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Not simply repel water: the diversified nature of corrosion protection by superhydrophobic coatings

Ludmila B. Boinovich,* Alexandre M. Emelyanenko, Alexander D. Modestov, Alexandr G. Domantovsky and Kirill A. Emelyanenko

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. E-mail: boinovich@mail.ru

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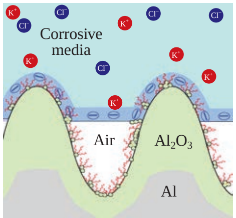
New mechanisms of the anticorrosion action of superhydrophobic coatings (SHCs), additional to electrolyte repellency, namely, the suppression of adsorption of aggressive ions, the barrier effect of a modified surface layer, and the specific charging of a hydrophobic layer in electrolytes, are considered and illustrated by the electrochemical behavior of an SHC on aluminum alloy in KCl solutions.



Field and laboratory studies on the corrosion of metals protected by superhydrophobic coatings (SHCs) showed a very high efficiency of the protective properties of SHCs.[1–8] The overwhelming majority of these studies related the improved corrosion resistance of the SHCs to their water repellency. This interpretation of the protective effect of the SHCs does not explain the fact that they give excellent anticorrosion results in some cases, while in other cases they fail to sustain the corrosion attack.[9] However, recent publications revealed physicochemical phenomena responsible for the protective properties of SHCs. Since the problem of corrosion protection is of great importance in both science and industry, the protection mechanisms have to be understood in detail.

Here, we consider various aspects of complex corrosion protection provided by an SHC with the emphasis on the newly described ones and analyze the corrosion behavior of an aluminum–magnesium alloy (AMG2) with SHCs in halide containing electrolytes.[†]

As shown earlier,[10] the applied method of surface texturing based on nanosecond laser treatment leads to the formation of a surface with a multimodal roughness (characterized by regular micron-sized surface ripples and trenches decorated by fiber- and globule-like aggregates composed of nanoparticles). Moreover, the surface layer enriched in oxides in different phase states,[11] as confirmed by EDX and XRD analysis. For the surface layer under the deposited nanoparticles, EDX analysis indicated high oxygen content to a depth of up to 100 μm below the bottom of the grooves produced by laser treatment.[10] After the chemisorption of fluorooxysilanes onto the laser textured surface, the samples had contact angles of 171–174° and rolling angles smaller than 2.4±1.2°.

The EIS data and potentiodynamic polarization curves (Figure 1) were used to study the corrosion protection properties of SHCs fabricated by laser treatment[10] on AMG alloy during long-term contact with 3 M KCl solutions. Both EIS and polarization curves give consistent data on the electrochemical behaviors of SHCs, indicating high protective properties of SHCs.

A low corrosion current (1.0×10^{-9} A cm^{-2}) for an SHC sample in contact with a solution for 120 min indicates a very low corrosion rate. After 10 days of immersion, the corrosion

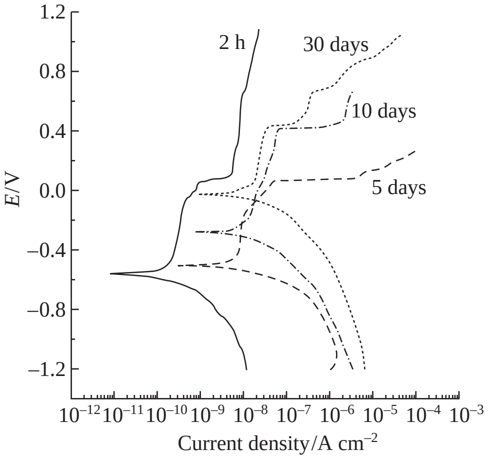


Figure 1 Evolution of the potentiodynamic polarization curves for the SHC immersed in 3 M KCl solutions for different times.

[†] The test samples were fabricated by intense nanosecond laser treatment followed by surface modification with fluorooxysilanes to decrease the surface energy, as described previously.[10] The electrochemical properties of the coatings were studied using a PARSTAT 2273 potentiostat/galvanostat (Princeton Applied Research) at room temperature in a three-electrode cell (PAR K0235 Flat Cell) with the sample as a working electrode. An Ag/AgCl electrode filled with saturated KCl solution served as a reference electrode, and a Pt mesh, as a counter electrode. The corrosion medium was a 3 M KCl solution in contact with air at 23 °C. Deionized water with a specific resistivity of 18 MΩ cm and chemically pure grade reagents were used to prepare the electrolyte solutions. Prior to electrochemical measurements the samples were immersed in the solution for a specified time. The potentiodynamic polarization curves were measured at a scan rate of 1 mV s^{-1} in a potential range from –1.2 to 0.6 V. A sinusoidal perturbation signal with an amplitude of 20 mV (with respect to open circuit potential) was used for the electrochemical impedance spectroscopy (EIS) measurements. Impedance spectra were acquired in a frequency range from 0.05 to 100 kHz with logarithmic sweep (20 points per decade). The wettability of coatings was characterized by contact and rolling angle measurements.

