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Influence of halloysite nanotube incorporation on the properties of PEO-coatings formed on MA8 magnesium alloy

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Abstract: The properties of the coatings formed on the MA8 magnesium alloy by plasma electrolytic oxidation in electrolytes containing halloysite nanotubes in the concentrations of 0, 10, 20, 30 and 40 g/l were investigated. It has been found that the presence of halloysite nanotubes in the composition of the coatings has a positive impact on protective properties of the coatings and leads to the increase of roughness and heterogeneity. Obtained coatings reduce corrosion current density in comparison with the base PEO layers.

Keywords: plasma electrolytic oxidation, nanoparticles, halloysite nanotubes, protective coatings

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Влияние внедрения нанотрубок галлуазита на свойства ПЭО-покрытий, сформированных на магниевом сплаве МА8

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Аннотация. Изучены свойства покрытий, формируемых на магниевом сплаве МА8 методом плазменного электролитического оксидирования в электролитах, содержащих нанотрубки галлуазита в концентрациях 30 ,20 ,10 ,0 и 40 г/л. Установлено, что наличие нанотрубок галлуазита в составе покрытий, приводит к увеличению шероховатости поверхности и положительно влияет на защитные свойства покрытий.

Ключевые слова: плазменное электролитическое оксидирование, наночастицы, нанотрубки галлуазита, защитные покрытия

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Introduction

Magnesium alloys are lightweight materials with excellent strength and vibration damping capacity that have found application in multiple engineering fields [1]. Interest in magnesium alloys has particularly increased among researchers from the biomedical materials science field since a potential use of Mg as a biodegradable material has been established. However, modern engineering and science face a problem of low corrosion resistance of magnesium alloys. This shortcoming crucially limits their usage as construction materials and alloys for bioresorbable implant fabrication.

One of the most promising methods of protective surface modification for light alloys is plasma electrolytic oxidation (PEO). PEO coatings combine improvement of corrosion resistance of a treated materials along with development of a new functional properties. PEO became widely investigated by the scientific community due to a broad range of adjustable process parameters and a prospect of coatings properties management. Ceramic-like coatings formed by the PEO can be improved through incorporating nanoparticles. PEO coatings with various nanoscale additives demonstrate improved hardness [2–4], corrosion [2, 3] and wear resistance [2, 4–6], biocompatibility [7]. Halloysite nanotubes are naturally formed nanoparticles that can be incorporated into PEO coatings and used as an nanocontainers [8] for loading, storage, and controlled release of active molecules such as drugs, corrosion inhibitors, proteins, etc.

Magnesium alloys with PEO-coating containing halloysite nanotubes are of great scientific interest because of their low density, bioresorbability, and improved corrosion resistance.

In this paper, the formation of protective multifunctional coatings on the MA8 magnesium alloy by the PEO in electrolytes with halloysite nanotubes was investigated. The electrochemical and mechanical properties of the obtained PEO-layers are represented.

Materials and Methods

The MA8 magnesium alloy sheets (Mn 1.30; Ce 0.15; Mg bal. (wt.%)) were used as a substrate. The size of specimens was 20 mm × 15 mm × 2 mm. The base electrolyte contained sodium fluoride (5 g/l) and sodium silicate (20 g/l). In this work, we used the halloysite nanotubes (Halloysite Ural, Russia) with a length of 1–3 μm, an outer diameter of 50–70 nm and inner diameter of 15–30 nm were used. The halloysite nanotubes were dispersed in the base electrolyte in concentrations of 0, 10, 20, 30 and 40 g/l with addition of anionic surfactant (sodium dodecyl sulfate) at concentration of 0.25 g/l. The corresponding coatings were named in reference to the concentration of the halloysite nanotubes in the used electrolytes: H0, H10, H20, H30, and H40, respectively. Samples surface morphology were studied using a Carl Zeiss EVO 40 scanning electron microscope (SEM) (Carl Zeiss, Germany). The thickness of the coatings was measured by eddy-current thickness gauge. The electrochemical tests were carried out using VersaSTAT MC (Princeton Applied Research, USA). The samples were studied in 3.5 wt.% NaCl solution. As a reference electrode was used the saturated calomel electrode (SCE).

