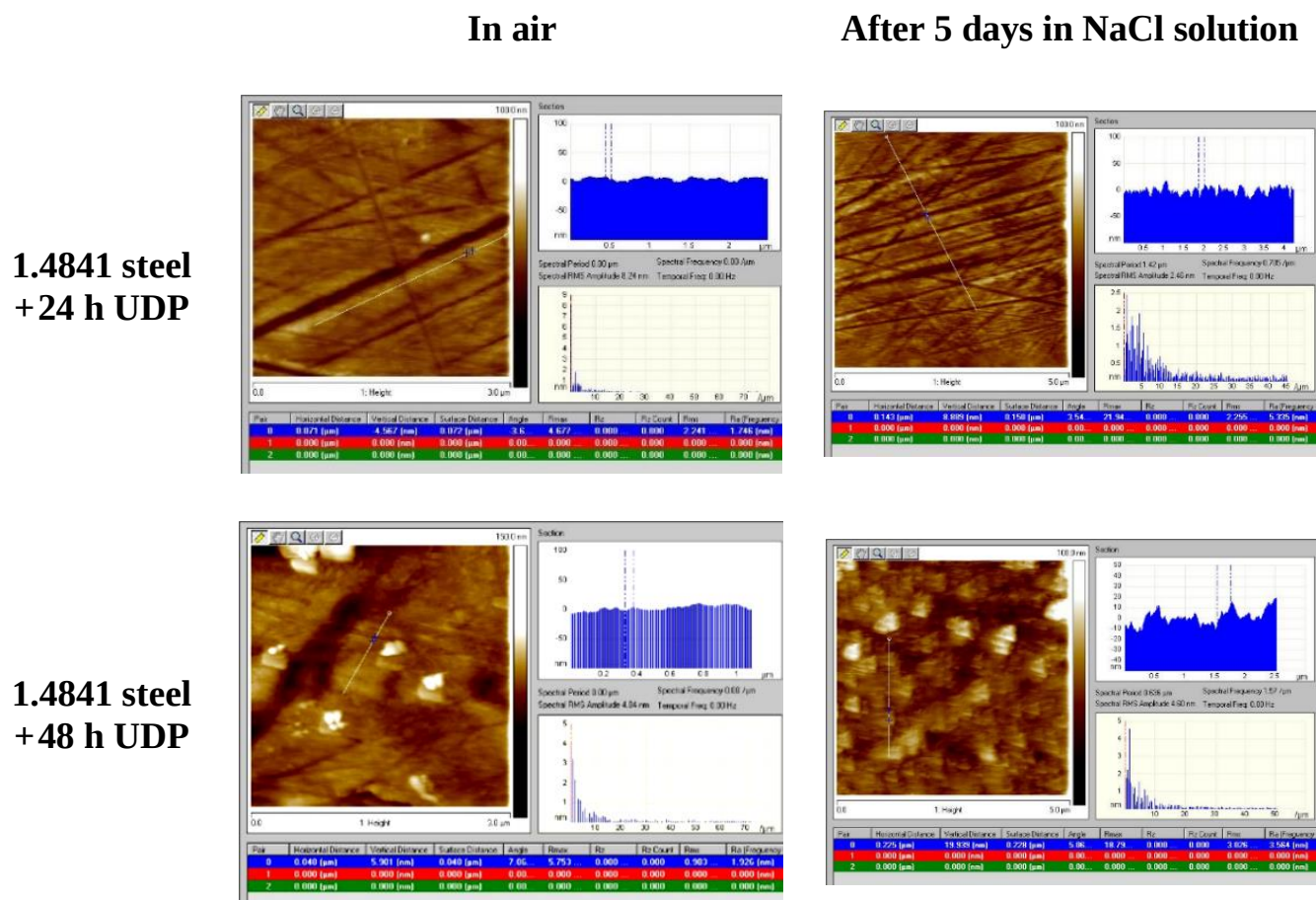


Figure 2b. Surfaces of 1.4841 steel after SAM deposition in different times and after corrosion experiment. AFM images were taken in contact mode, demonstrated in 2D and in section analysis.

