

## COATING SYSTEMS FOR MAGNESIUM-BASED BIOMATERIALS - STATE OF THE ART

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### Abstract

Magnesium and its alloys have the potential to be used for biodegradable orthopedic implants. However, the corrosion rate in physiological conditions is too high for most applications. For this reason, surface modification to slow the corrosion rate is of great interest. Such modifications must remain biologically compatible as well as protective in corrosive environments. What follows is a brief review of recent research in inorganic coatings and surface modifications to create coatings for magnesium-based biomaterials.

### Introduction

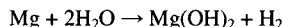
Magnesium (Mg) and magnesium alloys have the potential to be useful in creating better orthopedic implants [1]. Magnesium alloys can offer the strength and toughness required for load bearing implants where ceramics and polymers fall short. Other metals currently used for implants, such as stainless steels and titanium alloys, have elastic moduli that are much higher than natural bone, leading to unwanted stress shielding. The elastic modulus of magnesium and many magnesium alloys are much closer to bone [2]. Also, a second surgery is required to remove current metallic implants. Magnesium shows promise as the material for biodegradable implants that degrade in the body without requiring removal. It is found in abundance in the body, and the degradation by-products have been shown to be non toxic [3]. In addition, magnesium may actually serve to stimulate new bone growth [1]. With all of these favorable properties magnesium looks very promising for this application. However, there are some challenges to be overcome. Magnesium and its alloys in general have low corrosion resistance, which is important for metal implants given the very aggressive environment in the physiological system [4]. Toxic degradation products and loss of mechanical properties are the major concerns. The low corrosion resistance of magnesium leads to loss of mechanical properties too quickly. It also leads to rapid hydrogen gas evolution within the body. For these reasons, pure unaltered magnesium metal is not an ideal implant material. Furthermore, it is desirable to optimize the biological response to these implants to maximize recovery. The biological response to the surface of the implant is important for compatibility of the implant with surrounding tissue [5]. Since corrosion and biocompatibility are ultimately surface phenomena, surface modification through treatments or coating systems are an obvious route to optimizing implant properties.

A good coating or surface treatment will be one that will control corrosion of the implant, maintaining mechanical integrity for the duration the implant is required. To be effective on many types of implants, it will be ideal for the coating to cover complex surfaces completely to ensure corrosion does not occur too quickly. Also, the coating must have good adhesion to the metal substrate, and have acceptable wear resistance to protect the implant during the insertion operation and throughout the load cycles of the implant life. It is also of great concern that the implant be non-toxic and fully degradable itself after the duration required. Additionally,

good cellular response and attachment is desirable allow the implant to become fully integrated with the biological system. A suitable coating that meets these criteria will allow biodegradable magnesium implants to become a feasible alternative to current metallic orthopedic implants. What follows is a discussion of a few approaches taken to overcome the problems facing magnesium implants.

### The Corrosion of Magnesium

In order to determine how best to control the corrosion of magnesium, it is important to understand the mechanism of corrosion, especially in physiological environments. In general, magnesium metal corrodes in aqueous environments to form magnesium hydroxide and hydrogen gas [6]. The overall corrosion reaction of magnesium is:



Corrosion will in general form a surface coating of Mg(OH)<sub>2</sub> and/or MgO [6]. This forms a passivation layer that will generally slow the corrosion rate. The passive layer protects until the oxide layer is penetrated, exposing unoxidized metal to solution. When this happens, the corrosion rate accelerates locally. However, the corrosion degradation products passivate the surface again, slowing further corrosion [7].

When Magnesium is put into contact with other metals, galvanic corrosion will occur. This can be due to either external metals or internal secondary or impurity phases. Metals that have a low hydrogen overvoltage can cause severe galvanic corrosion. Examples are Ni, Fe, and Cu. Metals with lower hydrogen overvoltage like Al, Zn, Cd, and Sn are not as bad [6].

