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Preparation of layered double hydroxide on PEO-coated MA8 magnesium alloy: electrochemical and corrosion properties

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Abstract: The coating containing a layered double hydroxide (LDH) was obtained on the MA8 magnesium alloy. The coating morphology, its electrochemical and corrosion behavior were studied. Scanning electron microscopy confirmed the lamellar structure of the LDH. Maps of the element distribution on the surface (the aluminum content on the surface is 3.2 wt.%) and the diffraction pattern of the sample (the presence of a hydrotalcite phase) also confirmed the presence of LDH. The electrochemical and corrosion behavior of the base PEO-coating, an LDH-containing coating, and the LDH-containing coating after impregnation with sodium oleate was compared. According to the experimental data analysis the positive role of LDH in the protection of the magnesium alloy was established. Treatment of the LDH-containing coating with a 0.1 M solution of sodium oleate makes it possible to increase the impedance modulus measured at the frequency of 0.1 Hz by order of magnitude compared to the inhibitor free protective layer. The obtained LDHs have a positive effect on the stability of the protective properties in aggressive medium, which was shown by the decrease in corrosion current density for the investigated sample.

Keywords: magnesium alloys, layered double hydroxide, electrochemistry, corrosion, inhibition, plasma electrolytic oxidation

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Материалы конференции
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Получение слоистого двойного гидроксида на ПЭО- покрытии, сформированном на сплаве магния MA8: электрохимические и коррозионные свойства

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Аннотация. На магниевом сплаве MA8 было получено покрытие, содержащее слоистые двойные гидроксиды (СДГ) в своей структуре. Изучена морфология полученного покрытия, его электрохимическое и коррозионное поведение. Ламеллярная структура СДГ подтверждена анализом данных, полученных с помощью сканирующей

электронной микроскопии. Наличие СДГ также подтверждено картами распределения элементов на поверхности (содержание алюминия на поверхности 3.2 масс.%) и дифрактограммой образца (присутствие фазы гидроталькита). Было проведено сравнение электрохимического и коррозионного поведения базового ПЭО-покрытия, покрытия, содержащего СДГ, и покрытия, содержащего СДГ, после импрегнирования олеатом натрия. Согласно полученным экспериментальным данным, установлена положительное влияние СДГ на защитные свойства покрытия. Обработка 0.1 М раствором олеата натрия покрытия, содержащего СДГ, позволяет увеличить модуль импеданса, измеренного на частоте 0.1 Гц, на порядок по сравнению с покрытием без ингибитора. Полученные СДГ положительно влияют на устойчивость сплава с ПЭО-покрытием в агрессивной среде что следует из уменьшения плотности тока коррозии для исследуемого образца.

Ключевые слова: магниевые сплавы, слоистый двойной гидроксид, электрохимия, коррозия, ингибирование, плазменно-электролитическое окисление

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Introduction

Magnesium and its alloys are light materials with a density of about 1.8 g/cm³, which is lower than that of aluminum (about 2.7 g/cm³), titanium (about 4.5 g/cm³) and steel (about 7.8 g/cm³). Magnesium alloys have attracted considerable interest from researchers due to their good specific strength, lightness, high damping capacity, and good recyclability [1, 2].

Magnesium alloys do not have a protective oxide layer on their surface, unlike stainless steel, aluminum and titanium alloys. Therefore, Mg alloys are subject to strong corrosion in the marine atmosphere and other environment [2–5]. One of the well-known methods for applying ceramic-like coatings to metals and their alloys is plasma electrolytic oxidation (PEO), which is used to protect valve metals such as Al, Mg, Ti, Ta, Nb, and others [6–10]. This method is based on polarization of the material in electrolyte solutions at voltages that cause the flow of microdischarges on the surface of treated materials [11].

Currently, technologies aimed at obtaining the smart coatings are widespread [12]. To date, there is a need to develop eco-friendly self-healing coatings [13]. This type of coating has the property of self-healing in case of damage, which is based on the gradual release of corrosion inhibitors that prevent the material against degradation. In the aerospace industry the intensive aluminum corrosion was prevented using Cr(VI) salts, but this inhibitor has a negative (toxic) effect to environment. Alternative protection options were developed using coatings based on Zr/Ti, rare earth elements, including those based on LDH [12, 14–16].

