

# METAL OXIDE COATING ON BIODEGRADABLE MAGNESIUM ALLOYS

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## ABSTRACT

*Magnesium is a biodegradable metal that has potential in orthopaedics. It has several advantages over other metallic materials because it is biocompatible and degradable now being used for biomedical applications, including elimination of stress shielding effects, enhancing degradation properties and enhancing biocompatibility concern in vivo, eliminating the second surgery for implant removal. Bioabsorbable magnesium (Mg) and related alloys have been limited in their usage because of its lower corrosion resistance. Surface alteration and functionality, in addition to basic alloying, is an important technique to deal with Mg and its alloys' reduced corrosion resistance. Magnesium's rapid depreciation however is a double-edged sword because it's critical to match bone renewal to material corrosion. As a result, calcium phosphate coatings have been proposed as a way to slow down corrosion. There are various possible calcium phosphate phases and their coating methods and can give a few distinct properties to various applications. Despite magnesium's lower melting point and greater reactivity, calcium phosphate coatings require precise settings to be effective. Because of their toxicity, non-biodegradability, and much higher cost, the recently used inorganic conversion coatings are less appealing and their application is limited. Conversion coatings are a viable alternative technology that is based on a cost-effective, environmentally friendly, and biodegradable organic component. Surface chelating functional groups in these compounds allow them to link with the magnesium/surface hydroxide layer while also providing anchoring groups for the polymer topcoat. Nanoreservoirs with multilayer inhibitors for active self-healing corrosion resistance thrive in this environment. This study examines the organic conversion coatings for Mg and its alloys in depth.*

## KEYWORDS

*Magnesium, Calcium phosphate coating, Conversion coating, Biodegradable, Biocompatible.*

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## 1. INTRODUCTION

To replace and repair damaged body tissue implants are broadly utilized in biomedical field [1,4]. Depending on type of material use, implants can be differentiated into three classes [5,6]: (i) ceramic, (ii) metal, and (iii) polymer. Metallic implants have excellent mechanical properties and good biocompatibility, due to which they are broadly utilized in dental, cardiovascular and orthopaedics applications [1]. Conventional metallic implant materials incorporate Ti alloy, Co-Cr alloy and SS [7, 131]. However, there is a stress shielding issue because of the substantial difference in modulus of elasticity of metallic implants and human bone, as indicated in table 1, which leads to osteoporosis and bone fusion [1]. Also, metallic implant generates metallic ions due to corrosion or erosion near to implant if these implants have been there for longer period of time, this might prompt issues, like inflammation of tissue [8]. At last, additional medical surgery may require to eliminate implants [6]. Availability of biodegradable materials have prompted new improvements in implant innovation.

**Table 1.** Cortical bone mechanical properties as well as implant materials [1].

Materials	Young's Modulus (GPa)	UTS (MPa)	Yield strength (MPa)	% Elongation
Cortical bone	5-23	35-283	--	1.07-2.10
Stainless steel	193-200	480-620	190	40
Titanium alloys	100-125	550-985	420-780	12-16
Pure iron	195-230	200	150	40
Co-Cr alloys	210	450-960	310-440	10.7-18.5
Pure Mg (As-cast)	41-45	90-190	20.9	7
DL-PLA	70-120	40-200	--	3.10

The primary purpose of biodegradable implants is to encourage tissue development, cure specific injuries, and then vanish in vivo by a breakdown process with little tissue damage [1]. Among orthopaedic application, bone screw and metallic bone plates are ordinarily used to fix crack sites before new bone development [5]. During rehabilitation, it has been discovered that the implant's strength gradually diminishes as the strength of the new bone grows [1,132]. Magnesium-based alloys are currently getting a lot of consideration and are being explored as more recent types of biodegradable material [8,9]. This is due to a number of factors. For starters, magnesium-based alloys have superior mechanical qualities for load-bearing applications than polymers, including high strength and malleability, in addition, they are biodegradable in vivo [9, 10]. Second, magnesium-based alloys have modulus of elasticity that are near to natural bone as compared to ordinary metallic implants, eliminating the stress shielding effect [11]. Magnesium-based alloys offer excellent in-vivo degradability; hence, using magnesium alloy to remove a temporary implant can avoid the need for additional medical operations, so significantly reducing a patient's suffering [7]. Magnesium-based alloys also exhibit good biocompatibility, osteogenesis induction, anti-inflammatory characteristics, and other bio functional qualities [12,13].

Furthermore, it containing specific elements, for example Cu, Ag, Ga, and Sn may likewise have good antibacterial characteristics [14,15]. It indicates that magnesium-based alloys have extraordinary development potential as biodegradable materials.

