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Formation and electrochemical properties of the superhydrophobic nanocomposite coating on PEO pretreated Mg–Mn–Ce magnesium alloy

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ABSTRACT

This paper describes the methods of preparation and electrochemical properties of hydrophobic (HP) and superhydrophobic (SHP) nanocomposite coatings on the surface of magnesium alloy pretreated using plasma electrolytic oxidation (PEO). The most effective corrosion protection in brine solutions among the coatings under study was demonstrated by the nanocomposite superhydrophobic coating. For this coating, the values of the contact and rolling angles are $166^\circ \pm 3^\circ$ and $5^\circ \pm 3^\circ$, respectively. The impedance modulus ($|Z|_{f=0.005}$) value, which characterizes the anticorrosion properties, attains $2.5 \cdot 10^7 \Omega \text{ cm}^2$ for the SHP coating and $1.4 \cdot 10^6 \Omega \text{ cm}^2$ for the HP coating at the initial moment of immersion into a chloride-containing electrolyte, thus improving the resistance of the base PEO coating by almost 400 and 20 times, respectively. After 24 h of exposure, the protective properties of the SHP coatings are one order of magnitude higher than those of the HP coatings. The high corrosion resistance and considerable stability of the SHP coatings during their operation result from a small area of real contact with aggressive media due to a heterogeneous wetting regime and formation of a firm chemical bond between the molecules of the hydrophobic agent and the other coating components.

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1. Introduction

Magnesium alloys are attractive and promising for industry [1] due to their low density, high strength, and ease of processing. The main disadvantages, which substantially limit the practical application of magnesium alloys, consist in their low wear and corrosion resistances.

In a dry air atmosphere, the surface of magnesium (due to its high affinity to oxygen) is always coated with a thin layer of magnesium oxide. However, even a moderate level of relative air humidity leads to hydration of this oxide and formation of a brittle layer of magnesium hydroxide $\text{Mg}(\text{OH})_2$ weakly adhering to the metal. The contact of magnesium alloys with aggressive solutions, which contain, in particular, chloride ions, leads to a rapid destruction of the passive film and dissolution of the metal. In this case, the corrosion process is very fast [2,3]. Detailed information on the corrosion behavior of magnesium and its alloys in different environments has been reviewed in [4].

Among the methods of forming protective coatings on magnesium and its alloys, which are discussed, for example, in [5–8], plasma electrolytic oxidation (PEO) is becoming increasingly common [9]. This is due to the properties of coatings formed by PEO: high adhesion to the substrate [10], increased microhardness, and corrosion resistance in comparison with the alloy [11–15]. Despite good performance of these types of coatings, they have porosity that can attain 20 or more percent

[16,17]. It should also be pointed out that layers with even a small number of microdefects in their morphological structure have low protective properties. It was shown [2] that if a PEO layer in contact with a chloride-containing solution had micron-size defects, destruction of the metal became inevitable and the corrosion process occurred at the coating/metal interface.

Alloys of the Mg–Mn system form an important group of medium-strength wrought alloys, which are used at temperatures up to 200 °C. Doping of this system (in addition to manganese) with rare earth elements results in an increase in resistance to stress corrosion cracking [1]. However, papers on the formation of protective layers on the alloys of this system are rare in scientific literature [18]. Hydrophobic and superhydrophobic layers were selected for the protection of the magnesium alloy Mg–Mn–Ce against corrosion as a result of their high barrier properties [19–25]. At the same time, good adhesion of the PEO layers to the metal substrate and their complex surface topography made it possible to use them as a basis for the formation of composite coatings.

In this work, the anticorrosion properties of hydrophobic and superhydrophobic coatings on the Mg–Mn–Ce alloy were identified and the features of their changes depending on exposure time in 3% aqueous solution of sodium chloride were established. Three types of coatings that differ significantly from each other by wettability in chloride-containing electrolyte were selected for the study. Hydrophilic coatings were produced by plasma electrolytic oxidation in silicate-containing electrolyte as described in [18]. Hydrophobic coatings were formed by deposition of the hydrophobic agent from the solution onto the surface of the

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PEO layer by adsorption. The superhydrophobic coatings were fabricated on top of the PEO coatings by formation of a nanocomposite layer having both multimodal roughness and low surface energy through the deposition of a wetting film of a dispersion containing silica nanoparticles and molecules of the hydrophobic agent [26–29].

2. Experimental

2.1. Materials

The base material in this study was wrought magnesium alloy MA8 containing 1.5–2.5 mass% Mn and 0.15–0.35 mass% Ce, for which the hydrophobic and superhydrophobic coatings were designed. Rectangular plates of sizes 15 mm × 40 mm × 1.5 mm were used as samples for electrochemical studies. Typical plate sizes for wetting analysis were 15 mm × 10 mm × 1.5 mm. Preliminary treatment of a sample included grinding with sandpaper of different grits (600, 800 and 1200) and washing with distilled water. Abrading with the last paper was carried out with high purity ethanol rinsing.

To prepare both the hydrophobic and the superhydrophobic coatings, methoxy- $\{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8\text{-pentadecafluorooctyl})\text{oxy}]\text{propyl}\}$ -silane (synthesized in the laboratory) was used as the hydrophobic agent; decane and 99.9% ethyl alcohol were also used.