However, for magnesium, a smaller number of possible protection methods (in comparison to Al) can be observed [3, 15], since Mg is a rather active metal. Previously, the coating impregnation with 8-hydroxyquinoline [18] was proposed as an additional protection for magnesium with a PEO-layer. This treatment made it possible to significantly improve the corrosion resistance of the base PEO-coating.

In [14, 19], it was proposed to use LDH as a paint pigment for steel, with the preliminary incorporation of 2-mercaptobenzothiazole, which makes it possible to inhibit corrosion processes. LDH [17, 18] is the ionic solids with the general formula $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2]^{x+}[(A^{n-})_{x/n} \cdot mH_2O]$.



LDH has a hydrotalcite-like structure (the structure of brucite-like layers, that consist of mixed metal hydroxides, in which these metals are in an octahedral molecular geometry, and the interlayer space is filled with charge-compensating anions and water molecules [22, 23]. Due to the peculiarities of this structure, inhibitor molecules can be incorporated in the intercalated layers [14, 24–26] and subsequently be released to suppress corrosion [25].

In this paper, we propose the way of preparation and use of LDHs as nanocontainers for the protection of the PEO-coated MA8 magnesium alloy. Sodium oleate was chosen as a corrosion inhibitor [27].

Materials and Methods

Samples with the size of $20 \times 20 \times 2$ mm³ made of MA8 magnesium alloy were used in this work as a substrate. The specimens were preliminarily processed on a grinding machine using an emery paper with a grit of P320, then washed with isopropyl alcohol and air-dried.

The following coatings were formed on MA8 magnesium alloy: base PEO-coating (MA8-PEO), PEO-coating containing LDH (MA8-PEO-LDH), and PEO-coating containing LDH and treated with an inhibitor (MA8-PEO-LDH-oleat).

PEO treatment was carried out in an electrolyte containing 15 g/L Na₂SiO₃·5H₂O and 5 g/L NaF in the bipolar mode. The duration of the process was 600 s. During the entire oxidation process, the potential of the cathode phase was maintained equal to -30 V, and the potential of the anode phase increased linearly from 30 to 300 V. The pulse duration was 30 ms with a pause for each phase.

To obtain LDH the treatment of the PEO-coating [24, 25] was carried out in a solution containing 50 g/L EDTA-Na, 40 g/L NaOH, 5 g/L Al (aluminum granules were preliminarily dissolved in sodium hydroxide). The samples were immersed in the solution and soaked for 48 h at 60 °C (hot solution treatment).

Treatment with the inhibitor was performed in a solution containing 0.1 M sodium oleate for 24 h.

An AUW120D analytical balance (Shimadzu, Japan) was used for sample weighting. To control the coating thickness, a VT-201 eddy current thickness gauge (KID, Russia) was used. SEM images and element distribution maps were obtained using an EVO 40 electron microscope (Carl Zeiss, Germany). X-ray phase analysis (XRD) was performed on a D8 Advance diffractometer (Bruker, USA). Electrochemical measurements were carried out using a VersaSTAT MC electrochemical station (Princeton Applied Research, USA) in a 3.5 % NaCl solution in a three-electrode cell with an Ag/AgCl electrode as a reference electrode and Pt mesh as a counter one. The impedance spectra and polarization curves were processed using the ZView® and CView® programs, respectively (Scribner, USA).

Results and Discussion

The thickness of the resulting coatings for all samples was 15 ± 2 μm. The weight gain for the MA8-PEO-LDH sample was equal to 0.8 mg compared to MA8-PEO, and for the sample impregnated with the inhibitor, the weight gain was equal to 0.4 mg compared to MA8-PEO-LDH. For samples with PEO-coating containing LDH, a change in the color of the coating was noted. The original PEO-coating was white, PEO-coating with inhibitor free LDH was yellow. The color of the MA8-PEO-LDH coating did not change when treated with an inhibitor.

