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PMMA-Siloxane-Silica Coating to Enhance Corrosion Resistance of AZ31

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INTRODUCTION & AIM

Magnesium alloy AZ31 (with aluminium and zinc as the main alloying elements) is a biocompatible material; however, its application for implants is limited due to its low corrosion resistance. According to the literature, protective coatings can mitigate or control degradation, but many suffer from limited durability and poor adhesion.[1] PMMA-siloxane-silica coatings present a promising solution by enhancing both adhesion and corrosion resistance.[2]

This study focuses on the characterisation of coatings deposited on AZ31. It aims to improve corrosion resistance relative to a simulated environment such as Ringer's solution, which simulates extracellular body fluid, and to achieve strong and durable coating adhesion.

MATERIALS & METHODS

AZ31 magnesium alloy foil 2 mm thick distributed by Goodfellow, UK, was cut into specimens with an area of 2 × 2 cm. First, the surface was ground using silicon carbide paper up to 4000 grit and then polished sequentially with 3 µm and 1 µm diamond pastes, using ethanol as a lubricant.

A hybrid PMMA-siloxane-silica coating was synthesised from two separately prepared sols: Sol 1: tetraethyl orthosilicate (TEOS), and Sol 2: methyl methacrylate (MMA) + 3-methacryloxypropyl trimethoxy silane (MAPTMS), as schematically presented in Figure 1.

