IN VITRO CORROSION BEHAVIOR OF NEW MAGNESIUM ALLOYS FOR BONE REGENERATION

C. D. YFANTIS[1], D. K. YFANTIS[1], J. ANASTASSOPOULOU[1], T. THEOPHANIDES[1], M. STAIGER[2]

1 Faculty of Chemical Engineering, Dept. III: Materials Science and Engineering
National Technical University of Athens (NTUA), Zografou Campus 157 73, Athens
Greece
2 Department of Mechanical Engineering, University of Canterbury, Christchurch
New Zealand

Abstract: - Magnesium alloys are used in a variety of structural applications. Currently, there is an increasing amount of evidence suggesting that magnesium based alloys could have several biomedical applications. There is adequate evidence supporting the viability of magnesium as biodegradable scaffold for bone tissue regeneration. It is crucial that its corrosion rate has to be controlled by alloying. New Mg alloys have been *in vitro* tested by electrochemical and other methods. The corrosion rates of Mg12Li and Mg1Ca are quite encouraging because are compatible with the time needed for bone tissue regeneration.

Key-Words: - Magnesium alloys, corrosion, bone, tissue engineering

1 Introduction

Magnesium and magnesium alloys are used in a wide variety of structural applications including automotive, industrial, materials-handling, commercial and aerospace equipment due to their combination of lightweight, high mechanical strength and fracture toughness. From the point of view of biological performance, magnesium is essential to human metabolism and is naturally found in bone tissue [1]. Moreover, due to functional roles and presence in bone tissue, magnesium may actually be osteoinductive.

Currently, there is an increasing amount of evidence suggesting that magnesium based alloys could have several biomedical applications. In the field of interventional Cardiology [2], the concept of applying bioabsorbable coronary stents made of Mg alloys seems to be quite attractive.

In the field of orthopedic and maxillofacial surgery, Mg alloys could be a viable alternative to ceramics and polymers for the fabrication of biodegradable GBR (guided bone regeneration) devices, like plugs, rods or screws. From prior clinical reports in the beginning of the last century, we know that magnesium alloys did not perform well due to inappropriately high corrosion rates.[3,4] The screws and plates made of these magnesium alloys corroded too quickly and as a consequence, subcutaneous gas cavities appeared in treated patients. [3,4] Their poor corrosion resistance is an obvious disadvantage if they are to be used as permanent metallic biomaterials. At the same time, the fact that Mg alloys are inherently susceptible to corrosion attack makes them suitable candidates for the development of biodegradable devices with diverse biomedical applications.

2 Problem Formulation

The scaffold or three-dimensional (3-D) construct provides the necessary support for cells to proliferate and maintain their differentiated function, and its architecture defines the ultimate shape of the new bone [5] The selection of the most appropriate material to produce a scaffold to be used in tissue engineering applications is a very important step towards the construction of a tissue engineered product, since its properties will determine to a great extent, the properties of the scaffold.

There is adequate evidence supporting the viability of magnesium as a biodegradable, biocompatible and possibly biologically active scaffold. The unfortunate complication is that pure magnesium can corrode too quickly [6] in the physiological pH (7.4-7.6) and high chloride environment of the physiological system, loosing mechanical integrity before the tissue has sufficiently healed and producing hydrogen gas in the corrosion process at a rate that is too fast to be dealt with by the host tissue. It is a requirement that the

corrosion/degradation rate of the 3-D construct has to match cell/tissue growth in vitro and/or in vivo. Thus, the corrosion/degradation rate has to be controlled in such a way that the bioresorbable Mg scaffold maintains mechanical integrity for at least 6 months while the bone tissue heals, eventually being replaced by natural bone tissue. Consequently, more research is necessary to develop Mg alloys for this application.

3 Problem Solution

Alloying is an essential step to improve corrosion resistance of magnesium. The alloying elements are known to determine the corrosion characteristics of magnesium alloys. Alloying elements such as rare earth elements, calcium, zinc is suggested to alter the oxidation rate of magnesium alloys. Furthermore, the addition of lithium is known to alkalize the corrosion layer and therefore stabilize the formed magnesium hydroxides within the corrosion layer. Our team has concentrated its efforts in developing new magnesium alloys for bone applications.We studied their *in vitro* corrosion resistance by electrochemical tests, immersion test and XRD analysis and reached to some conclusions concerning their performance.

