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Effect of PEO-modes on the electrochemical and mechanical properties of coatings on MA8 magnesium alloy

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Abstract

Protective surface layers with a high corrosion stability and significant microhardness as compared to the substrate material were obtained on MA8 magnesium alloy by Plasma Electrolytic Oxidation (PEO) in a silicate-fluoride electrolyte. The phase and elemental composition of the coatings were investigated. It was found that the application of the bipolar PEO-modes enables one to synthesize on the alloy’s surface a high-temperature phase of magnesium silicate, forsterite (Mg$_2$SiO$_4$) having a good anticorrosion and mechanical properties.

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1. Introduction

Magnesium alloys possess low density, high durability and can be easily processed. They can therefore successfully compete with steel and aluminum alloys in automotive, aerospace and defense industries, as well as in production of personal computers and mobile communication devices. Their main disadvantage however is a low corrosion and wear resistance.

Exposure to aqueous corrosive media (e.g. containing chloride-ions) results in breakdown of the passive film and degradation of magnesium alloy. A limited number of protective coatings serve to prevent corrosion and wear of parts made of magnesium alloys. Conversion coatings based on chromates,

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fluorides, phosphates or permanganates have insufficient protection properties, however the application and disposal of corresponding electrolyte solutions is often too harmful for the environment [1].

2. Experiment

Rectangular coupons 5 mm × 30 mm × 1 mm in size made from MA8 magnesium alloy (1.5 to 2.5 wt.% Mn; 0.15 to 0.35 wt.% Ce; Mg – balance) were used. Prior to oxidation the samples were polished to achieve a surface roughness of $R_a = 0.12 \mu m$, washed by distilled water and alcohol. The electrical parameters during the PEO-process were controlled using an automated control system connected to a PC with appropriate software. A conventional reversible thyristor rectifier was used as a power supply [2].

Electrochemical properties of the surface layers formed on magnesium were investigated using a Series G300 potentiostat/galvanostat (Gamry Instruments) with computer interface. The measurements were carried out in 3% NaCl solution under ambient conditions in a three-electrode cell. The impedance spectra were acquired at a free corrosion potential over the frequency range from 0.01 Hz to 0.3 MHz. The experiments were controlled by DC105™ and EIS300™ software (Gamry Instruments).

Chemical compositions and elemental distributions across the coating were analyzed using a JXA 8100 JEOL Electron Probe Microanalyzer. The coating porosity was analysed on the cross-sectional SEM image using ImageJ 1.34p software.

3. Results and discussions

The analysis of cross-sectional SEM images of investigated PEO-coatings on MA8 magnesium alloy revealed that the coatings consist of an outer porous region and an inner denser region. The thickness of the coating obtained in the bipolar PEO-modes is about 16–20 µm whereas in the case of the unipolar mode it is significantly lower (8 to 10 µm).

Through thickness distribution of the elements constituting the PEO layer investigated using EPMA method is shown in Fig. 1. According to the EPMA-data, the elemental composition of the coatings is practically identical, comprising Mg, O, Si and F, whereas Mn appeared below detectable limits. For all coatings it is common that in the outer region, the silicon content is generally higher than that in the inner one; this should result from the mechanism of Si incorporation from the electrolyte indicating its more active role in formation of the outer coating part. Also, fluorine is present in relevant coatings and its content in the inner region was about 2.5 times higher than in the outer one.

According to the XRD data the PEO-layers formed in a different modes consist of MgO and Mg$_2$SiO$_4$. There is however a quantitative difference in the coating phase compositions, with higher peaks of Mg$_2$SiO$_4$ phase being observed for the sample formed in the bipolar mode in comparison those formed in the unipolar one.

Thus the application of the bipolar PEO-modes leads mainly to the increase in Mg$_2$SiO$_4$ content in the
coatings. This can be explained by more intensive discharges that occur during the treatment in the bipolar modes as compared to the unipolar one. Higher temperature of these discharges promotes transformation of the amorphous phase magnesium silicate in crystal state. Moreover, according to experimental results both the fluoride addition and the application of the bipolar current result in the morphological changes that may be linked to the chemical/phase composition as well.

The corrosion characteristics were obtained by Tafel-analysis of potentiodynamic polarisation curves shown in fig. 2. The curves numerations correspond to those of samples in Table 1 in which shows a microhardness ($H$), polarization resistance ($R_p$), corrosion current ($I_c$) and free corrosion potential ($E_c$) of the magnesium alloy MA8 samples of the with different PEO-coatings.

As follows from comparison of the electrochemical parameters with cross-sectional morphology, the layers obtained under bipolar conditions (samples #4, 5) are characterized by a relatively low porosity, with pores being generally narrow and going part through the thickness. These characteristics response for high protective properties of the formed layers.