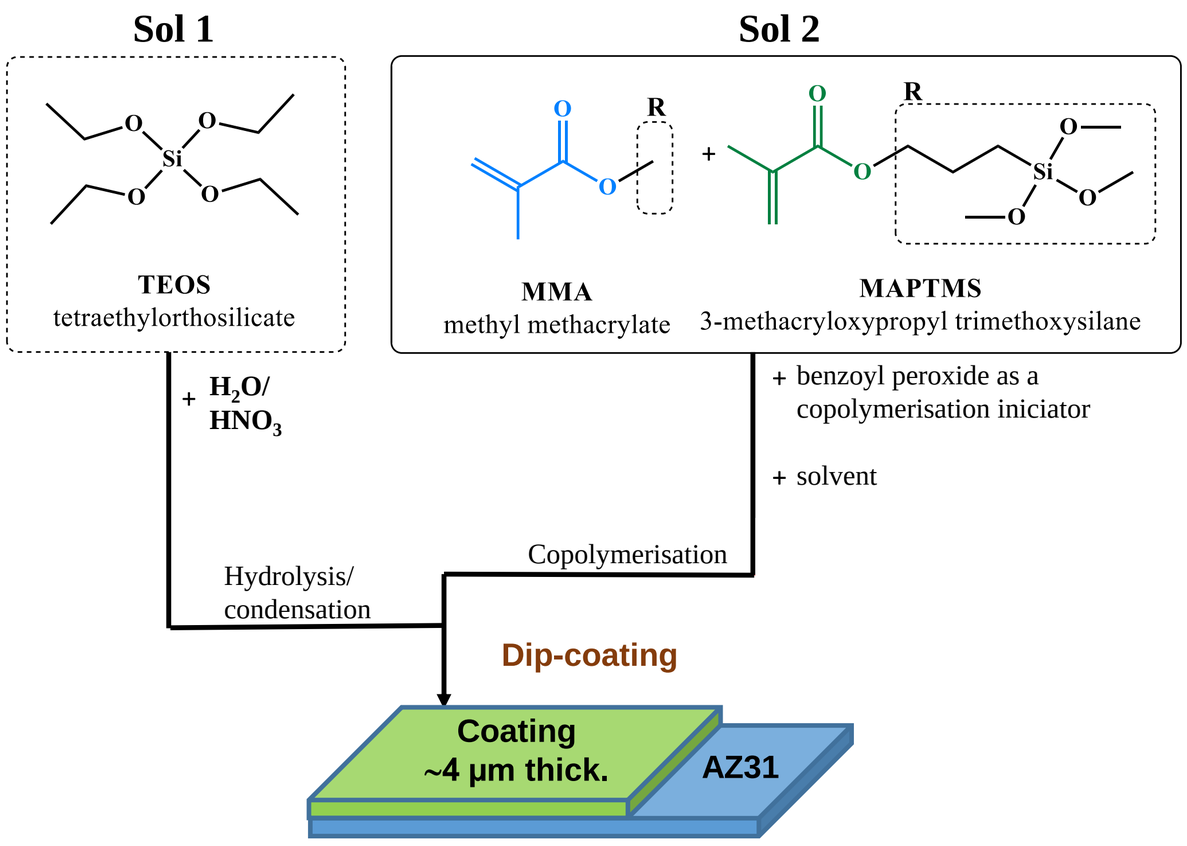

Figure 1. Synthesis and deposition of PMMA-siloxane-silica coating on AZ31 surface.

The coating was applied to AZ31 via a dip-coating process at a withdrawal rate of 14 mm/min. After deposition, it was thermally cured at 180 °C.

Surface morphology and elemental composition were characterised using scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) (Helios NanoLab™ 650). Coating adhesion was assessed utilising a revetest scratch test (CSM Instruments). Corrosion resistance was evaluated in Ringer's solution (composed of 8.6 g/L NaCl, 0.3 g/L KCl, and 0.33 g/L $CaCl_2 \times 2H_2O$) using electrochemical impedance spectroscopy (EIS) and hydrogen (H_2) evolution measurements.

ACKNOWLEDGMENT

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[2] P. Rodič, B. Kapun, I. Milošev, Durable Polyacrylic/Siloxane-Silica Coating for the Protection of Cast AlSi7Mg0.3 Alloy against Corrosion in Chloride Solution, Polymers 15 (2023) 3993. https://doi.org/10.3390/polym15193993.

RESULTS & DISCUSSION

Figure 2 shows the morphological and mechanical characterisation of the AZ31 alloy coated with the PMMA-siloxane-silica coating.

SEM/EDS analysis (Figure 2a) confirmed that the coating uniformly covered the magnesium surface and contained a high concentration of silicon (37 wt. %) and oxygen (63 wt. %) (carbon was intentionally excluded from the EDS analysis).

Figure 2b presents an optical image of the entire scratch path obtained during the adhesion test, indicating that the coating maintained strong adhesion up to a critical load of 11.7 N. SEM image in Figure 2c presents the evidence of early-stage deformation, including microcracking at the point of coating failure.

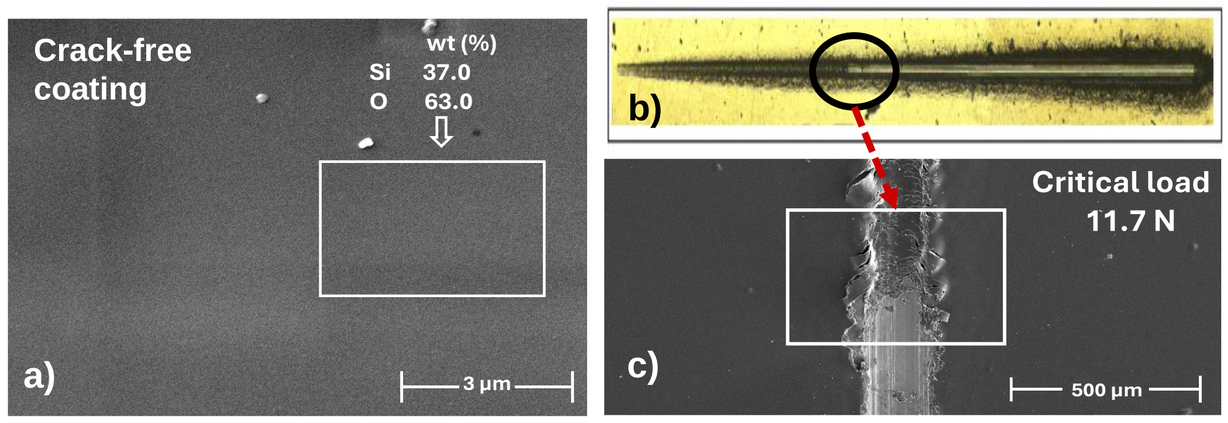

Figure 2. a) SEM image of the AZ31 alloy coated with the PMMA-siloxan-silica coating. The marked square indicates the region where EDS analysis was conducted. b) Optical image of the entire scratch path and c) SEM image of early deformation (microcracking) and critical failure.