Researchers and industry interest in magnesium-based alloy as biodegradable materials emphatically grown in the course of the last many years. Magnesium based alloys possess very good biocompatibility, excellent corrosion behaviour, and excellent mechanical properties when proper process parameters and right alloying elements are utilized. Likely uses of magnesium-based alloys are temporary cardiovascular devices and structural alloys for orthopaedic applications. Once these implants have served their limited purpose, the body consumes them, such as scaffolding, mechanical support and attaching to living tissue. Researchers and industry are exceptionally talking about the connection between magnesium-based alloys in-vitro and in-vivo characteristics, that could assist in reducing animal testing and backing simulations to choose alloys. Mechanical characteristics are typically portrayed by hardness test and tensile test. Additionally, information on stress corrosion and fatigue is anticipated to give a complete idea of stability over the course of degradation. Alloys made with magnesium are prone to pitting corrosion. A consistent corrosion morphology needs to be given special consideration since corrosion pits increase the intensity of stress during mechanical strain and contribute to the premature failure of implants [2, 132]. First and primarily, the mechanical and physical characteristics of magnesium-alloys do not yet match that of implant materials, and their rapid disintegration can cause mechanical instabilities before the bone healing process is completed [9,16]. Second, the rate of breakdown of magnesium-based alloys is very quick, particularly in a chloride medium like a human physiological fluid. The degradation product of Mg alloys is probably going to create some issues, for example, tissue inflammation [17]. Finally, corrosion of magnesium-based alloys is not uniform, which could lead to premature implant failure [18]. Various tests have been carried out to date with the goal of breaking through these barriers. Regardless of this advantageous property, magnesium alloys used in biomedical applications must be carefully monitored for their ability to corrode when in contact with ECF containing Cl iron. Due to low electronegativity of magnesium alloy, their corrosion rate is high in in-vivo. From one viewpoint, this implies that according to a thermodynamic perspective, a biomedical implant developed from magnesium alloy probably won't be viewed as a reasonable alternative in the exceptionally corrosive body fluid.

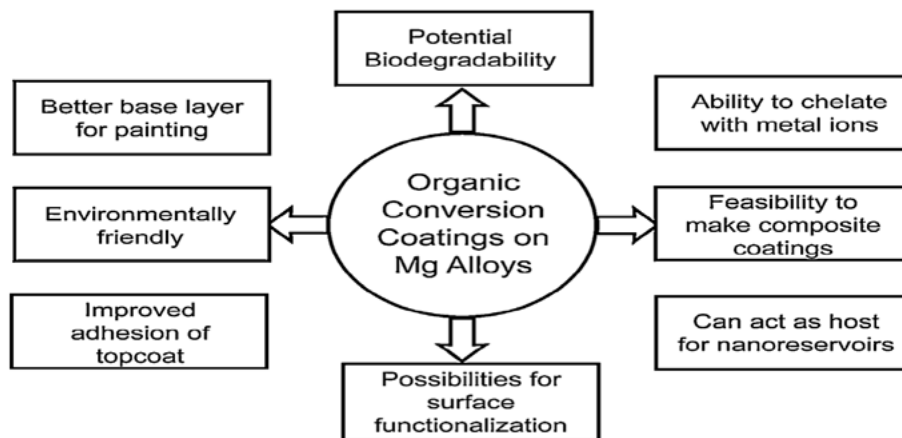
In general, three methods can be used to protect biomedical magnesium against in vivo corrosion: (i) adding defensive coatings to isolate body fluid and implant. (ii) alloying with biocompatible elements to protect surface from corrosion (iii) microstructural surface alteration. During initial phase of implantation, high corrosion resistance, and even the establishment of a homogeneous, controlled, and anticipated corrosion rate, are critical. Surface modifications of magnesium alloy for corrosion control includes micro arc oxidation (MAO), hydrothermal treatments, anodization, electrophoretic deposition (EPD), physical vapor deposition (PVD), electrochemical deposition (ECD), sol-gel deposition, magnetron sputtering, and a few other, less

known process for example, electrospinning, cold gas dynamic showering (CGDS), phosphatization, laser cladding [3,19,20]. However, regardless of numerous multi-pronged methodologies towards improvements of magnesium alloy for biomedical applications, significantly more exploration is needed to overcome their insufficiencies in demanding biomedical field. This argument is supported by the astounding amount of effort, resources, funds, and research capacity put into adapting a chemical like magnesium, which is fundamentally inappropriate for use in medicinal applications. At the end, simply by applying protective coatings along with suitable alloying elements, it became conceivable to use Mg alloy in biomedical applications because of its promising mechanical and natural properties as a cutting-edge biomaterial. Currently, much research and development is focused on the development of magnesium alloy for cutting-edge biomaterials, To address the stress shielding effect, future isoelastic arthroplastic implants could be employed [3, 21–25] if they have lower young's modulus and are acceptable with the nearby cortical bone. Paper is focusing on metal oxide coating on magnesium alloy to improve its performance in biomedical applications.

