Biocompatible coatings for corrosion control of magnesium alloys used as bio resorsorable implants

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• Introduction
• Composite Coating
• Electrochemical results
• In-vitro cell culture tests
• Conclusions
Introduction

Mg alloys are used in a wide array of technical applications:

<table>
<thead>
<tr>
<th>Automotive &amp; Aeronautics</th>
<th>Electronic devices</th>
<th>Energy storage</th>
<th>Biomedical</th>
</tr>
</thead>
<tbody>
<tr>
<td>• New epoxy-siloxane modified coating (International Patent) compatible with hydroxide and anodised layers. Outstanding corrosion resistance</td>
<td>• New epoxy-siloxane modified coating modified with conductive fillers Outstanding Corrosion resistance and conductivity</td>
<td>• Porous oxide/hydroxide layers for enhanced catalytic activity and charge storage</td>
<td>• Biocompatible composite coatings (functional silanes, polyether imide, Polycaprolactone, TiO$_2$ rich sol-gel coatings)</td>
</tr>
</tbody>
</table>

Bruscotti et al. CS 2013

Industry contract Protected

Ongoing

Zomorodian et al. SCT 2012
Acta Biom. 2013
### Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Natural bone</th>
<th>Stainless steel</th>
<th>Co–Cr alloy</th>
<th>Ti alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.8 - 2.1</td>
<td>7.9 - 8.1</td>
<td>8.3 - 9.2</td>
<td>4.4 - 4.5</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>3 - 20</td>
<td>189 - 205</td>
<td>230</td>
<td>110 - 112</td>
</tr>
<tr>
<td>Compressive yield strength (Mpa)</td>
<td>130 - 180</td>
<td>170 - 310</td>
<td>450 - 1000</td>
<td>758 - 1117</td>
</tr>
<tr>
<td>Fracture toughness (MPa m¹/²)</td>
<td>3 - 6</td>
<td>50 - 200</td>
<td>---</td>
<td>55 - 115</td>
</tr>
</tbody>
</table>
## Mg alloys

### Advantages
- Density close to that of the bone
- Bio-resorsable
- No need for second surgery (temporary implant)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Natural bone</th>
<th>Mg alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.8–2.1</td>
<td>1.74–2.0</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>3–20</td>
<td>41–45</td>
</tr>
<tr>
<td>Compressive yield strength (MPa)</td>
<td>130–180</td>
<td>65–100</td>
</tr>
<tr>
<td>Fracture toughness (MPa m$^{1/2}$)</td>
<td>3–6</td>
<td>15–40</td>
</tr>
</tbody>
</table>

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Drawbacks:

Unprotected Mg alloys
- High corrosion activity
- Release of H$_2$
- Risk of excess of Mg precipitates

Solution:
- To slow down the corrosion activity to biocompatible levels
- Surface treatments
- New thin functional coatings
### Composite PEI (polyether imide) coating

#### PEI coating composition

<table>
<thead>
<tr>
<th>PEI (wt%)</th>
<th>DETA (wt%)</th>
<th>Hydroxyapatite (HA) wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>15%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15%</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>15%</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>15%</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>15%</td>
<td>0.3</td>
<td>5</td>
</tr>
</tbody>
</table>

PEI coating applied on HF etched AZ31 by dip coating. Electrochemical experiments in Hank solution.
SEM results – PEI (ref.) coating

Coating surface

cross section before immersion in Hank's solution

Thickness < 5 µm
Increased HA contents lead to large agglomerates and larger defects in the coating.
EIS Results

Ref. Coating

Addition of a crosslinker
EIS Results

PEI - 0.3%DETA - 2%HA

EIS Results

PEI - 0.3%DETA - 5%HA
EIS Results

Evolution of the low frequency impedance

![Graph showing the evolution of low frequency impedance over time for different samples. The graph plots the impedance modulus (|Z|) in units of Ω cm² against time (in days). Different samples are represented by distinct line styles and markers, indicating variations in composition like 5% HA, 0.3% DETA, 2% HA, 0.3% DETA, 2% HA, 0.1% DETA, PEI, and PEI 0.3% DETA.]
EIS Results

Graph a: Graph showing the relationship between \( R_{pt} \) and \( \Omega \cdot \text{cm}^2 \) over time (d) for different samples.

Graph b: Graph showing the relationship between \( Y_{pt} \) and \( \Omega \cdot \text{cm}^2 \cdot \text{s}^n \) over time (d) for different samples.
EIS Results
SVET Results – PEI ref. coating

1h

5h

20h

µA/cm²
SVET Results – PEI + 5% HA coating
In vitro cell culture tests

MG63 Osteoblastic cells after 1 day

(a) PEI
(b) PEI+2%HA
(c) PEI+DETA
(d) PEI+DETA+2%HA
(e) PEI+DETA+5%HA

Higher magnification

Control
In vitro cell culture tests

MG63 Osteoblastic cells after 4 days

SEM images of coating c applied over glass coverslips and seeded with MG63 osteoblastic cells, at day 4. Bar: 200 µm (a, c) and 50 µm (b).
In vitro cell culture tests

MG63 osteoblastic cells cultured over the coating

CLSM (a, b) and SEM (c) images of coated AZ31 seeded with MG63 osteoblastic cells, at day 1 (a, b) and day 4(c).
Bar: 80 µm (a), 20 µm (b) and 50 µm (c).
Conclusions

• The corrosion resistance of AZ31 magnesium alloy was significantly improved by designing a novel PEI+HA composite coating.
• PEI alone resulted in a delay in the corrosion activity for more than 8 weeks.
• DETA (up to 0.3%) and 2% of HA prolonged the coating resistance to more than 12 weeks.
• High contents of HA (5%) create particle agglomeration, resulting in a reduction of the protective performance of the coating. However, local corrosion activity is delayed.
• The coatings showed good osteoblastic cytocompatibility, allowing cell adhesion and proliferation.
• The best cellular response was achieved for coatings modified with HA nanoparticles. Indeed corrosion resistance seems compatible with a bioresorbable implant lifetime.
Acknowledgments:

mnt-era.net

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