Figure 3a shows the EIS Bode plots for uncoated and coated AZ31 alloy samples with the PMMA-siloxane-silica coating.

The coated sample exhibited a substantial increase in impedance across the entire frequency range, indicating the formation of an effective barrier that significantly enhances the corrosion protection of the AZ31. At low frequencies, the impedance increased by more than 6 orders of magnitude.

Figure 3b presents the hydrogen evolution behaviour of the same samples vs immersion time. The uncoated AZ31 showed almost a linear increase in H_2 evolution with time (~2 ml/cm^2/day). The coated alloy demonstrated a complete prevention of hydrogen release over 160 hours, confirming the superior corrosion resistance provided by the coating in Ringer's solution.

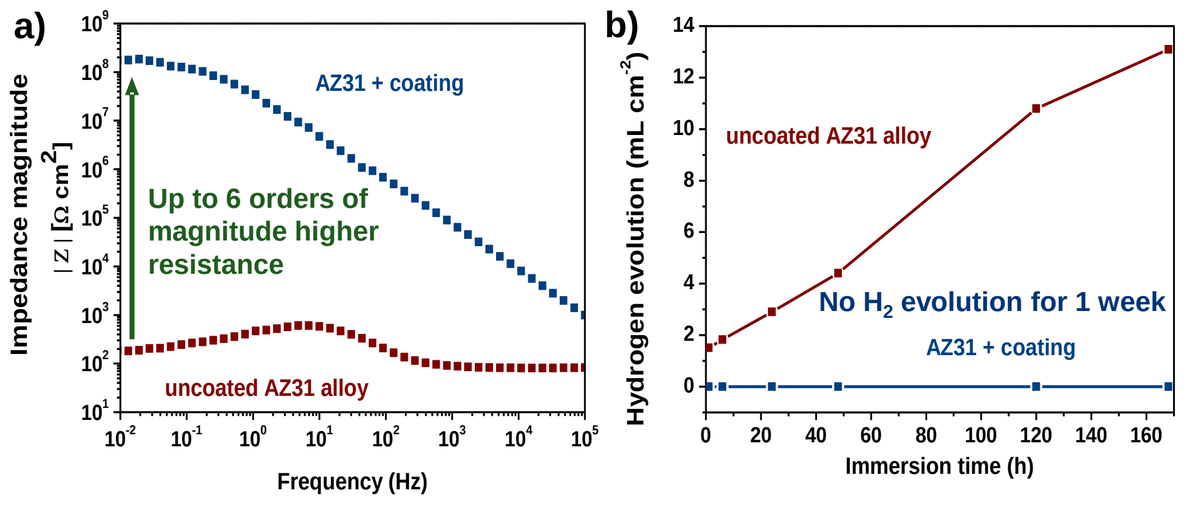

Figure 3. a) EIS spectra shown as Bode plots for uncoated and PMMA-siloxane-silica coated AZ31 alloy after 1 hour of immersion in Ringer's solution. b) Hydrogen evolution profiles of uncoated and coated AZ31 as a function of immersion time.

CONCLUSIONS & FUTURE WORK

In this study, a PMMA-siloxane-silica coating was deposited on a polished AZ31 surface.

The coating:
- ✓ is homogeneous and evenly covers the alloy surface,
- ✓ is strongly adhered to the polished AZ31 surface,
- ✓ significantly improved corrosion protection, up to six orders of magnitude in Ringer's solution, confirmed by EIS measurements and
- ✓ prevents H_2 evolution more than one week of immersion.

Future work will be focused on further long-term stability of the coating and further modifying the PMMA-siloxane-silica coating to tailor coating properties and also control degradation.