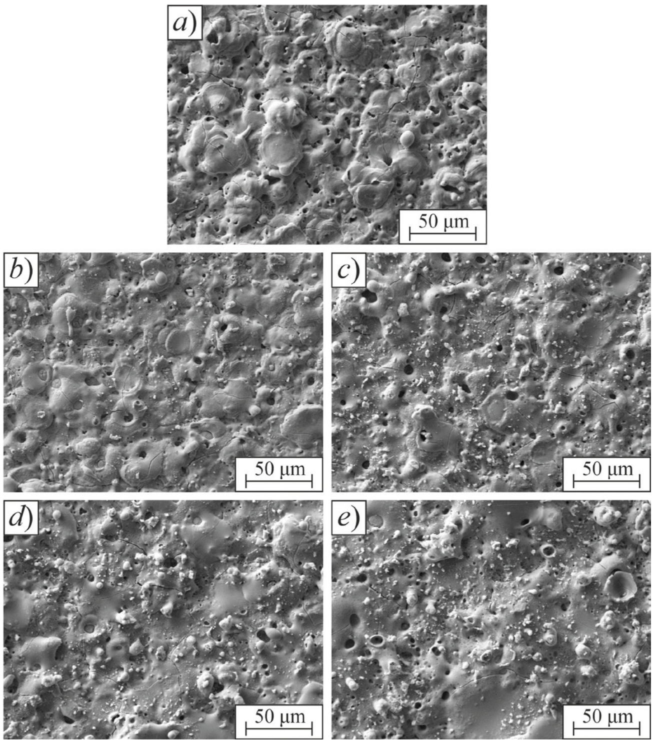

Fig. 1. SEM images of the coatings surface: H0 (*a*), H10 (*b*), H20 (*c*), H30 (*d*), H40 (*e*)

Results and Discussion

The SEM images of surfaces show significant differences in surface morphology of the studied specimens (Fig. 1). Samples obtained in electrolytes with high concentrations of halloysite nanotubes have a more rugged and irregular surface. Heterogeneity of the coatings increased with increasing content of halloysite nanotubes in electrolytes. Thus, clusters and aggregates of nanoparticles are primarily visible on the H20, H30, and H40, which were obtained in electrolytes enriched with nanoparticles.

The same tendency for roughness dependency on nanoparticles content is apparent according to results of optical laser profilometry (Table 1). Agglomerates occurrence rises with halloysite nanotubes content, as well as the surface roughness. The results of the thickness measurements are represented in the Table 1. It is plain to see, that the thickness of the layers is in direct proportion to halloysite nanotubes concentration.

Table 1

Thickness and roughness parameters of the studied samples

Sample name	R_a [μm]	R_z [μm]	Thickness [μm]
H0	1.8 ± 0.4	9.6 ± 2.2	51.4 ± 1.3
H10	2.0 ± 0.3	10.8 ± 2.8	54.8 ± 1.0
H20	2.5 ± 0.6	12.2 ± 2.9	55.0 ± 1.5
H30	3.0 ± 0.7	15.5 ± 2.9	68.6 ± 2.0
H40	3.4 ± 0.7	16.5 ± 3.1	78.8 ± 1.5

Notations: R_a and R_z are the arithmetical mean deviation of the profile, the ten-point height of irregularities, respectively.

The change in corrosion properties of the coatings containing halloysite nanotubes compared to the PEO-coating obtained in the electrolyte without nanoparticles was studied by potentiodynamic polarization test (Fig. 2).

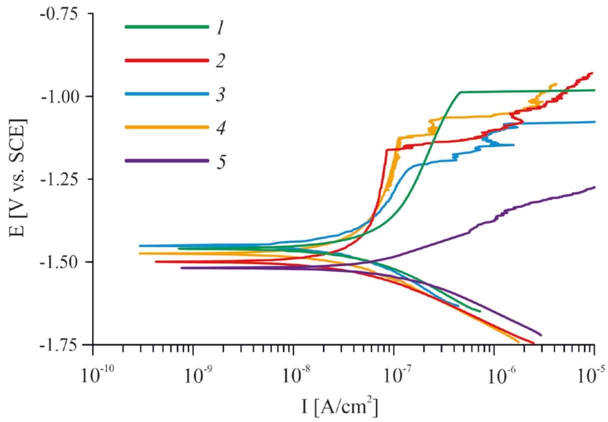

Fig. 2. Polarization curves for the H0 (*1*), H10 (*2*), H20 (*3*), H30 (*4*), H40 (*5*) samples

The corrosion parameters calculated from obtained data are represented in the Table 2. The results of tests demonstrate a decrease of the corrosion current density (I_c) and an increase of the polarization resistance (R_p) up to the concentration of nanoparticles of 20 g/l.