## 2. CONVERSION COATINGS ON MAGNESIUM AND ITS ALLOYS

Surface coating is formed by electrochemical or chemical treatment in the conversion coating process. Coating transforms a metal's or alloy's surface layer into a thin coating of metallic oxide or any other chemically related substances. The coating creates a corrosion-resistant surface that better adheres to the topcoat. A successful conversion coating should be (i) inert/insoluble (ii) self-healing (iii) resistant to mechanical damages, (iv) impermeable to liquids/gas (v) eco-friendly (vi) cost effective. Chemical conversion coatings are manufactured via non-electrolytic chemical reactions without the use of electricity, whereas electrochemical conversion coatings use an electrolyte and electricity [26]. The primary benefits of chemical conversion coatings are process speed, simplicity, low capital and working expenses, lower energy utilization, low-temperature process, high efficiency and less treatment time [26,27]. It was found that corrosion fatigue properties were improved by conversion coating [28]. A conversion coating, in general, functions by driving interfacial reactions and resultant coating/precipitation formation. A reduction in pH and a rise in  $Mg^{2+}$  concentration at the solution/metal contact initiate the interaction. The chemical has a minor dissolving effect on the hydroxide/oxide layer, which will aid further solution penetration into the layer. Many variables have impacts on the quality of conversion coating, for example, phase or compound structure, types of pre-treatment processes, concentration and composition of bath solution, pH of bath, temperature of bath, time of immersion, degree of stirring, and condition of post treatment [29]. By and large, different functional additives are used to accelerate coating formation and to control bath pH value. By changing experimental condition, thickness of coating can be varied from several hundred nano meter to a micro meter. The thickness of the coating might range from a few hundred nanometers to a few micrometres, depending on the trial circumstances used. It was observed that

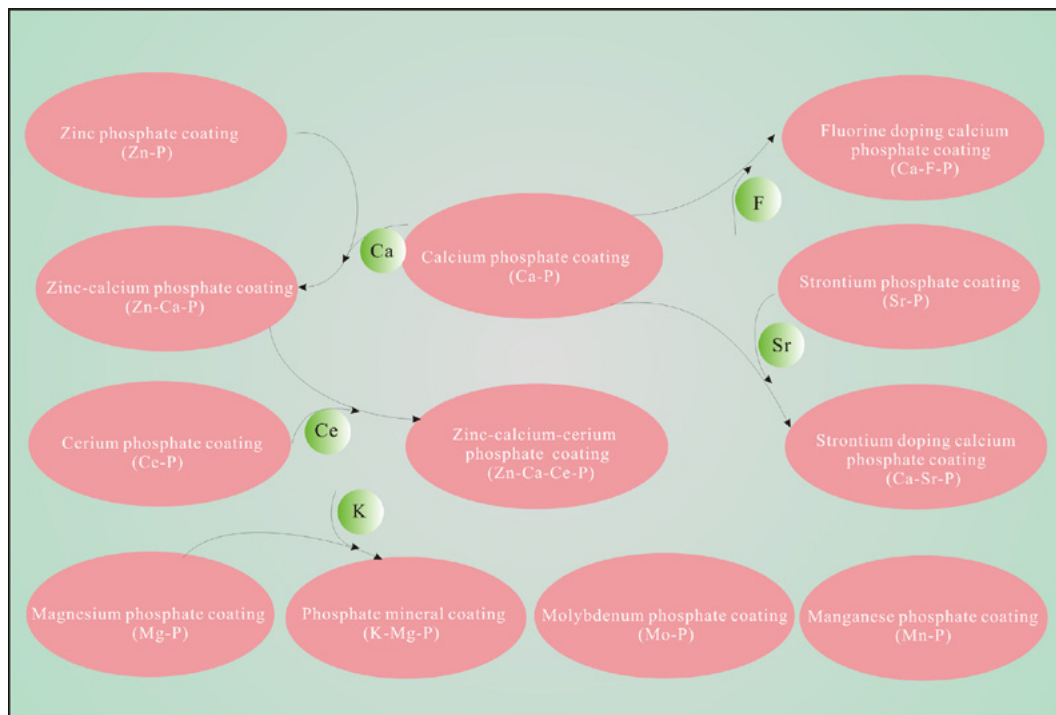
thickness of coating can be varied by addition of nanoparticles to the conversion solutions.