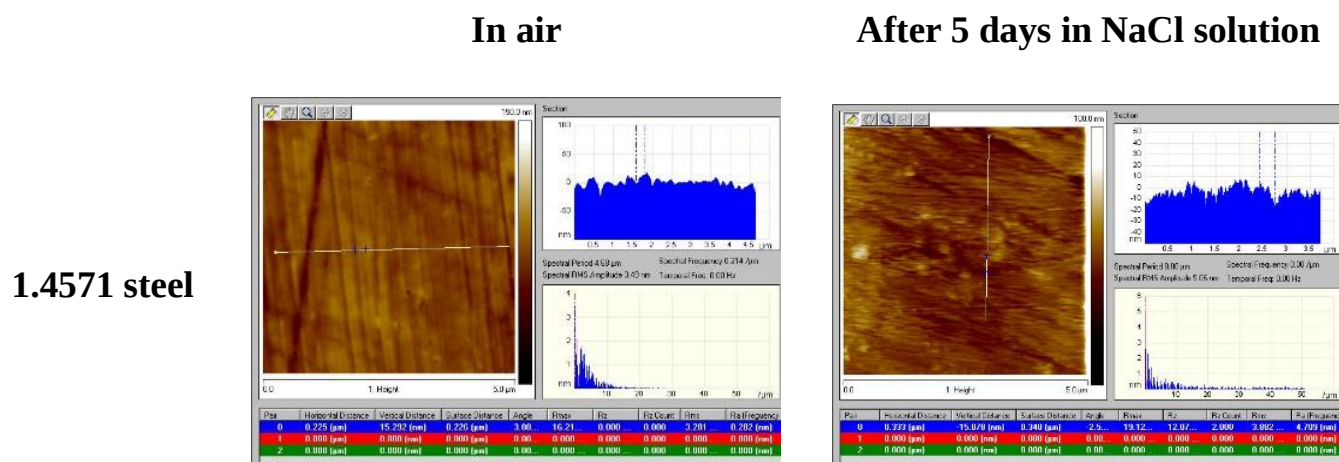


Figure 3a. Surfaces of 1.4571 steel in uncovered form. AFM images were taken in contact mode, demonstrated in 2D and in section analysis.

