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

1. Introduction

Magnesium (Mg) alloys have experienced increased interest in the area of biomaterials due to Mg being considered a resorbable biomaterial. Mg alloy implants can potentially be designed to degrade in the body, thus an implant would not remain in the body for longer than is needed to function, and 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 atomic 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 process all samples surface were prepped as follows:
- 400 grit SiC paper
- 800 grit SiC paper
- 1200 grit SiC paper
- 1 µm Alumina Slurry
- 0.05 µm Alumina Slurry
- Photostrip on paper

ALD — Following sample prep, Gantler™ Bonfiglioli ALD was used to apply TiO₂ to AZ31B substrate.
- Reactor Pressure: 0.15 Torr
- TiO₂: Ar Purge (50 sccm)
- Al₂O₃: Argon (1 sccm)
- Repeating of above process.
- Exposed to 400°C in-situ.

Atomic Force Microscopy (AFM) —
- AFM was used to confirm coating thickness on samples.
- A probe with tip radius of ~1.4 micrometers is used to scan the surface of the samples.
- Tip radius information was a known quantity to the tip that can be detected by the beam and photodetector.

Information about the sample surface topography is gained as the tip rastered across the sample.

3. Potentiostat

A three electrode system with solution can be modeled as a circuit. Each component in a electrochemical cell can be modeled with an electrical element. The process of collecting and analyzing data with the Potentiostat which applies either AC or DC current to the electrochemical cell.

4. Electrochemical Cell

Working Electrode — A linear sweep voltammetry is conducted and where the current is measured. In this case, the working electrode is a sample of the corroding metal.
Reference Electrode —
Electrode potential is constant, such as the Ag/AgCl electrode which the potentials of other electrodes can be measured with. Standard Calomel Electrode (SCE) is a standard electrode.
Counter Electrode —

device to provide the location of the second electron transfer reaction. A platinum mesh counter electrode was used in the electrochemical cell.

5. Electrochemical Impedance Spectroscopy and Anodic Polarization

Electrochemical Impedance Spectroscopy (EIS) —
EIS is used to investigate the impedance of a coating on a complex system using AC current over a range of frequencies. A Nyquist plot is a typical representation of data collected during EIS testing. The “Tafel” plot is used to describe the model for the Nyquist plot.

Anodic Polarization (AP) —
A change in the working electrode potential is caused by current (IC) flowing across an electrode-to-electrolyte structure. A Tafel plot in which potential is plotted vs applied current, is used to determine Tafel constants. From Tafel constants, corrosion potential Vcorr and corrosion current density Icorr can be calculated by the following model.

Using IC-lab software with the Tafel model, a linear regression is used to find the tangent lines to anodic and cathodic Tafel regions. The slope of the tangent lines will be the Tafel constants.

At the intersection of these tangent lines, values for the anodic and cathodic Tafel constants can be obtained.

6. Analysis of Data

From comparison plot (D), it can be seen that with the application of a thin film TiO₂ coating, AZ31B's signals remain by several orders of magnitude. Thus showing the corrosion resistance.

7. Future Work

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

8. Acknowledgments

A special thanks to B. Luda and the Boise State Center for Materials Characterization. This project is supported by Boise State University’s School of Materials Science and Engineering and the National Science Foundation Research Experience for Undergraduates in Materials and Sustainability (grant number DMR-1856780).