3.1 Materials and Methods

For in vitro corrosion testing five alloys were used, different magnesium alloys designated as AZ31, Mg-pure, Mg-12Li, Mg-Ca were used as test specimens. AZ31 is one of the most widely used magnesium casting alloys. The magnesium alloys Mg-12Li, Mg-1Zn and Mg-1Ca are not commercially available.

Test alloy	Element (wt%)					
	Mg	Al	Zn	Ca	Li	<0.001
AZ31	96.22	2.83	0.93	-	-	-
Mg-pure	99.98	0.005	0.004	-	-	-
Mg-Ca	99	-	-	1	-	-
Mg-Zn	99	-	1			
Mg-12Li	88	-	-	-	12	-

Table 1. Nominal composition of test alloys (wt%)

These alloys were therefore prepared by melting high-purity metals Mg, Li, Zn and Ca in a commonly used induction melting furnace under a dynamic flow of high purity argon gas. Firstly, pure Mg was melted in a stainless steel crucible. The other alloying elements were then added to the Mg melt by a successive addition method until the three nominal compositions mentioned in Table 1 were obtained. The melts were finally poured at 7500C into a steel mould to produce 120 mm x 60 mm x 10 mm ingots and allowed to air cool down to room temperature. For corrosion tests rectangular samples were machined. Before corrosion process, the samples were mechanically polished with SiC paper, 80, 120, 240, 300 and 600 grit paper and then with diamond paste 9 μm, 6 μm, 3 μm and 1 μm, in order to obtain surfaces with the same morphology and the same roughness. Subsequently, samples were cleaned for 5 min in an ultrasonic bath in 95% pure acetone and dried.

3.2 Test methods

Immersion test

An immersion test was carried out at room temperature. All test specimens were stored in sealed containers. After air drying, the specimens were weighed before corrosion testing. Three specimens of each alloy were immersed for 22 days in an aqueous solution of 0.1 M NaCl at a neutral pH. All test specimens were stored in sealed containers. The corrosion rate was calculated as follows

$$\mathrm{CR} = \frac{W}{Atp}$$

where CR is the corrosion rate, W is the weight loss, A is the original surface area exposed to the corrosive media, t is the exposure time, ρ is the standard density. The means and standard deviations of the corrosion rates were obtained from 3 runs for each alloy.

Electrochemical Corrosion Tests

Three specimens of each alloy were immersed in an aqueous solution 0.1 M NaCl (pH = 0). All test specimens were stored in sealed containers. Open circuit potential (OCP) of each alloy was monitored as a function of time (total monitoring time: 500 h). Another set of three specimens of each alloy was subject to linear polarization (LP). Triplicate corrosion tests for each alloy were performed using appropriate electrochemical setup (EG&G Princeton Applied Research Potentiostat/Galvanostat Model 362, Princeton, NJ, USA). The reference electrode was a standard calomel electrode (SCE), and the

auxiliary electrode was platinum. Each specimen was polarized from -20 mV to 20 mV, at a scanning rate of 0.3 mV / s.The polarization tests were repeated at least 3 times for each specimen until all repeated runs exhibited similar polarization curves. The corrosion rate was estimated with the following equation: $CR_{LP} = 0.82 \times I_{CORR} \times EW$

where CR_{LP} ($\mu g/d.cm^2$) stands for corrosion rate, EW is an equivalent weight of the corroding species in grams (g) and I_{CORR} is a corrosion curent density ($\mu A/cm^2$). The corrosion current density (I_{CORR}) was obtained graphically by finding the intersecting point of the cathodic Tafel slope and the anodic Tafel slope. The means and standard deviations of the corrosion rates were obtained from 3 runs per each alloy.

X-ray diffraction (XRD) analysis

After 5 days of immersion, X-ray diffraction spectra of the exposed specimens were obtained at room temperature using a Siemens D 5000 X-ray diffractometer with Cu Ka radiation. The diffraction angle (2θ) ranged from approximately 20^0- 120^0 with a 2θ scanning rate of $0,2^0$ per sec.