Fig. 2. Polarization curves for the MA8 alloy samples with the coatings obtained in the different PEO-modes

| Sample # | Electrolyte* | PEO-mode | Coating phase composition | Thickness (µm) | $H$ (GPa) | $R_p$ (Ω cm²) | $I_c$ (A/cm²) | $E_c$ (V) |
|----------|--------------|----------|----------------------------|---------------|----------|------------|-------------|---------|
| 1        | –            | without treatment | – | – | 0.6±0.1 | 4.9·10² | 5.3·10⁻³ | –1.56 |
| 2 S      | Unipolar potentiostatic | MgO | 8±1 | 0.4±0.1 | 1.1·10⁻⁴ | 2.2·10⁻⁶ | –1.56 |
| 3 SF     | Bipolar (phase A: $U^+ = 300$ V, phase B: $I^- = – 0.1$ A/cm², $t = 10$ min) | MgO, Mg₂SiO₄ | 11±3 | 0.9±0.4 | 1.5·10⁻⁵ | 1.7·10⁻⁷ | –1.53 |
| 4 SF     | Bipolar (phase A: $U^+ = 300$ V, phase B: $U^- = – 30$ V), $t = 10$ min | MgO, Mg₂SiO₄ | 20±2 | 2.1±0.6 | 6.7·10⁻⁶ | 3.9·10⁻⁷ | –1.55 |
| 5 SF     | Bipolar (phase A: $U^+ = 300$ V, phase B: $U^- = – 30$ V), $t = 10$ min | MgO, Mg₂SiO₄ | 16±2 | 4.8±0.9 | 3.3·10⁻⁵ | 7.8·10⁻⁶ | –1.50 |

* S – Na₂SiO₃·5H₂O, 15g/l; SF – Na₂SiO₃·5H₂O, 15g/l + NaF, 5 g/l

According to Table 1, surface layers formed in the bipolar PEO-mode possess a better anticorrosion properties compared to the coatings obtained under unipolar mode conditions. This must be related to the activation of magnesium surface by fluoride-ions and to the formation of a thicker coating with lower porosity. Incorporation of fluorne into the coating allows assuming a possibility of formation of MgF₂, most likely in the inner dense region, where the fluorine content is high (fig.1). Although it not be detected by XRD the presence of a chemically stable fluorides in the coating composition is implied by enhanced corrosion resistance of the layers formed in fluoridecontaining electrolytes.

The data of coating microhardness presented in Table 1 shows that the bipolar PEO-modes allows obtaining a harder layers. The effect is statistically significant and appears to be attributed primarily to the refined coating structure rather than phase composition. The application of protective PEO-coatings generally increases the impedance by 1.5–2 orders of magnitude compared to the uncoated sample. The
highest impedance value (especially in the low frequency range) is observed for sample #5 with the coating obtained in the bipolar mode from the electrolyte containing fluorine-ions.

Based on a conjoint analysis of the cross-sectional images and the impedance spectra, a suitable equivalent circuit was proposed as a result of the experimental data fitting. To better describe interfacial heterogeneities associated with the coating, the constant phase elements (CPE) were used in the circuit instead of capacitances. The impedance spectra fitting results shows in Table 2 ($n$ and $Y_o$ are the exponential coefficient and the frequency independent constant respectively).

Table 2. Parameters of the equivalent circuit for selected coatings

| Sample # | CPE$_1$ | R$_1$, kOhm·cm$^2$ | CPE$_2$ | R$_2$, kOhm·cm$^2$ |
|----------|---------|-------------------|---------|-------------------|
| 3        | 1.8·10$^{-7}$ | 0.82 | 15.0 | 1.3·10$^{6}$ | 0.59 | 18.0 |
| 4        | 7.3·10$^{-8}$ | 0.86 | 3.5 | 1.5·10$^{6}$ | 0.63 | 22.0 |
| 5        | 5.6·10$^{-8}$ | 0.85 | 14.0 | 3.9·10$^{7}$ | 0.64 | 61.0 |

The fitting of the impedance spectra enabled discrimination between the porous and the dense constituent of the coating and quantitative estimation of their individual characteristics. Moreover, the quantification provides a better insight into the effects of the process modes and parameters on the coating morphology and physical properties. The data obtained thereby show that the bipolar mode allows the coating with higher resistance of both the porous and the dense components to be obtained.

Compared to the unipolar mode, the resistances of the porous and the dense layer of the PEO-coating obtained in the bipolar mode increase two and five times respectively. Porosity evaluated for the PEO-coating obtained in the unipolar mode is about 18%; this is more than in three times higher than that for the coating obtained in the bipolar mode (~ 5%). According to Table 2, resistances $R_1$ and $R_2$ of the outer porous and the inner dense regions respectively are much higher for PEO-coating obtained in the bipolar mode compared to those of the unipolar one; this is also the case for average thicknesses of these regions estimated by corresponding reciprocal values of $Y_o$.

4. Conclusions

1. Protective coatings formed on the MA8 magnesium alloy in the bipolar PEO-modes have higher microhardness and better anticorrosion properties as compared to the layers obtained in the unipolar one.

2. It was established that introduction of the cathodic component in the coating formation mode enables one to obtain surface layers containing mainly magnesium orthosilicate with low porosity and high homogeneity.

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