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Electrochemical properties of the superhydrophobic coatings on metals and alloys

S.V. Gnedenkov[a], S.L. Sinebryukhov[a], V.S. Egorkin[a,*], D.V. Mashtalyar[a],
A.M. Emelyanenko[b], L.B. Boinovich[b]

[a] Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russia
[b] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

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ABSTRACT

Superhydrophobic layers were prepared by means of nanoparticle dispersions deposition on PEO (plasma electrolytic oxidation)-pretreated metal/alloy (titanium, low-carbon steel, and magnesium) substrates. The contact angles on the surface of the fabricated coatings were higher than 160°. The comprehensive analysis of the data obtained by electrochemical method provides the possibility to study variations in the surface conditions due to the electrochemical reaction associated with the corrosion process. It was found that the combined effect of PEO treatment and textured hydrophobic layer deposition results in inhibition of the corrosion reactions and ensures the anticorrosive behavior of the coatings. As follows from the electrochemical data analysis, the corrosion protection for nanocomposite superhydrophobic coatings formed on the PEO-layer is provided by small area of real contact with the electrolyte solution and higher ohmic barrier for corrosion reactions. In case of superhydrophobic layers, the mass transfer of electrolyte solution through the coating to the metal surface is substantially hindered.

1. Introduction

The development of superhydrophobic (SHP) nanocomposite coatings for metals and alloys with oxide layers and studies of their protective performance comprise important stages in the creation of corrosion-resistant coatings, which demonstrate consistent protective characteristics not only under the atmospheric conditions, but also in the aggressive media [1–18].

In the present study, electrochemical properties of superhydrophobic coatings on titanium, low-carbon steel, and magnesium alloy were investigated in 0.5 M aqueous NaCl solution.

The superhydrophobic coatings were fabricated atop of the plasma electrolytic oxidation (PEO, also known as Micro-Arc Oxidation – MAO) coatings by formation of a nanocomposite layer having both multimodal roughness and low surface energy [19–22]. High adhesion of the PEO-layers to the alloy substrate and their complex surface topography (porosity, roughness, etc.) along with controlled composition of surface layer enable one to use them as a basis for the formation of composite coatings [21,23,24].

Moreover, it is the presence of OH groups at particular surface [25,26], which is responsible for chemisorption of molecules of hydrophobic agent. It has been shown that the strong chemical interfacial bonding between hydrophobic agent and substrate leads to a higher stability and corrosion inhibition efficiency. Unlike other oxidation methods, PEO allows to control of hydroxyl groups concentration, morphology structure at surface of PEO-layer and its composition due to purposeful regulation of electrolyte content and electric modes of formation as well [27]. Therefore, PEO has some advantages in comparison to other oxidation methods for development of superhydrophobic coatings.

The thickness of composite superhydrophobic coatings includes the thickness of PEO-layer (8–10 μm for titanium [28], 20–30 μm for steel [29], and 15–17 μm for magnesium alloy [30]) and thickness of nanocomposite coating (1–3 μm) [22] immediately atop of PEO-layer. It should be noted, that thickness of the PEO-layer is strongly depends on the substrate material, chemical composition of the electrolyte solution, oxidation conditions (uni- or bipolar oxidation mode, current and voltage values, duty cycle) etc., and may exceed 100 μm. The part of superhydrophobic agent

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[*] Corresponding author at: 159, Prospect 100-Letiya Vladivostoka, Vladivostok 690063, Russia. Tel.: +7 4232312588; fax: +7 4232312590.
E-mail address: egorkin@ich.dvo.ru (V.S. Egorkin).

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penetrates in porous part of PEO-layers and partly contributes to the outer nanocomposite layer with multimodal roughness, containing the aggregates of nanoparticles [19]. Anticorrosion properties are controlled by not only thickness of inner and outer part of composite coating, but by properties and morphological structure of these layers [22].

For the sake of comparison, native oxide films formed during natural oxidation of the samples at ambient conditions and PEO-coatings were studied as reference samples. The improved corrosion resistance of materials that underwent the PEO process, both alone and as a part of composite coatings [27,31–33], on the one hand, and extremely high anticorrosive protection for various metals demonstrated by highly hydrophobic and superhydrophobic coatings [34,35], on the other hand, were crucial in our choice of coatings to be taken for the comparative analysis.

The results of formation of the composite superhydrophobic layers on the basis of the PEO-coatings on magnesium alloys were described only by few research groups [36–40]. There is no information on superhydrophobic coatings formed on PEO-pretreated low-carbon steel or titanium.

2. Experimental

2.1. Materials

Rectangular plates of commercially pure titanium VT1-0 (99.3 at. % Ti), low-carbon steel (99.2 Fe; 0.4 Mn; 0.2 Si; 0.2 C at.%), and wrought magnesium alloy MA8 (1.5–2.5 Mn; 0.15–0.35 Ce mass%) were used as samples.

N,N,N-trimethyl-1-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]propyl}-silane, was used as the hydrophobic agent to prepare superhydrophobic coatings.

