Supplementary material

1. The degradation mechanism of magnesium in aqueous solution can be presented as the following reactions:

General process: $Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2$, (S1)

odic reaction:
$$Mg \rightarrow Mg^{2+} + 2e^{-}$$
, (S2)

Cathodic reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, (S3)

Product formation:
$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_{2}$$
. (S4)

The optical images in Fig. 6 d show that white gel-like products were formed on the surface of a dissolving Mg sample.

The composition of the MAO coating includes the difficult to dissolve crystalline phases β -TCP and α -TCP (β -, α -Ca₃(PO₄)₂), as well as the amorphous phase. We hypothesize that the amorphous phase is primarily involved in the coating dissolution process. In the presence of calcium ions and phosphate ions, the following reactions can take place [13,28]:

$$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-} \tag{S5}$$

$$3Ca^{2+}(or Mg^{2+}) + 2OH^{-} + 2HPO_4^{2-} + (n-2)H_2O \rightarrow Ca_3(or Mg_3)(PO_4)_2 \cdot nH_2O.$$
 (S6)

2. The effective (through-end) porosity for MAO and MAO-PLGA coatings was calculated using the equation (S7) given in the source [29],

$$P = \left(\frac{R_{\rm ps}}{R_{\rm p}}\right) \times 10^{-(\Delta E_{\rm corr}/\beta_{\rm as})},\tag{S7}$$

where R_{ps} and β_{as} are the polarization resistance and the anodic Tafel slope of the substrate, respectively, and ΔE is the difference in the corrosion potential between the substrate and PEO-coated sample. It was found that the values of effective porosity for MAO and MAO-PLGA coatings are equal to 7.5% and 1.3%, respectively. This supports the conclusion drawn from the observation of the SEM images of the coatings (Fig. 2 d, f), which show that after modifying the surface of the MAO coating by depositing a PLGA layer, its internal structure becomes more dense.

3. EIS investigation.

To further understanding the corrosion processes occurring on the surface of the composites, an impedance spectroscopy study was performed, which allowed the construction of equivalent electrical circuits.

The number of spectrum points was limited to 100. The signal amplitude was set at 100 mV from open circuit potential for composite samples, and 50 mV for bare metal samples, with a sweep from -50 mV from open circuit potential, to prevent magnesium oxidation at low frequencies (less than 1 Hz). The frequency interval from 0.01 to 500 000 Hz was selected for imaging. Impedance values at low frequencies indirectly indicate the corrosion resistance of composites, and the larger the impedance value, the higher the corrosion resistance [30].

The obtained impedance spectra are shown in Fig. S1. It is worth noting that the spectrum of bare metal substrate starts at high frequencies with a parasitic component, which is due to the conductivity of the electrolyte. According to the obtained impedance spectra, modeling of equivalent circuits was carried out, which are shown in Fig. S2.

For magnesium alloys, in principle, there are 6 electrical circuits that can describe their corrosion behavior [31]. In this paper, the following circuits were used to describe the composites:

an equivalent circuit with two time constants, to describe the Mg sample (MA20 with an ultrafine-grained structure);
Randles equivalent circuit modified by a semi-infinite Warburg diffusion impedance element, to describe the Mg-MAO sample;

3) equivalent circuit with three time constants, to describe the Mg-MAO-PLGA sample.

A real electrochemical interface at the microscopic level is not the often assumed smooth, homogeneous and defectfree surface typical of a pure capacitor [32]. It contains a large number of structural features such as porosity, surface inhomogeneities and surface roughness [33], especially in the case of coatings. Due to the non-uniform current distribution resulting from the surface inhomogeneity, in this paper, all ideal elements in the form of capacitance and inductance have been replaced by a constant phase element (CPE).

For the Mg sample, it has the following elements in its composition:

R el — electrolyte resistance;

CPE EDL — capacitance of electric double layer or corrosion products layer;

R charge — resistance of charge transfer (through electric double layer);

R pass — active resistance of the inductive component associated with pitting corrosion or passivation;

CPE pass — element modeling the reactive load (instead of typical induction) of the inductive component associated with pitting or passivation.

The peculiarity of this scheme is that it is observed to contain an inductive load, potentially arising from the formation of chlorides on the coating surface [34]. The reason for the presence of inductive loop may be due to pitting corrosion associated with adsorption/desorption of intermediates on the electrode surface or due to accelerated anodic dissolution [35, 36]. Many



Fig. S1. Impedance spectra for composite samples: Nyquist coordinates (a, c, e); Bode coordinates (b, d, f); Mg (a, b). c, d - MAO coating; e, f - MAO-PLGA coating.



researchers have reported that in the structure of pure magnesium alloys, induction loading is associated with the process of pitting and hydrogen formation in the electrolyte-surface contact of the sample [20, 37].

The following elements were used in modeling the spectra of the Mg-MAO sample:

R el — resistance of the electrolyte;

CPE MAO — capacitance of the MAO coating on the alloy surface;

R MAO — charge transfer resistance (through the MAO coating layer);

CPE diff — constant phase element simulating a semi-infinite Warburg diffusion impedance element (since the slope of the impedance hodograph at low frequencies is different from 45 degrees). This element is responsible for the diffusion of charged particles through the MAO coating. This phenomenon may arise due to the combination of the fine-grained structure of the material and the presence of calcium phosphate particles in the coating surface.