**Figure 1.** Potential advantages of organic conversion coatings [26]

Inorganic coatings, in which the chemical reacting with the surface of metal to generate highly adhesive coatings and corrosion resistance coatings, are among the various chemical conversion coatings explored and used in practise. Figure 1 depicts the most widely used inorganic conversion coatings on magnesium alloy. Chrome manganese, phosphate treatments, chrome-pickle, dichromate and ferric nitride pickle are most normal industrial conversion coatings. For biomedical applications fluoride and calcium phosphate containing conversion coatings are significant [27]. Chemical breakdown of rare earth and phosphate-based conversion coatings occurs at acidic and alkaline pH levels, respectively [30]. Phosphates in water may also promote nutritional replenishment. Molybdate conversion coatings decreased oxidising capacity isn't up to par. Heavy metal contamination is the main source of worry. When reactive magnesium comes into contact with certain inorganic materials, it can become anodic. As a result, research into non-toxic and environmentally acceptable conversion coatings for magnesium and related alloys is crucial. In this case, organic conversion coatings (OCCs) are crucial. Precipitation and chemical dissolution interact to form chemical conversion coatings. Chemical conversion coating generally carried out in bath of phosphate, fluoride, chromate and carbonate [32]. Because of its low cost and convenience of application, conversion coating can be employed in a various biomedical field. Regardless of the fact that chromate-based coatings offer outstanding corrosion resistance to Mg alloys, they have been outlawed because of concerns about the human health and environment. As a result, biomedical applications of phosphate conversion coatings [33, 34], fluoride [35], and MAO coating have gotten a lot of interest. Figure 2 depicts a few phosphate-based conversion coatings, which are typically Zn, Mg, Mn, Ce, Sr, and Ca phosphates. Ce, Sr, K, F, and Ca doped phosphates are rare. Regrettably, several conversion coatings have riverbed-like topologies on surfaces, limiting their robustness. In this case, it's also necessary to change the coating. Due to high biocompatibility, high temperature resistance, insoluble in water and chemical stability of calcium phosphate and zinc phosphate, they have been accounted as a possible option in contrast to chromate coating for biomedical applications [36]. The morphology and structure of those layers

exceptionally relies upon the temperature of process, composition of conversion bath and pH value [37].



**Figure 2.** Mg alloys with phosphate-based conversion coatings [31]

A lot of strategies have been utilized for improving Mg-based biomedical implants and devices. Calcium phosphate (Ca-P) coatings are non-toxic and have excellent osteoconductivity. As a result, numerous researchers are concentrating their efforts on Ca-P coatings in bone replacement, orthopaedics, and other fields. The elements P and Ca combine to develop a HA layer and is the primary component of natural bone. The critical aspect is changing the phase and increasing the concentration of HA in Ca-P coatings, which are fundamentally non-crystalline and contain relatively lesser amount of HA. HA can develop across specified range of Ca/P proportions under sub-alkaline and neutral circumstances, as per calculation of the thermodynamic chemical reaction [34], HA is exclusively produced in a narrow range of Ca/P proportions in sub-alkaline and neutral circumstances.

One of the researchers [38] established a Ca-P coating on magnesium consisting of Mg (H<sub>2</sub> PO<sub>4</sub>)<sub>2</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Ca (H<sub>2</sub> PO<sub>4</sub>)<sub>2</sub>, and Mg 3 (H<sub>2</sub> PO<sub>4</sub>)<sub>2</sub> to reduce corrosion of AZ31B in SBF. The morphology of the surface, EDS finding, and cross-sectional area of the Ca-P coating on a surface with a thickness of roughly 20 m reveal a regular petal-like crystal made up of small long blocks. In comparison to its substrate, the Ca-P coating has a corrosion current density that is two times lower. As the immersion period in SBF grows, the hemolytic rate of AZ31B increases without and with coating at first, then reduces to a safe level. The load bearing capacity of the Ca-P coating for AZ31B decreases noticeably while submerged in SBF, and after 120 days of submersion, the loading capacity was reduced to 85%. Even yet, it's impossible to say which elements are significant in the progression of corrosion resistance.