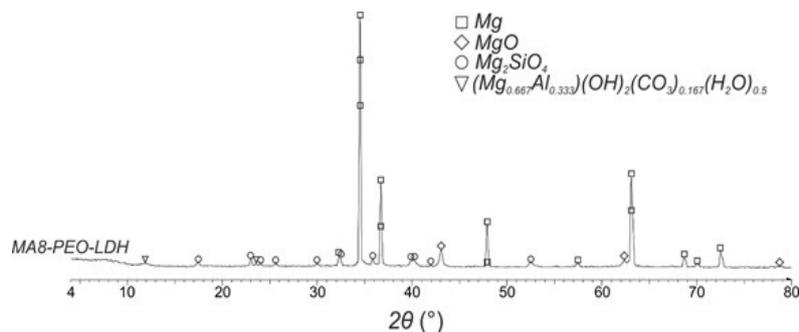


Fig. 1. XRD patterns of MA8, MA8-PEO, MA8-PEO-LDH samples

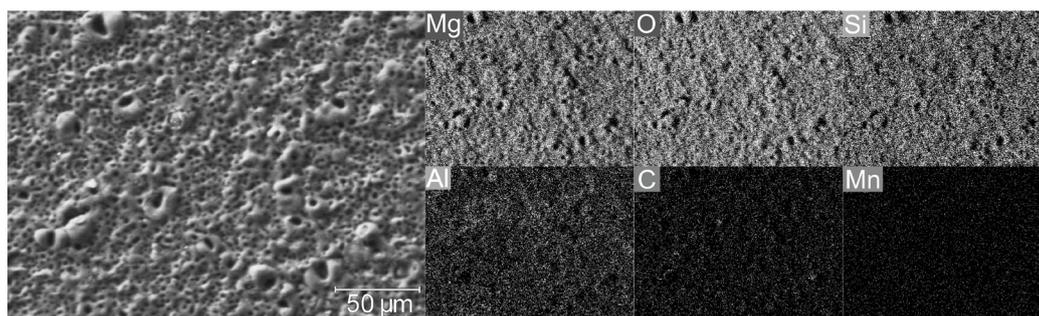


Fig. 2. SEM image and EDX maps of the MA8-PEO-LDH

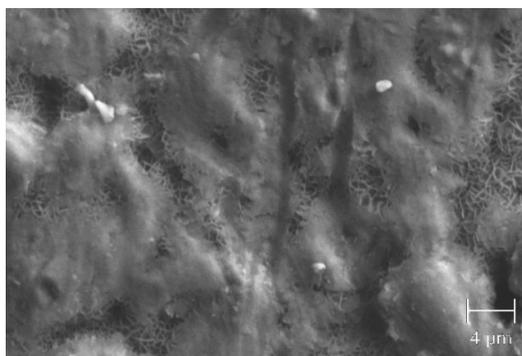


Fig. 3. SEM image of the MA8-PEO-LDH

The XRD patterns (Fig. 1) and EDX maps of the distribution of elements (Fig. 2) indicate the formation of the layered double hydroxide (Mg-Al-LDH) phase ($\text{Mg}_{0.667}\text{Al}_{0.333}(\text{OH})_2(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}$). The main phases of the base PEO-coating such as (Mg, MgO (periclase), Mg_2SiO_4 (forsterite)) are presented in the MA8-PEO-LDH sample. The element composition of the sample is as follows (wt.%): O, 46.0; Mg, 26.6; C, 15.1; Si, 7.8; Al, 3.2; Na, 1.3.

The surface morphology of MA8-PEO-LDH is shown in the SEM image (Fig. 2). This protective layer has a structure, which is typical for PEO-coating. According to the EDX maps, one can note the homogeneity of the distribution of Mg, Si, O in the PEO-coating. Aluminum is also homogeneously distributed over the sample surface (3.2 wt.%). This means that the process of formation of the LDH was successful. The high-resolution SEM image (Fig. 3) of the LDH-containing PEO-coating shows areas with a lamellar structure, which corresponds to LDH, that is in accordance with [3, 12, 20, 25]. It should also be noted that not whole PEO-coating was covered with LDH crystallites, since PEO-coating structure was detected among the LDH. Fig. 3 shows that LDH formation was mainly occurred in porous part of the PEO-layer.

