

Effects of Silver Nitrate Addition on the Antibacterial and Corrosion Resistance of Plasma Electrolytic Oxidation Coatings on AZ31 Magnesium Alloy

Experimental setup and coating preparation

AZ31 magnesium alloy was used as the substrate. The specimens were sequentially ground with SiC papers (80~1500 grit), ultrasonically cleaned in ethanol and deionized water, and dried prior to coating. The electrolyte contained $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (12 g/L), $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (6 g/L), K_2TiF_6 (1 g/L), and NaOH (2 g/L), with AgNO_3 additions of 0~0.4 g/L and 25 mL/L ethanol as a dispersant. Magnetic stirring was applied for 60 min to ensure uniform dispersion.

Plasma electrolytic oxidation was performed in a bipolar pulsed mode (1000 Hz, 25% duty cycle) with a positive voltage of 400 V and a negative voltage of 100 V. The coatings were labeled A0~A4 according to the AgNO_3 concentration.

Phase composition of the PEO coatings

Figure 1 XRD patterns of PEO coatings on AZ31 magnesium alloy with different AgNO_3 additions. The coatings are mainly composed of MgO and Mg_2SiO_4 phases formed through plasma electrolytic oxidation, while $\text{Mg}_3(\text{PO}_4)_2$ is not clearly detected due to its amorphous or low-crystallinity nature. No distinct Ag-related phases are observed, which is attributed to the low Ag content (<3 wt.%) and its nanoscale or amorphous distribution below the XRD detection limit. With increasing AgNO_3 addition, the intensity of MgO peaks increases, indicating enhanced oxidation reactions during the PEO process.

X-ray photoelectron spectroscopy (XPS) was employed to verify the presence and chemical states of Ag species in the PEO coatings with AgNO_3 addition. As shown in Figure 2, the survey spectra indicate that the coatings are mainly composed of O, C, and Mg signals, which is consistent with the EDS results, while weak Ag 3d signals are detected after AgNO_3 incorporation. To further clarify the role and chemical states of Ag in the coatings, high-

resolution Ag 3d spectra were analyzed, as presented in Figure 3. The Ag 3d_{5/2} and Ag 3d_{3/2} peaks can be deconvoluted into AgO , Ag_2O , and Ag_2CO_3 components, with Ag_2O being the dominant species, indicating that Ag(I) oxides are thermodynamically more stable during the PEO process.

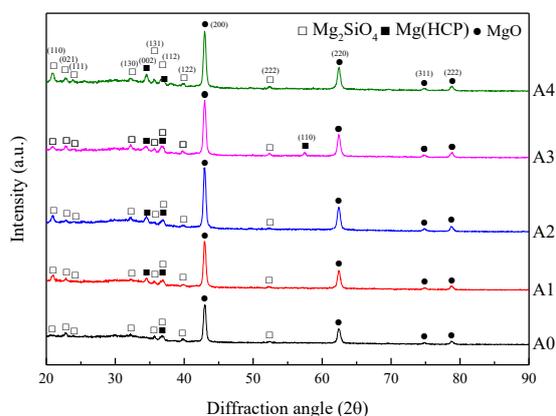


Figure 1 XRD patterns of PEO coatings with different AgNO_3 additions.

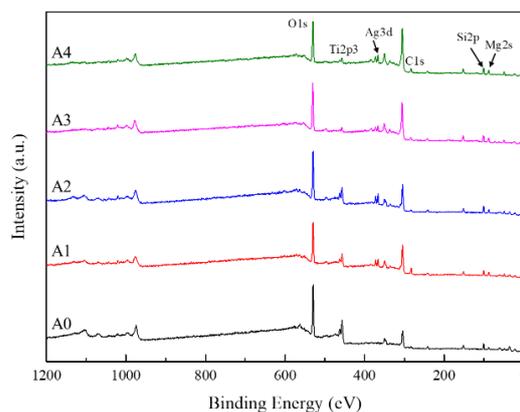


Figure 2 XPS survey spectra of PEO coatings with different AgNO_3 additions.