3.3 Results – Discussion

Immersion test

A mean corrosion rate (CR_{WL}) of 142.8 mg/day.cm^2 for Mg-pure, 0.4 mg/day.cm^2 for Mg12Li, 0.8 mg/day.cm^2 for Mg1Ca, 0.2 mg/day.cm^2 for Mg1Zn and 12,5 mg/day.cm^2 for AZ31, were estimated by weight loss respectively.

Electrochemical Corrosion Tests

Stabilized corrosion potentials (Ecorr) referred to Ag/AgCl were observed: - 1550 mV for Mg-pure after 120 h of immersion, -1495 mV for AZ31 after 240 h of immersion, -1485, -1475, -1460 mV for Mg1Ca, Mg12Li, Mg1Zn, respectively after 538 h of immersion. A mean corrosion rate (CRLP) of 1214.5 mg/day.cm2 for Mg-pure, 2 mg/day.cm2 for Mg12Li, 2.7 mg/day.cm2 for Mg1Ca, 1mg/day.cm2 for Mg1Zn and 102,8 mg/day.cm2 for AZ31, were estimated by linear polarization, respectively.

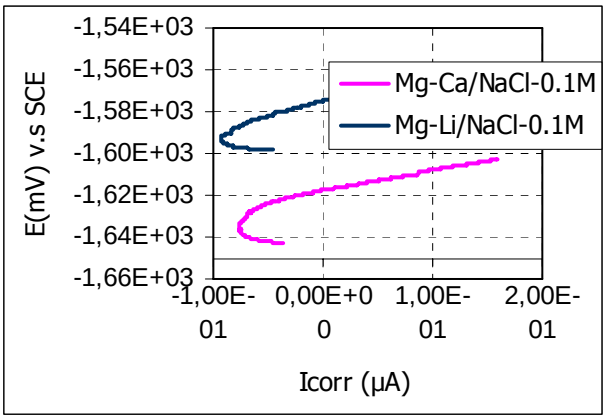

Fig 1. Representative LP curves for Mg1Ca and Mg12Li.
Mg-pure, AZ31, Mg1Zn produced similar curves.

X-ray diffraction (XRD) analysis

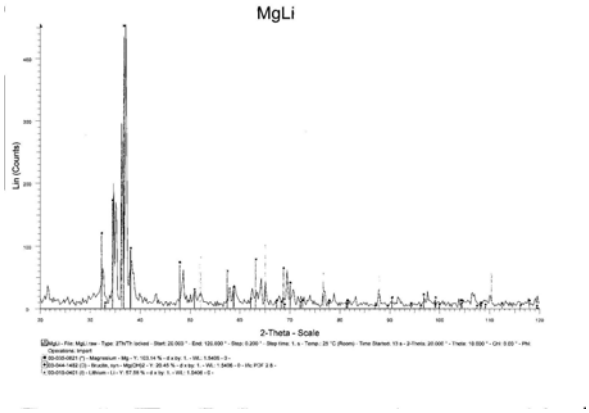

Fig 2. Representative XRD pattern for Mg12Li.
Mg-pure, AZ31, Mg1Zn, Mg1Ca produced similar patterns.
Mg and Mg(OH)2 (brucite) was clearly detected in the XRD results. This result is in agreement with the corrosion mechanism of magnesium which includes the formation of a partially protective Mg(OH)2 surface layer. Peaks of lithium were detected in the XRD analysis of the corroded Mg12Li alloy. The highest peak of lithium correspond to 36.300^0. It is interesting to observe that ZnO and CaCO3 (aragonite) were not detected from the XRD patterns of Mg1Zn and Mg1Ca, respectively. This may be probably due to the relatively poor adhesion of these corrosion products to the alloy surface.
The OCP is measured under static conditions after a prolonged period of time, when the specimen potential has reached steady-state relative to the reference electrode, as the electrical double layer adjacent to the specimen surface in the given electrolyte has stabilized. The OCP is a quasi-thermodynamic measure, and consequently obtaining corrosion tendencies from the

determination of corrosion potentials is necessary but not sufficient to ascertain whether a given magnesium alloy will suffer corrosion under the given set of the bone tissue milieu.