The lowest current density was demonstrated by the sample with coating obtained in the electrolytes containing halloysite nanotubes in concentration of 20 g/l. The corrosion current density for the H20 sample decreased twofold in comparison with the H0 sample (from $1.2 \cdot 10^{-7}$ A/cm^2 for base PEO layer down to $4.9 \cdot 10^{-8}$ A/cm^2 for H20 coating). The H20 samples also exhibited the highest polarization resistance of $1.2 \cdot 10^6$ Ω·cm^2, which is almost two times higher than R_p value for H0 coating. Such results can be explained with nanoparticles incorporation, which leads to partial pores filling with chemically stable halloysite nanotubes. Plasma discharge temperature enables sintering of the halloysite nanotubes on the bottoms of the pores and sealing of incompletely closed channels with sintering products.

Table 2

Corrosion parameters of the obtained coatings

Sample name	R_p [Ω·cm^2]	I_c [A/cm^2]	E_c [V]
H0	6.4×10^5	1.2×10^{-7}	−1.46
H10	8.6×10^5	5.7×10^{-8}	−1.50
H20	1.2×10^6	4.9×10^{-8}	−1.45
H30	1.1×10^6	5.6×10^{-8}	−1.47
H40	2.9×10^5	1.1×10^{-7}	−1.52

A decrease in protective characteristics of coatings obtained in electrolytes with concentrations of halloysite nanotubes above 20 g/l can be observed. The main reason for a such tendency is an increase in heterogeneity of the coatings due to the more intensive nanoparticles incorporation, which led to the porosity increase. As a result, the value of R_p for H40 sample is even lower than for the base PEO coating.

Conclusion

It has been established that PEO-coatings formed on the MA8 magnesium alloy in electrolytes containing halloysite nanotubes have improved electrochemical characteristics in comparison with the surface layers obtained in the electrolyte without nanoparticles. Based on obtained results, it has been concluded that the coatings formed in an electrolyte with a 20 g/l nanoparticle concentration have the highest protective properties in the corrosive medium. The incorporation of nanoparticles led to an increase in the roughness parameters, which are comparably high for all PEO coatings containing halloysite nanotubes. Formed coatings are perspective for biomedical applications due to their suitable roughness parameters and corrosion resistance.

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REFERENCES

1. **Kulekci M. K.,** Magnesium and its alloys applications in automotive industry, The International Journal of Advanced Manufacturing Technology. 39 (2008) 851–865.
2. **Kaseem M., Fatimah S., Nashrah N., Ko Y. G.,** Recent progress in surface modification of metals coated by plasma electrolytic oxidation: Principle, structure, and performance, Journal of Physics D: Applied Physics. 117 (100735) (2021) 2110–2120.
3. **Asri R.I.M., Harun W.S.W., Samykano M., Lah N.A.C., Ghani S.A.C., Tarlochan F., Raza M.R.,** Corrosion and surface modification on biocompatible metals: A review, Materials Science and Engineering. 77 (2017) 1261–1274.
4. **Mashtalyar D.V., Nadaraia K.V., Imshinetskiy I.M., Sinebryukhov S.L., Gnedenkov S.V.,** New approach to formation of coatings on Mg-Mn-Ce alloy using a combination of plasma treatment and spraying of fluoropolymers, Journal of Magnesium and Alloys. Vol. 10 (4) (2022).
5. **Nadaraia K.V., Suchkov S.N., Imshinetskiy I.M., Mashtalyar D.V., Sinebrykhov S.L., Gnedenkov S.V.,** Some new aspects of the study of dependence of properties of PEO coatings on the parameters of current in potentiodynamic mode, Surface and Coatings Technology. 426 (2021) 127744.
6. **Atapour M., Blawert C., Zheludkevich M.L.,** The wear characteristics of CeO_2 containing nanocomposite coating made by aluminate-based PEO on AM 50 magnesium alloy, Surface & Coatings Technology. 357 (2018) 626–637.
7. **Mashtalyar D.V., Nadaraia K.V., Plekhova N.G., Imshinetskiy I.M., Piatkova M.A., Pleshkova A.I., Kislova S.E., Sinebryukhov S.L., Gnedenkov S.V.,** Antibacterial Ca/P-coatings formed on Mg alloy using plasma electrolytic oxidation and antibiotic impregnation, Materials Letters. 317 (2022) 132099.
8. **Zahidah K.A., Kakooei S., Ismail M. C., Raja P. B.,** Halloysite nanotubes as nanocontainer for smart coating application: A review, Progress in Organic Coatings. 111 (2017) 175–185.

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