Table 1

Electrochemical characteristics of the samples in 3.5% NaCl

| Sample | β_a , mV | β_c , mV | E_c , mV, vs Ag/AgCl | I_c , mA/cm ² | R_p , $\Omega \cdot \text{cm}^2$ | $ Z _{f=0.1\text{Hz}}$, $\Omega \cdot \text{cm}^2$ |
|-------------------|----------------|----------------|------------------------|----------------------------|------------------------------------|---|
| MA8 | 43.3 | 169.9 | -1512.2 | 16.67 | $8.7 \cdot 10^2$ | $6.7 \cdot 10^2$ |
| MA8-PEO | 97.2 | 251.6 | -1411.2 | 0.41 | $7.4 \cdot 10^4$ | $8.4 \cdot 10^3$ |
| MA8-PEO-LDH | 135.3 | 543.7 | -1422.2 | 0.35 | $1.4 \cdot 10^5$ | $1.7 \cdot 10^4$ |
| MA8-PEO-LDH-oleat | 44.9 | 267.6 | -1391.8 | 0.26 | $1.7 \cdot 10^5$ | $2.1 \cdot 10^5$ |

Notations: β_a , β_c , E_c , I_c , R_p , $|Z|_{f=0.1\text{Hz}}$ are the anodic and cathodic slope of Tafel curves, corrosion potential, corrosion current density, polarization resistance and impedance modulus at 0.1 Hz, respectively.

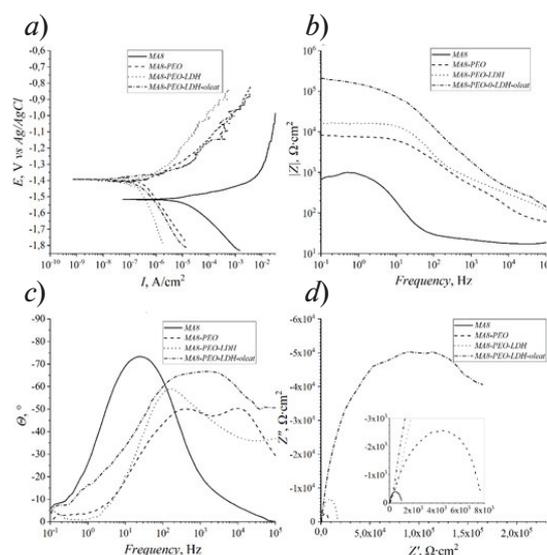


Fig. 4. Potentiodynamic curves (a); impedance spectra of MA8 samples with and without coatings; Bode plots (dependence of impedance modulus $|Z|$ (b) and phase angle θ (c) on frequency); Nyquist plots (d) (dependence of the imaginary part of the impedance Z'' on the real part of the impedance Z')

The analysis of the potentiodynamic polarization curves (Fig. 4, a) shows a shift in the corrosion potential to the positive direction for coated MA8 samples. The curves for MA8 with different types of protective coatings lies in the same region. A decrease in the corrosion current density indicates a positive effect of LDH formation on the surface of PEO-layer. The results of electrochemical impedance spectroscopy (Fig. 4, b, c, d) show high protective properties of the LDH-containing coatings. The analysis of the Bode plot clearly shows the positive effect of the presence of LDH in the structure of the protective coating, an increase in impedance modulus is noted over the entire frequency range. Treatment with sodium oleate also increases the impedance values as compared to the specimen with inhibitor free LDH-containing coating. The electrochemical characteristics of MA8 alloy sample with and without protective coatings are presented in Table 1.

Conclusion

The Mg-Al-LDH was formed on the PEO-coating containing MgO and Mg₂SiO₄ using hot solution treatment. The obtained LDHs have a positive effect on the stability of the coating obtained by the PEO method in the corrosive environment. The impedance modulus measured at the lowest frequency (0.1 Hz) resistance was increased as compared to one for sample without coating. The corrosion current density decreased after forming a ‘smart coating’ on MA8 Mg alloy. Inhibitor treatment also improves the corrosion resistance of the protective coating. This work allows us to suggest the effective way of self-healing coating formation on the surface of PEO-treated magnesium alloy.

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