2.2. PEO coating formation

PEO treatment was conducted in a silicate–fluoride electrolyte containing 15 g/l $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 5 g/l NaF [18]. Coating formation was carried out using the same equipment for plasma electrolytic oxidation as in [18], consisting of a computerized control and monitoring system and connected to a computer with the appropriate software. All samples were processed for 10 min in the bipolar mode of PEO, in which the anodic pulses periodically alternate with cathodic ones. During the anodic component of the process, the voltage values increased from 30 to 300 V at a rate of 0.45 V/s; the cathodic component was in potentiostatic mode fixed at a value of 30 V. The duration ratio of the anodic and cathodic pulses was equal to 1, so the duty cycles were 50%, and the polarization frequency was 300 Hz. The root-mean square values of the voltage were used in the formation process in this work. The applied electrical regime and waveforms of the voltage are schematically presented in Fig. 1.

2.3. Formation of hydrophobic and superhydrophobic layers

The initial PEO coatings were hydrophilic and characterized by contact angles of $45.9^\circ \pm 2.9^\circ$. Then, to improve the corrosion resistance of the samples, the PEO coatings were further processed by the hydrophobic and superhydrophobic treatments.

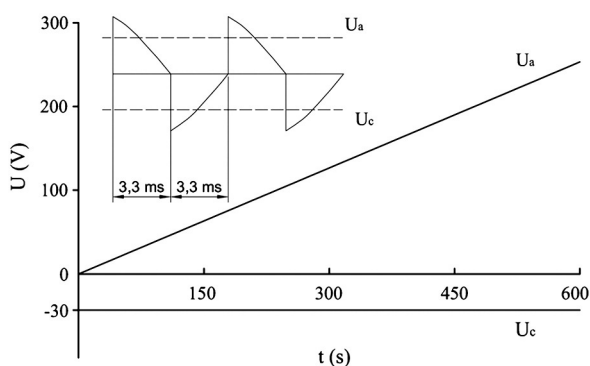


Fig. 1. Schematic illustration of the applied electrical regime and waveforms of the voltage pulses.

Since attaining the hydrophobic and superhydrophobic states of the surface is based on chemisorption of the hydrophobic agent at the surface OH groups [30,31], the initial PEO coatings were boiled in a $\text{Na}_2\text{O} \times \text{SiO}_2 \times \text{H}_2\text{O}$ solution for 15 min to increase the surface density of chemisorption-active sites. The decrease in the contact angle of the PEO coating to $22^\circ \pm 7^\circ$, which occurs after boiling, indicates an increase in the density of surface hydroxyl groups. The same agent, methoxy- $\{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8\text{-pentadecafluorooctyl})\text{oxy}]\text{propyl}\}$ -silane, was used to prepare both the hydrophobic and the superhydrophobic coatings on the PEO surface.

Modification of the surface to attain hydrophobicity was performed by two methods. In the first method, in order to form the hydrophobic coating, the sample was immersed in a 2% solution of hydrophobic agent in 99% decane for 2 h, followed by washing once in an ultrasonic bath in 99.9% ethyl alcohol and three times in distilled water for 5 min. The hydrophobic coating was formed as a result of chemisorption. The contact angle of the sample increased to $131^\circ \pm 2^\circ$. In the second method, superhydrophobic coatings characterized by contact angles higher than 160° and rolling angles less than 7° were produced in ambient conditions by deposition of a wetting film of aerosil nanoparticle suspension in decane on the PEO coating, as described in [26,27]. In the latter case, the hydrophobic agent performs two functions. First, it reduces the free surface energy of the material. Second, having three reactive terminal groups, $-\text{Si}(\text{OCH}_3)_3$, it provides a chemical bond between the nanoparticles in the aggregates and between the nanoparticles and the PEO layer [27,31].

The role of the complex surface topography of the PEO coating should be emphasized. The key point for the formation of stable hydrophobic and superhydrophobic layers on top of the metal surface is the adhesion strength. The adhesion strength in turn is determined by two factors. The first one is the formation of a chemical bond between components of the coating and chemically active sites on top of the metal surface. The surface of PEO treated metal generally contains more hydroxyl groups responsible for chemical bonding with the hydrophobic agent than the native magnesium surface. Moreover, the density of hydroxyl groups on a PEO treated surface can be effectively controlled by boiling in a $\text{Na}_2\text{O} \times \text{SiO}_2 \times \text{H}_2\text{O}$ solution [30]. The second factor is the real area of contact between the metal surface and the hydrophobic or superhydrophobic layer. The more developed area of magnesium alloy surface after PEO pretreatment provides a significant increase in effective contact area, and thus in effective adhesion strength.

In addition, the complex surface topography of the PEO coating facilitates the achievement of multimodal roughness, which is necessary to reach the stable superhydrophobic state [32].

2.4. Cross-section preparation, scanning electron microscopy and elemental analysis of the surface

The SHP coating cross-section was prepared by means of Ar^+ etching of the sample using Ilion+™ Precision Cross-Section System model 693 (Gatan Inc., USA) according to [33]. The etching was performed for 1 h with the ion gun beam energy equal to 4 keV. The etching ion beam was oriented in the SHP-layer/PEO-coating/Mg alloy direction. The area of etching was limited by a special shield consisting of a steel sample blade. SEM images of the surface of the samples and data on their elemental composition were obtained with a Hitachi S5500 scanning electron microscope equipped with an energy dispersive X-ray microanalysis system. Taking into account the multimodal roughness of the analyzed surface and an electron beam diameter of about 10 nm, the accuracy of estimating the elemental content of a nanoscale edge object is significantly about $0.1 \mu\text{m}^3$. The nanoscale gold layers were deposited on the surfaces of the test samples to reduce image distortion associated with charging of the non-conductive coating.

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