For the Mg-MAO-PLGA sample, the spectra have the following elements:

R el — electrolyte resistance;

CPE MAO — capacitance of the MAO coating on the alloy surface;

R MAO — charge transfer resistance (through the MAO coating layer);

CPE PLGA — capacitance of PLGA coating on the alloy surface;

R PLGA — charge transfer resistance (through the PLGA coating layer);

R prod — charge transfer resistance through the absorbed product layer on the composite surface;

CPE prod — capacitance of the layer of absorbed products on the composite surface.

The parameters of the models are summarized in Table S1.

With changing the state of the composites, the resistance of the electrolyte remains constant, which indicates the correctness of the experiment. It should be noted that when PLGA is applied to the surface of the MAO coating, the parameter CPE MAO-T decreases by three orders of magnitude, which indicates a decrease in the capacitance of this layer. At the same time, the parameters CPE MAO-P and R MAO remain constant. These facts lead to the conclusion that the specific surface area of MAO coating decreases when a polymer layer is applied to it, which in turn can increase the corrosion resistance of the MAO layer.

Mg		Mg-MAO		Mg-MAO-PLGA	
R el, $\Omega \cdot cm^2$	78	R el, $\Omega \cdot cm^2$	80	R el, Ω·cm ²	85
CPE EDL-T, F·cm ⁻² ·s ⁿ	1.4×10^{-5}	CPE MAO-T, F·cm ⁻² ·s ⁿ	3.1×10 ⁻⁶	CPE MAO-T, F⋅cm ⁻² ⋅s ⁿ	3.1×10 ⁻⁹
CPE EDL-P	0.87	CPE MAO-P	0.91	СРЕ МАО-Р	0.86
R EDL, $\Omega \cdot cm^2$	1521	R MAO, Ω·cm ²	3.1×104	R MAO, $\Omega \cdot cm^2$	3.1×104
CPE pass-T, F·cm ⁻² ·s ⁿ	2.4×10^{-4}	CPE diff-T, F·cm ⁻² ·s ⁿ	7.5×10 ⁻⁵	CPE PLGA-T, F·cm ⁻² ·s ⁿ	4.9×10 ⁻⁷
CPE pass-P	4.12	CPE diff-P	0.29	CPE PLGA-P	0.6
R pass, Ω·cm ²	821	-	-	R PLGA, Ω·cm ²	3.7×10^{5}
-	-	-	-	R prod, Ω·cm ²	1.9×10^{6}
-	-	-	-	CPE prod-T, F·cm ⁻² ·s ⁿ	-5.4×10^{-8}
-	-	-	-	CPE prod-P	-1.7

Table S1. Calculated model parameters for composite samples.

References

- 28. S. Amukarimi, M, Mozafari, Biodegradable magnesium biomaterials road to the clinic, Bioengineering. 9 (2022) 107.
- 29. M. Kaseem, S. Fatimah, N. Nashrah, Y.G. Ko, Recent progress in surface modification of metals coated by plasma electrolytic oxidation: Principle, structure, and performance, Progress in Materials Science 117 (2021) 100735.
- 30. S. Gollapudi, Grain size distribution effects on the corrosion behaviour of materials, Corros. Sci. 62 (2012) <u>90 94</u>.
- 31. S. Feliu, Electrochemical Impedance Spectroscopy for the Measurement of the Corrosion Rate of Magnesium Alloys: Brief Review and Challenges, Metals (Basel) 10 (2020) 775.
- 32. I. Tiginyanu, P. Topala, V. Ursaki (Eds), Nanostructures and Thin Films for Multifunctional Applications, Springer International Publishing, Cham, 2016, <u>576</u> p.
- B. Morończyk, E. Ura-Bińczyk, S. Kuroda, J. Jaroszewicz, R. M. Molak, Microstructure and corrosion resistance of warm sprayed titanium coatings with polymer sealing for corrosion protection of AZ91E magnesium alloy, Surf. Coat. Technol. 363 (2019) <u>142–151</u>.
- 34. C. Crimu, G. Bolat, C. Munteanu, D. Mareci, Degradation characteristics of Mg0.8Ca in saline solution with and without albumin protein investigated by electrochemical impedance spectroscopy, Materials and Corrosion 66 (2015) <u>649 655</u>.
- 35. A. E. Coy, F. Viejo, F. J. Garcia-Garcia, Z. Liu, P. Skeldon, G. E. Thompson, Effect of excimer laser surface melting on the microstructure and corrosion performance of the die cast AZ91D magnesium alloy, Corros. Sci. 52 (2010) <u>387 397</u>.
- 36. J.-W. Chang, X.-W. Guo, P.-H. Fu, L.-M. Peng, W.-J. Ding, Effect of heat treatment on corrosion and electrochemical behaviour of Mg-3Nd-0.2Zn-0.4Zr (wt.%) alloy, Electrochim. Acta. 52 (2007) <u>3160 3167</u>.
- M. Sun, A. Yerokhin, M. Ya. Bychkova, D. V. Shtansky, E. A. Levashov, A. Matthews, Self-healing plasma electrolytic oxidation coatings doped with benzotriazole loaded halloysite nanotubes on AM50 magnesium alloy, Corros. Sci. 111 (2016) <u>753 769</u>.