Physiological environments are typically very aggressive environments for metals. Corrosion tests carried out in simulated body fluids (SBF), which are fluids that contain many of the ions commonly found in the body, give some indication of how a metal will perform in an actual environment. In simulated body fluid, the rapid corrosion of magnesium can mainly be attributed to the presence of chloride ions. The Cl<sup>-</sup> is absorbed into the Mg(OH)<sub>2</sub> surface and MgCl<sub>2</sub> is formed. This compound is quite soluble, and thus increases the rate of corrosion by destroying the passivation layer of magnesium hydroxide [8]. The effect of the Cl<sup>-</sup> can be seen when corrosion is compared to a sample in a similar solution with a minimal amount of Cl<sup>-</sup>. Pitting and surface cracking is the major mechanism of corrosion in SBF due to Cl<sup>-</sup> ions [9, 10].

Alloying the magnesium with appropriate elements to overcome problems of corrosion and biocompatibility has been the focus of much research, and will be important to perfecting magnesium implants [2, 11, 12]. Alloying elements that create passivation layers that are more stable than Mg(OH)<sub>2</sub> can slow down corrosion, but often alloys with multiple phases exhibit microgalvanic corrosion [6].

### Biocompatibility

Increasing the biocompatibility of the implant is also important. For the implant to have the maximum effect and a speedy

recovery time, the manner in which the cells and tissue react to the implant is critical. [13] Toxicity is crucial for the purposes of a biodegradable implant. If the implant is to degrade in vivo, then the inclusion of toxic elements or compounds must be eliminated from the implants. This condition eliminates many of the common techniques used for corrosion resistance of magnesium in other applications. For example, heavy metals and chromate conversion coatings that have been used for magnesium corrosion resistance [14] should not be used. In addition to toxicity, cellular response while the implant is in place is of great importance. The biocompatibility of titanium implants has been investigated fairly extensively. A magnesium implant will also need to exhibit good biocompatibility if it is to be effective.

### **Coatings**

A simple but effective method to reduce corrosion is to coat the metal so as to provide a barrier between the metal and the environment. Corrosion resistant coatings are commonly used for metals in many applications. In this case, we want the coating to keep the corrosive ions in the physiological system (especially  $\text{Cl}^-$ ) away from the magnesium until sufficient time has passed and the bone is healed. Once this has occurred, it is desirable that the coating yield to the environment and degrade along with the magnesium leaving no harmful traces.

#### Anodization

A common practice is to use anodization to form a protective corrosion resistant layer on metals. Anodization uses and electrical current to form a thick, dense passivation layer that is more protective than the natural layer that develops. Magnesium oxide layers can be formed by anodizing Mg which slow short term corrosion rate in SBFs like Hanks solution [15, 16]. Furthermore, qualities of the coating like density can be optimized by controlling the voltage profiles during anodization [17]. The corrosion protection of the oxide layer can be increased by performing the anodization in a silicate solution, creating  $\text{Mg}_2\text{SiO}_4$  on the surface as well as MgO [18]. However, magnesium oxide layers will convert to magnesium hydroxide in aqueous solutions, and magnesium hydroxide is soluble in chloride solutions such as body fluid [19]. Xue, for example, found anodization greatly increased polarization resistance in a NaCl solution, but after 2 hours the resistance decreased by a factor of 2 [18]. Because these films are not stable in biological solutions, anodization alone is unlikely to produce the protective coating required for many bioapplications. Instead, anodization can be used as a pretreatment to another coating system. For example, anodized layers can be used to control the amount and rate of calcium phosphate compounds precipitated on the surface in SBFs [20].

#### Metal coatings

Metal coatings have been used to prevent degradation of magnesium. Pure magnesium coating on a magnesium alloy particularly susceptible to corrosion has been shown to decrease the corrosion. If alloying elements increase the corrosion potential, then a high purity deposition coating of pure magnesium on the surface will slow the corrosion [21]. Coatings of other metals may be achieved as well. Physical vapour deposition coating of aluminum has been successfully applied to magnesium AZ31 alloy [22]. The coating did corrode in a NaCl solution, however, and aluminum is not the best choice for biocompatibility. Still, a metal coating for corrosion resistance is a viable option for protection, provided the coating metal has a low toxicity.