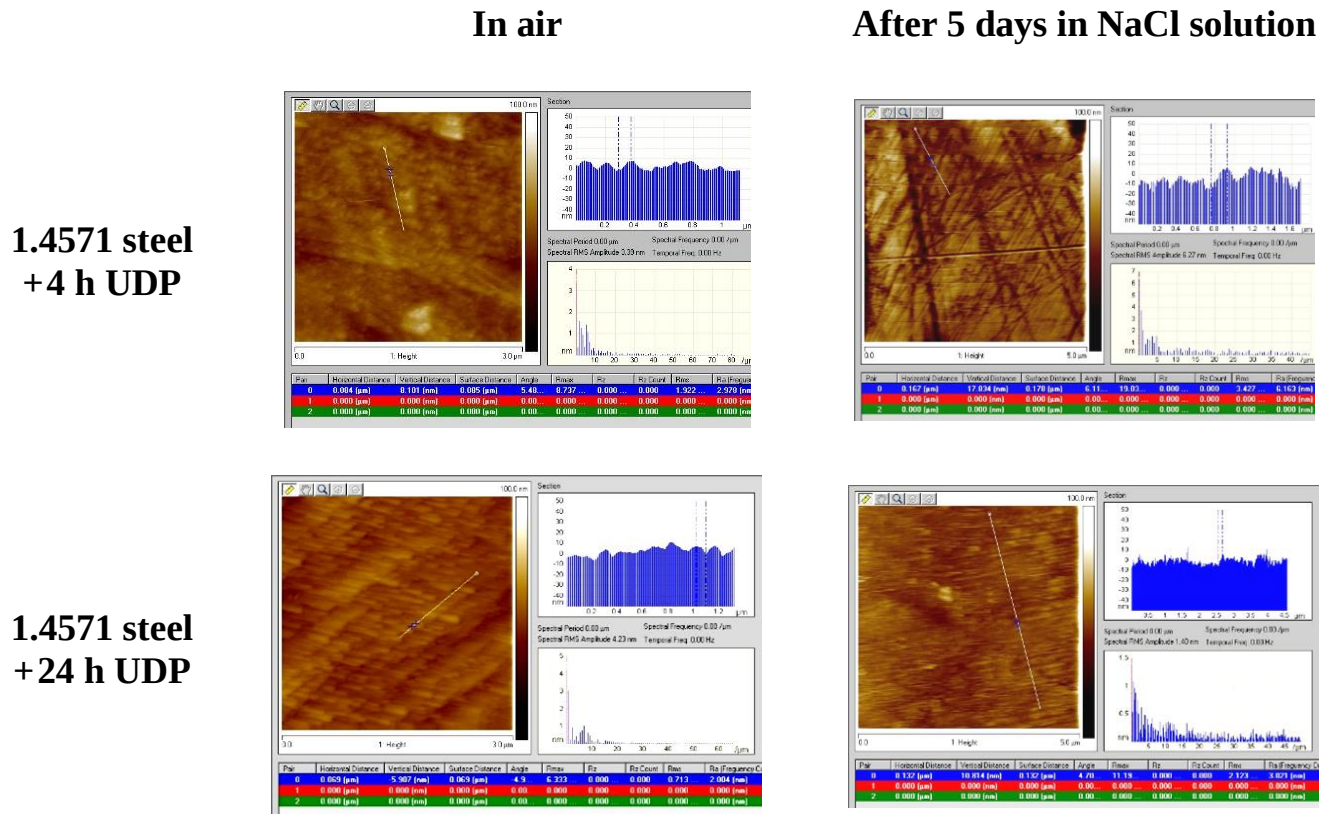


Figure 3b. Surfaces of 1.4571 steel after SAM deposition in different times and after corrosion experiment. AFM images were taken in contact mode, demonstrated in 2D and in section analysis.

The roughness parameters provide numerical evidence on the observation of AFM images.

3.3. Roughness parameters

There are three different roughness parameters that can characterize a surface (R_a denotes the arithmetic average height parameters, R_q means the root mean square roughness, R_{max} is sensitive to the height of peaks and to the deep scratches) [37].

Table 2. Summary of the roughness parameters measured on ARMCO pure iron, on mild steel and on 1.4841 and 14571 steels.

Metal	R_q [nm]	R_a [nm]	R_{max} [nm]
ARMCO pure iron	3.21	2.24	46.2
+4 hours NaCl	137.0	108.0	1009
Mild steel	3.65	2.48	47.6
+4 hours NaCl	178.0	136.0	1134

Metal	R_q [nm]	R_a [nm]	R_{max} [nm]
1.4841 steel	5.22	4.17	55.60
+5 days NaCl	7.11	5.14	102.0
1.4841 steel+4 h SAM	3.55	2.39	48.12
+5 days NaCl	6.58	4.76	83.7
1.4841 steel+24 h SAM	5.75	4.23	53.01
+5 days NaCl	6.2.0	5.19	68.10
1.4841 steel+48 h SAM	6.89	4.95	63.19
+5 days NaCl	9.51	6.76	181.00
1.4571 steel	7.14	5.46	58.30
+5 days NaCl	7.24	5.93	112.0
1.4571 steel+4 h SAM	4.03	3.10	37.10
+5 days NaCl	4.93	3.59	68.50
1.4571 steel+24 h SAM	4.85	3.90.	52.30
+5 days NaCl	5.39	3.63	73.10
1.4571+48 h SAM	3.89	3.06	43.00
+5 days NaCl	8.31	7.52	146.30