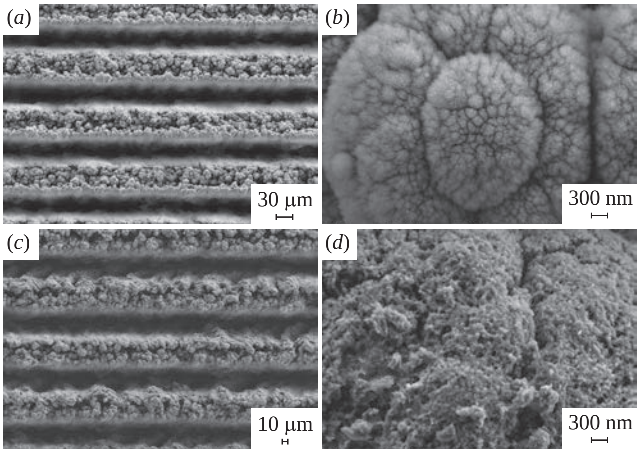


Figure 2 SEM images of superhydrophobic coatings on the surface of AMG alloy (*a*), (*b*) before and (*c*), (*d*) after a 60-day immersion in a 3 M aqueous solution of KCl.

current was less than 5×10^{-9} A cm^{-2}. The longer immersion of SHC did not cause a perceptible increase in the corrosion current, which remained lower than 10^{-8} A cm^{-2} after a month of continuous immersion in a brine bath. The wettability studies with the same type of SHC in 3 M KCl solution[11] indicated the high stability of a superhydrophobic state upon long-term continuous contact with a corrosive medium.

The SEM images of samples immersed in 3 M KCl solutions for 60 days (Figure 2) reveal only minor defects explaining high barrier properties detected by EIS and low corrosion currents derived from the above polarization data. Thus, although the electrochemical properties of as-prepared SHCs in a corrosive KCl solution show some degradation with time, they nevertheless indicate very high corrosion resistance.

It is generally accepted that several conditions are necessary for the corrosion of metals to proceed. They are the presence of active corrosion sites serving as anodes and cathodes, the availability of electrical contact, a continuous electrolyte phase between the anode and the cathode, and, finally, the presence of components of cathodic reactions, which assimilate the electrons formed on the anodic ionization of metal.[12,13]

Note that SHCs are simultaneously characterized by a water contact angle greater than 150° and a low wetting hysteresis. The above properties ensure that the coated material is wetted by aqueous media in a heterogeneous wetting regime, where air is trapped inside the grooves of the textured surface (Figure 3). The liquid only contacts the material at the surface of the protrusion peaks, so that the area of real contact between the liquid and the material (the wetted area) is considerably smaller than 10% of the apparent contact area.[14]

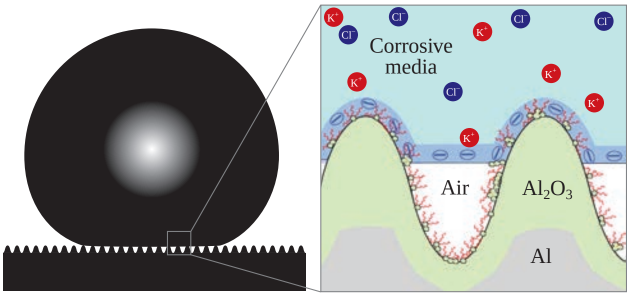


Figure 3 Optical image of an aqueous droplet on the SHC and a schematic illustration of main mechanisms defining the improved corrosion resistance of metals with SHCs: air cushions impede penetration of aggressive solution into the solid surface; the crosslinked layer of hydrophobic molecules blocks the adsorption sites and hinders the mass transfer of charges, halide ions and water molecules; negatively charged solid/liquid and air/liquid interfaces repel anions; the textured metal surface enriched in oxides forms an additional barrier for charge transfer.

Let us consider how the properties of the SHC, such as the layer of a hydrophobic agent, texture elements and air bubbles, contribute to the anticorrosive properties.

The images indicate that the surface texture consists of texture elements having characteristic sizes of different scales, such as tens of microns, microns and tens of nanometers. Thus, the characteristic surface roughness should be qualified as a multiscale one.