Zirconium [23] and zinc [24] are possible candidates in this respect. The unfortunate downside to metallic coatings on magnesium is galvanic corrosion when any defect in the coating is present. If the coating metal is more noble than the substrate, the substrate will corrode preferentially [9]. A gap in the coating will lead to severe galvanic corrosion of the substrate underneath, and loss of mechanical properties will follow. Since magnesium has a lower corrosion potential than all other engineering metals the applications of metallic coatings is limited.

#### Calcium Phosphates

One of the most biocompatible coating options for orthopedics is calcium phosphate coatings. Coatings of apatite have been researched extensively for use in biomedical applications [25, 26]. Several biologically important types of apatite are hydroxyapatite (HA), octocalcium phosphate (OCP), tricalcium phosphate (TCP), dicalcium phosphate dihydrate (DCPD) and amorphous calcium phosphates, often containing other secondary ion substitutions. The mineral component of bone itself is an apatite, but also contains other ions such as carbonate and phosphate groups. The mineral portion of bone is built up on a collagen matrix. The similarity of some of these apatites to bone minerals, such as stoichiometric HA, gives them good biocompatibility. Calcium phosphate coatings have been used to increase the integration of the implant to the bone [27, 28]. HA coated titanium implants have been found to increase cell proliferation and bone formation [29]. Because calcium phosphate compounds can be fairly insoluble in physiological conditions and are very biocompatible they are a perfect candidate for a protective coating for magnesium implants. To provide adequate corrosion protection, the coating must be complete and adherent to the substrate. The quality of the coating created is dependent on the process and process parameters used for formation.

#### Plasma Spray

The most popular commercial procedure to attach calcium phosphate coatings to a metallic implants is the plasma spray method. This entails using a jet of neutral gas, inserting the material or precursors for the material to be coated into the jet and plasmatizing by some means, for example a DC arc. The plasma spray is deposited onto the substrate where the coating forms. The process makes precise control of the coating thickness possible, as well as the composition by control of the feed powders [30]. Plasma sprayed hydroxyapatite has been used to coat implants to increase biocompatibility of implants [31, 32]. However, the high temperatures required for this process means care must be taken to avoid the presence of unwanted phases, as well as decomposition of the coating and/or substrate [30]. For Mg and its biocompatible alloys, the temperatures reached with plasma spray will be great enough to melt or change the substrate, making this technology difficult to apply to Mg. Plasma spray is also limited by the line of sight to the substrate, making complex shapes and porous structures difficult to coat uniformly. Other techniques to apply calcium phosphate coatings to metallic substrates have been attempted to overcome problems related to plasma spray such as poor integrity and adhesion, low crystallinity, and mechanical failure of the coating [33]. Some of these methods might be more appropriate for magnesium based materials.

#### Chemical Vapor Deposition

Coatings can be created by chemical reactions of gaseous chemicals near a heated substrate. This technique is known as chemical vapor deposition. Coating with this method allows the

production of multilayer and composite coatings as well as complex shapes without line of sight. [34] For example, CVD has been used as an alternative to plasma spray to create a stable, crystalline, bioactive hydroxyapatite coating on 316 L stainless steels [35]. Most CVD processes are fairly high temperature, often requiring the substrate to be stable at temperatures above 600 deg C. However, there are lower temperature processes being explored to limit temperatures to around 180 deg C [14].

#### Pulsed Laser Deposition (PLD)

PLD uses a laser to vaporize a target and allow the vapor to condense on the surface of the substrate. This method allows for greater control of the crystallinity and composition and thickness of the coating [26]. Pulsed laser deposition has been studied on other implant materials, notably titanium [33, 36-38], however their protectiveness in corrosive solutions on magnesium is not widely reported.

#### Ion Beam Assisted Deposition (IBAD)

IBAD can produce coatings with good adhesion and allows precise control of the coating chemistry, including the Ca:P ratio. Yang et al reported using IBAD to coat AZ31 [39]. Calcium phosphate coatings created were heat treated transform into HA. Annealing improved the mechanical properties. Coatings were tested in a 3% NaCl solution for corrosion properties. Coated samples were more protective, although pitting did occur through cracks in the coating.