The results of the immersion test and electrochemical corrosion test prove that the in vitro corrosion properties of magnesium alloys are dependent on their chemical composition. Hence, the addition of Ca, Li and Zn significantly reduce both the corrosion rate obtained by weight loss and that obtained by linear polarization. The corrosion rates estimated by linear polarization are 3-5 times higher than the respective corrosion rates estimated by immersion test.

As mentioned earlier, an appropriate corrosion/degradation rate has to be achieved in order to apply magnesium alloy as a scaffold for bone regeneration. Thus, the corrosion/degradation rate has to be controlled in such a way that the bioresorbable Mg scaffold maintains mechanical integrity for at least 6 months while the bone tissue heals, eventually being replaced by natural bone tissue.

The minimum bone volume needed for the placement of a standard diameter (3,75 mm) dental implant is approximately 0,282cm^3. [7]Therefore, a minimum volume of 0,282cm^3 of bioabsorbable magnesium alloy should be implanted *in situ*. This volume corresponds to 490.11 mg Mg-pure, 508.16 mg AZ31, 483.20 mg Mg-Ca, 31.28 mg Mg-Zn and 350.46 mg Mg-Li.

The *in vitro* corrosion/degradation time based on CR_{WL} is approx. 3 days, 40 days, 19 months, 71 months and 28 months for Mg-pure, AZ31, Mg1Ca, Mg1Zn and Mg12Li, respectively. The *in vitro* corrosion/degradation time based on CR_{LP} is approx. 10 hours, 5 days, 6 months, 17 months and 6 months for Mg-pure, AZ31, Mg1Ca, Mg1Zn and Mg12Li, respectively.The *in vitro* corrosion/degradation time of Mg1Ca and Mg12Li, especially those based on CR_{LP}, are quite favourable. However, care should be taken in extrapolating the clinical behavior of magnesium alloys from *in vitro* tests because the corrosive environment *in vivo* is of different nature than *in vitro.* Therefore, the corrosion behaviour and biological performance of Mg1Ca and Mg12Li alloys in an animal model has to be investigated.

3.4 Conclusion

Within the limitations of this study, the following conclusions were drawn:

- The in vitro corrosion properties of magnesium alloys are dependent on their chemical composition. Hence, the addition of Ca, Li and Zn significantly reduce both the corrosion rate obtained by weight loss and that obtained by linear polarization.
- The corrosion rates estimated by linear polarization are 3-5 times higher than the respective corrosion rates estimated by immersion test.
- The *in vitro* corrosion/degradation time of Mg1Ca and Mg12Li, especially those based on CR_{LP}, are quite favourable and promising.

References:

[1] Theophanides T., Anastassopoulou J. Magnesium: current status and new developments, theoretical, biological and medical aspects. The Netherlands: Kluwer Academic Publishers, 1997 p.1-5

[2] Heublein B., Rohde R., Kaese V., Niemeyer M., Hartung W., Haverich A. "Biocorrosion of magnesium alloys: a new principle in cardiovascular implant technology? Heart 2003;89:651-656

[3] Witte F., Kaese V., Haferkamp, Switzer E. "In vivo corrosion of four magnesium alloys and the associated bone response" Biomaterials 2005;26:3557-3563

[4] Staiger M., Pietak A.M., Huadmai J., Dias G. "Magnesium and its alloys as orthopedic biomaterials: A review." Biomaterials 2005;26:1-7

[5] Salgado A.J., Coutinho O.P., Reis R.L. "Bone tissue engineering: state of the art and future trends." Macromol. Biosci. 2004;4:743-765

[6] Yfantis A, Paloumpa I, Schmeisser, D. Yfantis D. Surface and Coatings Technology, 151-152, (2002), p.400-404

[7] Yfantis C, Yfantis D, Anastassopoulou J., Theophanides T, Staiger M "Magnesium alloys and bone regeneration: Preliminary evaluation of their *in vitro* corrosion behavior." 1st Congress of the Hellenic Biomaterial Society, Athens 2006 (in greek)