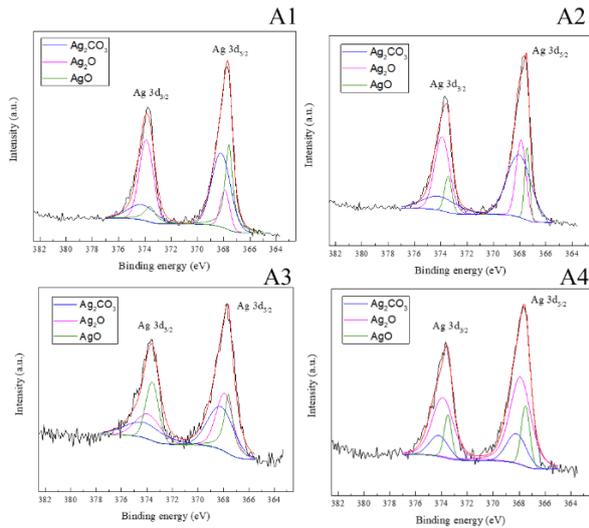


Figure 3 Deconvoluted Ag 3d XPS spectra of PEO coatings with different AgNO₃ additions.

Coating morphology and mechanical properties

Figure 4 shows EPMA–WDS elemental maps of PEO-coated surfaces prepared with different AgNO₃ additions. The coatings are mainly composed of Mg and O, with additional Si, P, and Ag signals derived from the electrolyte, confirming the incorporation of Ag into the PEO coatings.

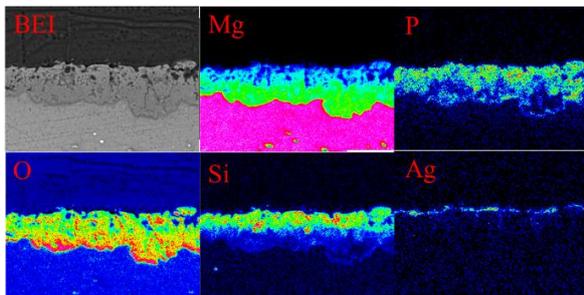


Figure 4 EPMA–WDS elemental maps of the A4 PEO-coated surface.

The adhesion strength of the coatings was evaluated by scratch testing, using the critical load L_{c3} corresponding to coating failure as the criterion (Figure 5). The A2 coating exhibited the highest lateral adhesion strength of **35.87 N**, whereas a decreasing trend was observed for A3 and A4. This reduction is attributed to the increase in pore size, which adversely affects the coating adhesion.

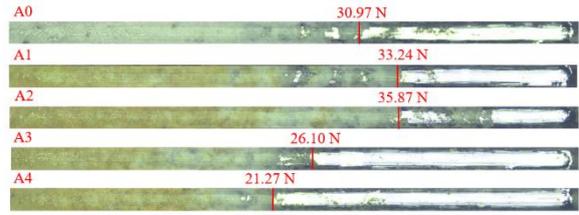


Figure 5 L_{c3} values obtained from scratch tests of PEO coatings with different AgNO₃ additions.

Biocorrosion and antibacterial performance of the coatings

Potentiodynamic polarization results in SBF (Figure 6) indicate that PEO-treated samples exhibit markedly enhanced corrosion resistance compared with bare AZ31, with I_{corr} and R_p improved by over three orders of magnitude.

AgNO₃-containing PEO coatings show a marked reduction in CFU and achieve 100% antibacterial efficiency within 45 min.

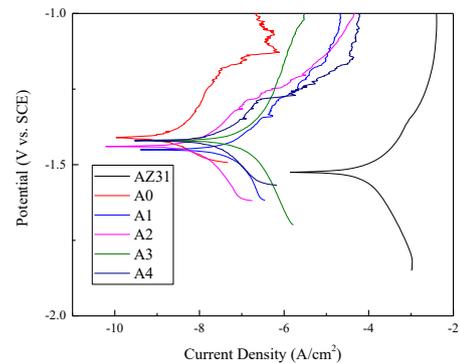


Figure 6 Potentiodynamic polarization curves of PEO coatings with different AgNO₃ additions in SBF

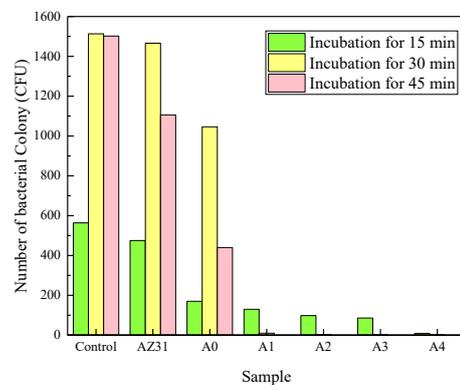


Figure 7 *E. coli* colony counts on PEO coatings with different AgNO₃ additions (15–45 min)