#### Solution Coatings

Solution chemistry methods for coating metals with calcium phosphates have a number of advantages. Simple and low cost setup, the ability to coat complex and porous materials, and the ability to use low temperatures make solution chemistry synthesis of calcium phosphates attractive for Mg substrates. The oxidation of Mg creates a local pH rise which promotes calcium phosphate deposition in solutions containing calcium and phosphate ions [40]. This can be leveraged to easily create coatings in simple solutions.

However, this method also has its drawbacks, as magnesium is highly reactive in aqueous environments it tends to corrode during the coating process. Furthermore, for calcium phosphate compounds, substitutions by  $Mg^{2+}$  ion in the crystal lattice of compounds like Hydroxyapatite are known to promote defects, limit crystallization [41], and decrease the stability of the created compound [42]. Hiromoto and Yamamoto reported HA coatings created on Mg and alloys in single step solution treatments [43]. Coating solution ionic concentration and pH affect the coating deposited. They reported reduction in corrosion current density of  $10^3$  to  $10^4$  times lower in 3.5% NaCl than uncoated Mg using potentiodynamic polarization (PDP). Hu et al. reported creation of a DCPD coating in solution on AZ91 alloy by titrating  $K_2HPO_4$  into a  $Ca(NO_3)_2$  solution [44]. The DCPD coating was transformed into HA over time in SBF, and the corrosion resistance of the coating increased to 4210 ohms from 331 on uncoated mg. By PDP tests, corrosion current density dropped from 70 to  $2.6 \mu A/cm^2$ . Tomozawa reported solution chemistry techniques to form HA on pure Mg in solution [45]. Findings included increasing temperature to 333K and above increased HA formation and also  $Mg(OH)_2$  formation. However, by increasing Ca concentration HA formation could be increased without affecting  $Mg(OH)_2$  formation, which may be undesirable to have underneath the coating, due to its high solubility. Xu et al. reported in vivo studies using calcium phosphate coatings

prepared by solution methods on Mg Mn Zn alloys [46]. The surface properties of the coated samples were much more friendly to cell growth and overall osteoconductivity than uncoated samples. Because these solution coatings can avoid using any toxic elements, the biocompatibility is good. However the issue remains creating a coating that is dense and adherent enough to remain crack free and fully protective in solution for the required amount of time.

#### Electrodeposition

Calcium phosphate coating formation can be assisted by the application of external potentials and currents. These processes are collectively referred to as electrodeposition. The setup for these methods is inexpensive and relatively simple, and the process can be done at low temperatures. The processing parameters can be easily controlled to optimize the coating created.

#### Electrochemical Assisted Deposition (ECAD)

ECAD uses the reduction of water in an aqueous solution to promote the precipitation of calcium phosphates on the surface of a metallic substrate. Reduction of  $H_2O$  generates  $H_2$  gas and leaves behind  $OH^-$  at the cathode. This leads to a local rise in pH at the surface of the substrate. An increase in pH decreases the solubility of calcium phosphates in solution, leading to precipitation at the surface.

The ECAD process for calcium phosphate can be controlled using a number of methods [26]. A constant potential can be held between the working electrode (the surface to be coated) and the counter electrode, typically made of an inert material such as platinum or graphite. Constant potential between the working and counter electrodes means the potential between the solution and the electrode is not directly controlled. Potential and current are therefore related to aspects of the coatings such as cell geometry, solution composition, counter electrode material, etc.

This method has been used to form coatings of HA on AZ91D and have been shown to reduce corrosion currents by the electrochemical methods PDP and electrochemical impedance spectroscopy (EIS) [47].