First, we discuss the role of the layer of a hydrophobic agent deposited onto the textured metal surface to decrease the surface energy. The appropriate deposition of this layer onto a textured surface implies the chemisorption and lateral crosslinking inside the layer. The occupation of active corrosion sites by the hydrophobic molecules arrests them for the adsorption of corrosive ions or molecular oxygen, and this is the first important effect of the hydrophobic agent at the interface. The decreased adsorption of halide anions inhibits the anodic reaction, while hindering the adsorption of O_2 or H_3O^+ suppresses the cathodic reaction. Indeed, the data presented in Figure 1 clearly indicate the inhibition of both cathodic and anodic reactions. The second important point is related to the charging of an interface where corrosion occurs. Metals/oxides in electrolytes have positively charged surfaces in neutral solutions;[15] thus, the aggressive anions are electrostatically attracted. In contrast, for a variety of hydrophobic materials, the isoelectric point in electrolytes is at pH 2–4; and their surfaces in neutral solutions are negatively charged. It was described in the literature[16–18] that, among the negative ions such as halide or hydroxide (OH^-) anions, the latter has the highest adsorption energy and the highest saturation coverage, whereas Cl^- has the lowest saturation coverage. The negative charging of an SHC causes a redistribution of ions inside the double electric layer leading to the depletion of halide anion concentration in the vicinity of a solid surface. Finally, the well-ordered layer of a chemisorbed hydrophobic agent acts as a barrier for charge transfer. Thus, the layer of hydrophobic molecules deposited onto the textured metal surface renders the metal surface less susceptible to corrosion. However, the above mechanisms of corrosion protection may be hindered by the desorption of hydrophobic agents from a solid/liquid interface and the formation of defects in the hydrophobic layer. Recently,[19] we found that this partial desorption takes place at a low adsorption energy or due to hydrolysis. The formation of wetting defects at the SHC/aqueous phase interface and the presence of aggressive entities like halide ions in our study caused the mass transfer of solution components through the coating, extensive localized attacks and the corrosion processes of aluminum. At the same time, as follows from the data on the evolution of wettability[11] or from the electrochemical parameters of the coatings (Figure 1), the desorption of hydrophobic molecules in concentrated KCl solutions is essentially inhibited for our SHC.

The surface layers including the textured part of the metal itself also play a very important role in corrosion inhibition. The laser treatment procedure used to impart multimodal roughness simultaneously modifies the composition of the surface layer[10] with the formation of nanocrystalline alumina phases to a depth of 100 μm.

The nanoparticles act as the main texturing elements ensuring the achievement of multimodal roughness and, finally, the superhydrophobic state of the surface. As for a surface layer containing Al_2O_3, it follows from the earlier studies,[10] that this layer demonstrates good barrier properties against the transfer of charges, halide ions and water molecules.

Let us consider the water repellent effect. On the one hand, due to heterogeneous wetting, a very small portion of the solid surface is exposed to the corrosive medium, thus essentially reducing the number of active corrosion sites. On the other hand, under the conditions of open circuit potential (free corrosion), the heterogeneity of surface properties results in the formation of corrosion pairs (cathodic and anodic sites). However, at the earlier stages of contact with a corrosive medium, the SHC provides direct contact with liquid to a very limited part of the surface. According to Tomashov,[13] the uniformity of the wetted part of the surface impedes the formation of corrosion pairs. On the contrary, the desorption of individual hydrophobic molecules leads to the nonuniformity of a hydrophobic layer and the subsequent formation of corrosion pairs. Nevertheless, the destructive effect of the desorption of hydrophobic molecules can be minimized by the appropriate choice of a hydrophobic agent and surface pretreatment.[10,11,19] It is worth noting that a transition from heterogeneous to homogeneous wetting regime still may take place, for example, under an excess hydrostatic pressure or due to the partial desorption of a hydrophobic agent. Such a transition will be accompanied by losing the entrapped air and will result in partial degradation of corrosion resistance properties associated with the low portion of wetted area and the suppression of anion adsorption. Even in that case, the negative hydrophobic surface charging and the barrier properties of a textured layer will still contribute to better corrosion resistance in comparison with bare metal.

Thus, we highlighted various aspects of the complex corrosion protection provided by SHCs and showed that, in addition to water repellent properties, an important aspect of the corrosion resistance of metals with SHCs is related to the protective properties of chemisorbed hydrophobic molecules, to the modified surface layer of the metal and to the specific charging of a hydrophobic layer in electrolytes. The presented mechanisms indicate the dominant role of the stability and structure perfection of the layer of hydrophobic molecules atop the textured surface.[9] They provide an explanation for the fact that the superhydrophobic coatings give excellent anticorrosion result, when the layer of hydrophobic molecules demonstrates chemical stability. In contrast, in the case of the intense desorption of hydrophobic molecules from the surface, SHCs fail to sustain the corrosion attack. The presented mechanisms will promote choosing the best strategy to control the efficiency of corrosion protection properties.

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