0.5 M solution (pH = 7) of chemically pure NaCl in distilled water was used as a testing liquid for both wetting and electrochemical studies.

2.2. Coatings formation

PEO-coatings on titanium were formed in phosphate electrolyte (aqueous solution of 10 g/l $Na_3PO_4 \cdot 12H_2O$) in unipolar polarization mode – anodic voltage increase from 30 to 270 V (4 V/s) with subsequent stabilization at 270 V for 9 min, as described in [28]. Low-carbon steel was oxidized in silicate-containing electrolyte (20 g/l Na_2CO_3 + 30 g/l $mNa_2O \cdot nSiO_2$; $m/n = 2$). Oxidation was performed in bipolar PEO-mode with voltage raising from 30 to 300 V at the rate of 0.45 V/s in anodic period and a constant cathodic voltage of 30 V [29]. Magnesium alloy was treated in 15 g/l $Na_2SiO_3 \cdot 5H_2O$ + 5 g/l NaF aqueous solution [30]. The coating formation process was performed using the bipolar mode. The anodic component was ramped from zero up to 250–300 V at the rate of 0.25–0.28 V/s. Potentiostatic cathodic component had a voltage of 25–30 V. The polarization signal's frequency was equal to 300 Hz, duty cycle was 50%. In our earlier studies it was shown that the chemical stability of superhydrophobic state of the alloy surface is based on the chemisorption of hydrophobic agent at the surface OH groups [21,25]. For example, to increase the surface density of chemisorption active sites on magnesium alloy substrate, the initial PEO coatings were boiled in a $Na_2O \times SiO_2 \times H_2O$ solution for 15 min [22,25].

The methods of deposition superhydrophobic coatings were described in details in [19,20].

Formation of the superhydrophobic coatings on all above-mentioned metals and alloys was based on self-organization of nanoparticles in a wetting film of the dispersion, containing silica nanoparticles with the size 10–60 nm, hydrophobic agent, and low volatile dehydrated dispersion medium. The superhydrophobic coatings were obtained atop of PEO layers by formation of nanocomposite layer, possessing both the multimodal roughness and the low surface energy. The mechanism of formation of multimodal roughness due to aggregation process of silica nanoparticles in the nanocomposite layer was considered in detail in [19].

To fabricate superhydrophobic coatings on the metal surface N,N,N-trimethyl-1-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-oxy]-propyl}-silane was used as a hydrophobic agent. The application of the above-mentioned hydrophobic agent was motivated by its following properties. On one hand it allows to decrease the coating surface energy due to presence of long-chain fluorocarbon tail. On the other hand this fluorooxysilane contains three terminal oxymethyl groups. Chemisorption of this molecule on free hydroxyl groups on the surface of either PEO layer, or silica nanoparticle is achieved by the reaction

$$-2Si-O-CH_3 + HO-X \Rightarrow -2Si-O-X + CH_3OH$$

(where X denotes either metal from PEO layer or Si from silica nanoparticle). This allows using the above hydrophobic agent as a binder of nanocomposite coating to the substrate and between nanoparticles [26,41].

2.3. Electrochemical studies

Electrochemical measurements were performed at room temperature using a VMC-4 electrochemical station (Princeton Applied Research, USA). The corrosion characteristics such as polarization resistance R_p, corrosion current I_C, and free corrosion potential E_C were calculated from potentiodynamic tests according to the Stearn-Geary relationship [42] on the basis of potentiodynamic polarization curves. Measurements were carried out in a three-electrode cell with 0.5 M NaCl aqueous solution as an electrolyte. Platinum coated niobium mesh was used as a counter electrode. A silver/silver chloride electrode filled with saturated KCl solution served as a reference electrode. The exposed sample surface area was 1 cm^2. Prior to the electrochemical measurements, the samples were kept in the solution for 30 min in order to stabilize the free corrosion potential. The potentiodynamic polarization curves were registered at a sweep rate of 1 mV/s. The samples were polarized from −100 mV vs. E_C in the anodic direction. Electrochemical impedance spectroscopy (EIS) measurements were conducted at an open circuit potential in the frequency range from 1.0 MHz to 0.01 Hz (logarithmic sweep, 7 points per decade), with a 10 mV (rms) sine-wave perturbation signal. The experiments were controlled and analyzed with the aid of VersaStudio (Princeton Applied Research, USA), ZView and CorrView software (Scribner Associates, USA).

2.4. Characterization of wettability

In contact angles measurements, we have used the method of digital video image processing of a sessile drop of the testing liquid on the investigated surface. The home made experimental setup for obtaining optical images of sessile drops and software for subsequent determination of drop parameters using the Laplace curve fitting routine were described earlier [43,44]. The typical volume of drops varied in the range from 10 to 30 μl. The initial contact angles were measured at 3–5 different positions on the surface of each sample, with at least 10 sequential images of the drop captured at every position. The reproducibility of contact angle measurements, determined as the root-mean-square scattering for 10 images of the same drop, did not exceed 0.2 degrees for all samples. To measure the rolling angle, the 10–15 μl drop