Alternately, the coating process can be performed potentiostatically, where the working electrode is held at a constant voltage compared with a reference electrode. The reference electrode is placed near the working substrate in order to maintain a constant potential difference between the solution and the coating. This is useful for keeping the potential at a desired level to cause reduction of  $H_2O$ , without rising to levels that can reduce other actors the solution. In this setup, the current will decrease as the substrate becomes coated and the exposed area of the electrode drops. Lower  $OH^-$  production at the cathode can lead to a pH drop near the working electrode, and therefore a drop in deposition rate. DCPD coatings have been created on Mg alloys using the potentiostatic method, and while coatings do reduce corrosion rates, total coverage from thick, dense coatings that completely protect the substrates remain an issue [48].

To keep the hydroxide ion production constant, constant current, or galvanostatic methods have been used to coat magnesium with this method. The standard three electrode cell is used, but the controls are set to keep current applied between the working and counter electrodes constant.  $H_2O$  is the only molecule undergoing oxidation and reduction in solution, then the rate of  $OH^-$  production near the surface remains constant, keeping the pH profile roughly equal during the process. The voltage can spike during the process, especially after the substrate is partially coated. Song found that galvanostatic method of coating to form a

calcium phosphate coating that was protective in SBFs, dropping the measured corrosion current significantly over a 48 hour test [47]. Wen used the galvanostatic method to coat AZ31 with HA. PDP results show protective effects. Corrosion potential ( $E_{\text{corr}}$ ) was increased and corrosion current density ( $I_{\text{corr}}$ ) decreased. Post treatment in an alkali solution can result in greater stability of the coating, resulting in a lower rate of mass loss over 30 days [49]. Calcium phosphate and chitosan composite coatings have also been reported on Mg alloys by Wu et al. [50]. By performing the deposition in a solution containing a HA suspension as well as chitosan, composite coatings could be formed during the deposition process.

Finally, the voltage profile can be controlled to whatever is allowed by the control systems used to monitor a 3 cell system. Other voltage profiles used in this process include pulsed profiles. Ion diffusion in the coating solution can limit the rate of coating, needing longer than the current can source. Additionally, the reduction of water at the cathode produces hydrogen gas when the voltage is high. The net result of these factors can be loose, porous coatings [51]. Pulse duration can be modified to change properties of the coatings, including crystal size, with longer durations leading to larger crystals [42], others To limit this pulsed current deposition on MgZnCa alloys has been studied, with the results being increased  $E_{\text{corr}}$  by PDP and decreased  $I_{\text{corr}}$  [51].

One downside of ECAD methods is the lack of complete dense adhesive coatings [48], and others. Hydrogen evolution at the surface of the metallic substrate creates gas bubbles that block chemical formation of the ceramic at the interface, resulting in volcano-like interfaces as reported by Kumar et al. [52]. Unfortunately the evolution of hydrogen gas is unavoidable for these type of ECAD coatings in aqueous solutions, and is indeed necessary to raise the pH at the surface and drive the coating process.

For electrodeposition processes that are not based around pH solubility, it is possible to avoid the reduction of water by performing the reactions in no aqueous solutions. Due to the need for an eclectically conductive fluid, ionic liquids present themselves as a alternative plating medium. Bakkar and Neubert have reported successful plating of Mg substrates with metallic Zn to increase corrosion resistance [24]. Ionic liquid composition, applied current density, and substrate alloy composition was found to affect the coating created.

### **Surface Treatments**

Another method for increasing the corrosion resistance of a magnesium alloy is to modify the surface structure of the metal itself. Magnesium alloys undergo microgalvanic corrosion when multiple phases exist in an alloy, one more cathodic than another [9]. This can be detrimental to the corrosion resistance, as it accelerates local corrosion at the anodic phase. Furthermore, there exists differences in energy between the grains and grain boundaries in magnesium and magnesium alloys. Galvanic cells therefore can form between grains and grain boundaries. For pure Mg, grain boundaries are more cathodic than grains, leading to undercutting of grains near the boundaries [19]. Local corrosion can cause a loss of mechanical properties at rates faster than predicted by bulk corrosion rate measurements. For load bearing implant design, controlling and eliminating localized corrosion is desirable.

