TiO₂ Coatings Formed by Atomic Layer Deposition for Enhanced Corrosion Performance of Mg-biomaterials

1. Introduction

Magnesium (Mg) alloys have excellent increased attention in the area of biomaterials due to Mg being considered a biodegradable biomaterial. Mg alloy implants can potentially be designed to degrade in vivo, thus an implant would not remain in the body for longer than is needed to perform its task. Mg and many of its alloys, are considered to be biocompatible and non-toxic in the body; however, due to the high rate at which Mg degrades a negative host response is expected. A novel approach to inhibit corrosion rate using thin film coatings on a Mg alloy (AZ31B) via interfacial layer deposition (ALD) is proposed. TiO₂ is grown in an atomic layer-by-layer fashion during ALD allowing sub-nanometer thickness control of growth, with excellent coating uniformity and step coverage. TiO₂ coatings and their impact on the corrosion resistance of AZ31B were characterized using atomic force microscopy, scanning electron microscopy, electrochemical impedance spectroscopy, and linear polarization measurements.

2. Atomic Layer Deposition on AZ31B

Sample Prep – AZ31B Sample size ~20 x 20 mm. Prior to ALD exposure, all samples surfaces were prepared as follows:

- 460 grit SiC paper
- 800 grit SiC paper
- 1200 grit SiC paper
- 3 µm alumina slurry
- 1 µm alumina slurry
- 0.05 µm alumina slurry
- Photoresist on sample

ALD – Following sample prep, Gemstar™ Benchtop ALD was used to apply TiO₂ to AZ31B substrate.

- TiO₂ Deposition Rate: 6 Å/min
- H₂/Ar: 50/50
- Ti(OEt)₂: 0.05% (v/v) in H₂, 0.5% (v/v) in Ar
- Pluse Repeat: 60 sec
- TiO₂ Thickness: 25nm, 50nm, 100nm

3. Potentiostat

Potentiostat – A linear polarizing system with solution can be modeled as a circuit. Each component in a potentiostatic cell can be modeled with circuit elements. A current of collecting and analyzing data with the Potentiostat which applies either AC or DC current to the electrochemical cell.

4. Electrochemical Cell

Working Electrode – The samples potential is controlled and where the current is measured, in our case a Platinum counter electrode is a sample of the corroding metal.

Reference Electrode – Electrode whose potential is constant, serves as a reference standard against which the potentials of other electrodes can be measured. Standard Calomel Electrode (SCE) is based on the reaction between elemental mercury and aqueous solution of potassium chloride in water.

Counter Electrode – The reaction of the counter electrode is to provide the location of the second electron transfer reaction. A platinum mesh counter electrode was used the electrochemical cell.

5. Electrochemical Impedance Spectroscopy and Anodic Polarization

Electrochemical Impedance Spectroscopy (EIS)

EIS measures the impedance of an electrochemical system using AC current over a range of frequencies. A Nyquist plot is a typical current magnitude data collected during EIS testing. The Tafel equation is used to derive the model for the Nyquist plot.

With equivalent circuit, the EC lab software calculates values for polarization resistance (R_p) and solution resistance (R_s).

Anodic Polarization (AP)

A change in the working electrode’s potential is caused by current (IC) flowing across an electrode-to-electrolyte interface. A Tafel plot on which potential is plotted vs. applied current, is used to approximate Tafel constants. From Tafel constants, R_p is calculated, potential (E) and corrosion current density (i_c) can be determined by the following model.

Using EC lab software with the Tafel model, a linear regression is used to plot tangent lines to anodic and cathodic Tafel regions. The slope of these tangent lines are the Tafel constants.

At the intersection of these tangent lines, values for E_p and i_c can be obtained.

6. Analysis of Data

EIS Data – EIS testing was conducted with the following parameters:

- Frequency range: 0.01 Hz – 1 MHz
- 5 cycles applied
- 5 points sampled from 10 Hz to 1 MHz
- Amplitude of 0.01 V

Data from EIS testing was fitted and polarization resistance (R_p) was calculated for each sample. From the following model it can be shown that:

\[
E_p = \frac{1}{2} \left( \frac{E^{\text{corr}}}{R_s} \right) + \frac{1}{2} \left( \frac{E^{\text{corr}}}{R_p} \right)^{1/2}
\]

AP Data – AP testing was conducted with the following parameters:

- Energy range: 0.01 V – 2.5 V
- Sweep rate: 10 mV/s
- Scan range: 0.045 to 0.2 V
- Solution composition (SCE)
- Solution resistance (R_s)
- Data recorded every 0.1 seconds

AP testing gives another method to calculate i_c by extrapolating Tafel constants E_p.

7. Future Work

Further research will be conducted with different probe molecules during the ALD process and analysis of any corroducants that may be left on the sample. Modification of electrochemical impedance spectroscopy testing, monitoring hydrogen evolution, using different solutions (synthetic physiological buffer), as well as conducting electrochemical testing at elevated temperatures.

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Microscopy of Tested Samples

Optical Microscopy of coating surfaces.

AFM provides accurate analysis of coating thickness although this technique is limited to a small area of the sample.

9. Conclusion

The ENF testing was conducted on the following samples:

- No Coating
- 25nm TiO₂
- 50nm TiO₂
- 100nm TiO₂
- 40nm TiO₂
- 80nm TiO₂

Data suggests original Tafel behavior for samples with coatings applied (linearly of zero order) giving consistent values for E_p and thereafter.

Graphs of ORR and ORR for samples without TiO₂ and TiO₂ coatings.