After the corrosion tests the change in all three types of surface roughness parameters show almost twenty-time higher values in case of the ARMCO pure iron and mild steel than measured on air. On the other hand, the steels 1.4571 and 1.4841 suffer much less irregularity caused by aggressive chloride ions; the changes are less than twice at the R_q and R_a values and not higher than twice in case of the R_{max} values, which is very sensitive to the heights and peaks. It is interesting that after the corrosion experiments, the ratios of R_{max} values are similar at both stainless steels but the R_q and R_a changes are less at the 1.4571 steel. The presence of the SAM layer after 4 hour long deposition time can save the surface but only a 24 hour long immersion can produce compact layer, which is reflected in less roughening: even after 5 day long corrosion experiments the ratio between the surface roughness of the starting nanofilm covered metal surface and that one's after corrosion tests are maximum two, even in the case of the surface sensitive R_{max} values. The influence of the SAM layer in 4 and 24 hour-long deposition time results in almost similar effectiveness at both types of stainless steels, but the layer developed in 48 hours decreases the anticorrosion efficiency, which is reflected in higher roughness.

On the basis of comparison of roughness values and the wettability parameters we cannot decide whether the wetting is a Wenzel or a Cassie–Baxter type. The Wenzel model allows the comparison of the wettability parameter with the roughness values. Whether the roughness increases the wettability or not it depends on the surface layer composition of the

metal oxide and the coactiveness by amphiphiles. The problem is that the shorter deposition time could not be enough to cover the oxide layer with the amphiphilic molecules fully; the uncovered surface allows the adsorption of air bubbles (Cassie–Baxter model). The decision between the two types of wetting models needs further experiments.

3.4. Influence of the alloy composition on the wettability

The passive films could play important role in corrosion resistance. The main elements in the stainless steel passive films are oxides of alloying elements, mainly Cr and Ni as well as of the bulk metal. It is proved that the oxide layer is more compact and show higher protection ability in corrosion processes than hydroxides [38–40]. In our previous paper we demonstrate the distribution of alloying components on different steel surfaces [28].

The composition of the surface oxide layer also influences the attachment of the phosphonic groups in the amphiphilic molecules; this significantly influences the surface wettability. Please, remember that the contact angle value of the steel 1.4841 (where the sum of the alloying component is about 27%) is 60.2° and in the case of steel 1.4571 (with circa 31% alloying component) 65.6° . Of course, not only the sum of the metals in the alloy influences the wettability but the types and concentration of the metal oxide on the solid surface. The surface coverage with chromium oxides is much higher in case of the 1.4841 than at the 1.4571 stainless steel. In the first case mainly chromium oxide (and, of course, iron oxides/hydroxides) cover the alloy surface, and at the 1.4571 steel surface is partly occupied by nickel oxides, too. The other alloying components are in similar concentrations in both steels except the Ti that in the 1.4571 steel is in 0.7%. The surface distribution of the alloying elements was demonstrated earlier [28].

4. Conclusion

These experiments demonstrated that the sensitivity of stainless steels against corrosion (which is mainly due to their alloying components and the surface passive layers), could be increased with special surface treatments, *i.e.* with amphiphilic nanolayer deposition that decreases the water wettability of the metal and – parallel – reduces the sensitivity against corrosion. The corrosive environment was sodium chloride that increases the rate of pitting corrosion with destroying the passive layer and initialization of shallow or deep pits. The stainless steels are more sensitive to pitting than to general corrosion. The self-assembled layer deposition time affects the quality of the nanolayer: longer time results in better protection. But too long (48 h) adsorption allows formation of irregular second nanolayer with “islands” of the amphiphilic molecules that do not improve the anticorrosion activity. These experiments also proved that the presence of Cr alloying metal in the steel at higher concentration can reduce the corrosion processes better and increase the anticorrosion activity, which is mainly due to higher chromium oxide surface layer.

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