A method for removing these effects is to modify the surface to homogenize it. If it is possible make the surface completely amorphous, it will eliminate the formation of galvanic cells between grains and boundaries.

### **Bulk Metallic Glasses**

Making the matrix a completely amorphous bulk metallic glass is the obvious approach to completely remove corrosion difference due to crystal structure in the metal. Casting metallic glasses requires specific favorable alloy compositions and extremely high cooling rates to freeze the liquid metal without the formation of crystalline grains [53]. This makes it difficult to create fully amorphous structures of dimensions larger than a few millimeters. Alloy compositions can be optimized to form BMGs. Recently MgZnCa alloys at compositions with good glass forming ability have been of interest for biomedical and other applications [54-58]. As these ternary alloys do not contain toxic elements, enabling them to be used in degradable implants.

Amorphous MgZnCa alloys have been tested in vivo to show reduced hydrogen evolution [58]. Amorphous alloys above 28 at. % Zn showed particularly good passivation properties, due to zinc oxide layer. However, the BMG samples created were sheets only 0.5mm thick, so again, dimensional constraints due to the formation of BMGs may limit the use of fully glassy materials for larger implants. Gu et al. reported similar results for 2mm thick MgZnCa BMG samples, including reduced corrosion rate and increased response in cell culture tests [54].

An alternative to forming bulk metallic glasses for the substrate is to make the surface amorphous on a crystalline material using a surface treatment technique. Ion implantation provides a possible route of creating a modified surface like this. Accelerating ions to high velocities and implanting them into the surface of the substrate can cause a collision cascade that destroys the long range order of crystals in the metal, leaving a glassy surface. Chatterjee has demonstrated such formation in aluminum substrates by ion implantation [59]. Glassy surfaces can also be formed after ion beam mixing a coated surface layer with the substrate [60].

### **Ion Implantation**

Ion implantation offers a method of surface modification to increase corrosion resistance. Advantages of ion implantation include modification of the existing substrate surface, often creating a gradual transition between the modified surface and the bulk of the material. This generally tends to make strong, adherent treatments that do not have the problems of adhesion, thermal stresses, and crackings that separate secondary coating phases tend to have. Plasma immersion ion implantation (PIII or  $PI^3$ ) of Al, Zr, and Ti has been used to create corrosion resistance on AZ91. The mechanism is introducing the elements near the surface increases the density of the corresponding oxide during corrosion, resulting in a more protective passivation layer [61]. However, for biodegradable implants, additional elements may not be desirable if they are linked to toxicity like Al, or do not degrade such as Ti. However, using a thin implanted layer at the surface as opposed to complete alloying can decrease the amount of toxic ions required. Of course, toxic ions should be avoided if possible, limiting the species that may be used. Wan et al. used Zn ions due to their biocompatibility, but found Zn ion implantation in MgCa alloys increased corrosion rate rather than decreasing it [62]. Oxygen ion implantation has also been attempted but with little success against chloride solutions [63]. Nitrogen ion implantation has been used to improve corrosion resistance of magnesium as well. Nakatsugawa et al. reported N ion implantation reducing the corrosion rate of AZ91D to 15% of the untreated metal in 5% NaCl [64]. Similarly, Tian et al. used PIII to improve the corrosion resistance of AZ31B [65]. With ion

implantation, the implant energy and dosage are critical to maximizing the implant performance.

### Conclusion

Effective surface treatment of biodegradable implants will be able to slow corrosion for the period of time necessary to retain the mechanical strength required of the implant. The corrosion rate must be low enough that hydrogen evolution and corrosion products do not cause problems for the surrounding tissue. To do this, the coating must be adherent and consistent on the substrate. The coating system must protect the substrate from corrosion due to chloride ion attack and galvanic corrosion between phases. Defects such as cracks and voids in the coating should be avoided to prevent localized corrosion compromising the mechanical integrity of the device. Furthermore, the coating must be fully biocompatible and biodegradable. Toxic elements should not be incorporated into the coating system. When coatings can be created that fully provide the corrosion protection necessary, biodegradable orthopedic implants will become possible.

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