THE EFFECT OF ALUMINUM ON THE BIODEGRADATION BEHAVIOR OF MAGNESIUM-BASED INDUSTRIAL CASTING ALLOYS IN SALINE

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Abstract

In the recent years, magnesium and its alloys are widely used in different engineering fields for their low density and high specific strength. Biomedical aspects of magnesium alloys, especially in orthopedic applications, have been investigated owing to their biodegradability and good bio-compatibility for more than a decade. The mechanism of degradation of magnesium implants is based on corrosion in biological environment. However, magnesium alloys suffer from low corrosion resistance, especially in the aqueous solutions containing chloride compounds like human blood plasma. In this study, chemical processes and bio-corrosion behavior of AZ31 and AZ91D alloys were investigated in normal saline (NS) medium to determine the effects of aluminum content of magnesium alloys. The results have shown that the corrosion rate could be decreased with the increase in aluminum content.

Keywords: magnesium, corrosion, biodegradation, aluminum, saline.

1. INTRODUCTION

In biomaterial science, biodegradable metals are breaking the current paradigm to develop only corrosion resistant metals. Especially, metals which consist of trace elements existing in the human body are promising candidates for this approach. The aim of coating biodegradable implants is to support tissue regeneration, concurrent implant replacement through the surrounding tissue and healing in a specific application by material degradation [1]. Biodegradable metals have an advantage over available biodegradable materials such as ceramics, polymers or bioactive glasses in load bearing applications that require a higher tensile strength and a Young's modulus that is closer to bone [1-3]. Magnesium alloys are promising to be used as a new sort of biomedical implants, including the vascular stent, and tissue-engineering scaffold [4-9].

Magnesium and its alloys degrade in aqueous environments via corrosion which produces hydrogen gas (H2) and magnesium hydroxide (MgOH2). So, in aqueous solutions magnesium corrosion is relatively insensitive to various oxygen concentrations in aqueous solutions which occur around implants in different anatomical locations. The overall corrosion reaction of magnesium in aqueous environments was given below:

\[ \text{Mg(s)} + 2 \text{H}_2\text{O(aq)} \leftrightarrow \text{MgOH}_2(\text{s}) + \text{H}_2(\text{g}) \]

The corrosion morphology of magnesium and its alloys depends on the alloy chemistry and the environmental conditions [10-12].

Dissolved ions from metal implants are always an anxiety to induce hypersensitivity, inflammation and allergy. Magnesium alloys AZ31, AZ91 and some rare earth alloys have been shown to be non-allergenic in a patch test in accordance with the ISO standard [13].
The ability of magnesium based materials to degrade has led to a multitude of medical applications. With years of research, current studies are now focused on the interaction of biomaterials with biological molecules, cells or tissues and the cellular mechanisms as to how the materials are biologically influenced by the dissolution of corrosion byproducts from the bulk of the material [14-16].

Advanced studies are also investigating how polymer coatings with polyaprolactone (PCL) and polylactic acid (PLA) polymer coatings influence the corrosion behavior and drug eluting kinetics for biodegradable stent applications. Extensive studies on magnesium stents, including both animal studies and studies on human subjects, as well as exploration by topographic imaging modalities are well underway. Orthopedically implanted magnesium materials have been shown to achieve enhanced bone response and excellent interfacial strength. Magnesium materials have also been used for different types of fixation devices for orthopedic surgery, such as screws, plates, and fasteners. Recent studies have also shown that the implantation of a magnesium device shows minimal changes to blood composition within a 6 month study post-implantation without causing damage to excretory organs like the liver or the kidneys [14].

2. EXPERIMENTAL

When evaluating corrosion characterization using organic/inorganic media, weight by loss methodology is the safest technique as there is no applied electrical voltage to accelerate the corrosion process; however, a significant amount of experimental time is required to evaluate and characterize corrosion reactions and rates. Alternative methods include accelerated corrosion methods using a potentiostat that primarily serves to maintain a constant potential difference between the working electrode and the reference electrode [14].

In this study weight loss method was used to determine the biodegradation behavior of AZ31 and AZ91D specimens in normal saline solution (%0.9 NaCl in ultra-pure water). Chemical compositions of test specimens were given in Table 1 and Table 2 respectively.

<table>
<thead>
<tr>
<th>Table 1 Nominal and real chemical compositions of AZ91D.</th>
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<tbody>
<tr>
<td><strong>AZ91D</strong></td>
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<tr>
<td>Nominal, wt.%</td>
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<td>Measured, wt.%</td>
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<table>
<thead>
<tr>
<th>Table 2 Nominal and real chemical compositions of AZ31.</th>
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<tr>
<td><strong>AZ31</strong></td>
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<td>Nominal, wt.%</td>
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</tbody>
</table>

AZ31 and AZ91D specimens were machined and grinded and then cleaned with ethanol in an ultrasonic cleaner before weighting. Test pieces were exhibited in Fig. 1a and Fig. 1b.
The weight loss was measured after each experiment and the corrosion rate \( r \) was calculated in mg.cm\(^{-2}\).day\(^{-1}\) according to equation 1.

\[
r = \left( \frac{w - w_i}{A \times t} \right) \times 1000
\]

(1)

Where:

- \( r \): corrosion rate (mg.cm\(^{-2}\).day\(^{-1}\))
- \( w_i \): initial weight before immersion (g)
- \( w \): weight of specimen after immersion (g)
- \( A \): surface area of specimen (cm\(^2\))
- \( t \): duration of immersion (day)

### 3. RESULTS

Specimens were removed from saline at 10h, 20h and 30h of immersion times, cleaned with ethanol to remove remaining saline from surface, dried at room temperature and weighted. Weight loss during immersion was calculated for each specimen and the results were given in Table 3.

![Fig. 1](image)

**Table 3** Weight loss results due to immersion in normal saline

<table>
<thead>
<tr>
<th></th>
<th>Initial Weight</th>
<th>After 10h</th>
<th>After 20h</th>
<th>After 30h</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31</td>
<td>0.0794</td>
<td>0.0793</td>
<td>0.0792</td>
<td>0.0790</td>
</tr>
<tr>
<td>AZ91D</td>
<td>0.0728</td>
<td>0.0724</td>
<td>0.0721</td>
<td>0.0719</td>
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</tbody>
</table>
4. CONCLUSIONS

AZ series magnesium alloys are used for their properties in industrial applications such as casting. Currently, aluminum containing magnesium alloys are investigated by several research groups in biomedical applications and a lot of data from various in-vitro and in-vivo experiments are available today. Some researchers argue that the aluminum containing magnesium alloys are not safe to use in humans. In this point using rare earth elements as alloying element seems to be obviously one successful way to obtain usable implant materials.

Most rare earth elements show a beneficial effect on magnesium corrosion in-vivo [14].
But rare earth elements are used as additives in alloys with various compositions. Overall impact of several rare earth elements in magnesium alloy production should be thoroughly investigated.

Test results have revealed some interesting degradation behavior of magnesium alloys with different aluminum content. AZ91D alloy with approx. 9% aluminum degraded rapidly (almost six times faster) in the first 10h of immersion tests. But after 20h of immersion corrosion rates became similar and at the end of the tests (at 30h) the two compositions have almost reached the same corrosion rates. Authors think that rapid corrosion at the beginning of the tests has created an aluminum-rich protective layer on the AZ91D specimens which slows down the corrosion reactions. Furthermore, it can be argued that the formation of aluminum-rich layers decreases the amount of free Al$^{3+}$ ions in human tissues. Further analysis of the protective layer will reveal the chemical composition of corrosion products.

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LITERATURE