To seal the structural design, one of the researchers [39] applied a Ca-P coating to MAO oxidised Mg by immersing it in a Ca-P bath. The upper layer is made up of dicalcium phosphate dihydrate (DCPD) and HA, according to the findings. At various temperatures, flake-like and round-shaped morphologies appeared on the surface of the substrate, demonstrating that temperature has an impact on coating structure. The volume of hydrogen produced in MAO and soaked MAO after 300 hours of immersion in SBF was around 17.75 and 1.11 mL/cm<sup>2</sup>, respectively. After submerging the coated specimen in SBF, bone-like apatite formed. The thickness was about 42 m after 4 weeks of soaking in SBF Ca-P coatings. It has been observed that corrosion performance of coating enhanced. Instead of the Zn-P coating's dry-riverbed-like structure, one of the researchers [36] coated Mg alloy AZ31 with a Ca-doped zinc phosphate (Zn-Ca-P) coating that had a flower-like structure. The structure of Zn-Ca-P coatings were found to be tightly connected to the microstructure, including particle size and secondary phases, as well as the chemical composition of the substrate [40]. Form, orientation, and size of AlMn particles were discovered to take a significant effect on Zn-Ca-P coatings characteristics. Corrosion of the -Mg network near an upright AlMnSi particle almost likely results in an obstructed and deeper hole. Horizontal particles, on the other hand, may form a flat, open, and shallow trench. Because of this, small pits rather than deeper holes are where phosphate nuclei can easily accumulate. The outer layer of AM30 therefore develops a coarse grain coating. Under magnetic field, one of the researchers [41] developed Mn-P conversion coating on AZ91D Mg alloy. The findings demonstrated that, during the production of the phosphate conversion layer, superpositioning magnetic fields might speed up the synthesis of minute hydrogen gas bubbles as well as their speedy desorption from the surface. Following that, it was discovered that Mg<sup>2+</sup> cations are evenly distributed throughout the alloy, regardless of its microstructure. Immersion in a solution treatment bath can provide a smooth and homogeneous phosphate conversion coating when the magnetic field is delivered perpendicular to the substrate rather than parallel to the substrate. It's worth mentioning that Ce-P, Zn-Ca-Ce-P, and Mn-P coatings have yet to be shown biocompatible. The biocompatibility of Sr-p ZnCaP and CaP coatings, on the other hand, is excellent [33,42].

## 2.1. FLUORIDE CONVERSION COATING

The use of fluoride conversion coatings as biomaterials appears to be a viable option [43, 44]. Fluoride conversion coating is created by a chemical reaction with Mg alloys in a hydrofluoric acid (HF) solution bath. Fluorine in bones can help with calcium and phosphorus digestion and improve bone strength. The major component of fluoride conversion coatings, magnesium fluoride (MgF<sub>2</sub>), is water insoluble and binds to the Mg-alloys surface satisfactorily. Because of their great biocompatibility, outstanding corrosion resistance, and cell responsiveness, magnesium alloys with MgF<sub>2</sub> coatings have been explored in the biomedical applications [45]. It has been observed that HF concentration has great impact on protective efficiency and performance of coating. One of the studies [46] suggested that a MgF<sub>2</sub> coating on the LAE442 alloy could decrease the corrosion rate in-vivo. Despite the fact that the

substrate was slightly protected, the MgF<sub>2</sub> layer deteriorated completely after a month of implantation. Despite this, fluoride levels in the adjacent bone did not rise over the first six weeks after implantation. In MgF<sub>2</sub> coated Mg implants, there was restricted pitting erosion but no subcutaneous gas pits. Regardless of the fact that fluoride conversion coating could offer safety during the initial phases of implantation, due to the relatively thin coating, in terms of prolonged use, it must be very effective. The detrimental effects of high fluoride on bone are also present at the same time, fluoride release during Mg implants breakdown and its harmfulness for implanted tissue has been unclear yet. One of the researchers [47] used a novel method to make fluoride conversion coatings by immersing an AZ61 sample in Na [BF<sub>4</sub>] liquid salt for varied durations of time at 430°C and 450°C, then heating the sample to eliminate any remaining salts and external layer. The two-layer structure of the 2- $\mu$ m coating made of a larger interior MgF<sub>2</sub> layer and a minor exterior NaMgF<sub>3</sub> layer [47]. As the treatment period increases from 2 h at 450 °C, the corrosion current density,  $i_{corr}$ , of the coatings decreases, implying higher corrosion resistance in SBF. The untreated substrate had an  $i_{corr}$  that was around four times lower than the material that had been treated for 12 hours at 450°C. Even though a few deformities are seen on the surface of coating, these imperfections don't arrive at the substrate. The coatings are a superior alternative for fluoride treatments of magnesium alloys because they are finer than standard conversion coatings. The biocompatibility of the coating still has to be established. To increase the corrosion resistance of the conversion coating, researchers [45] employed a two-step immersion approach to develop a uniform and thinner MgF<sub>2</sub>/polydopamine (PDA) coating on Mg-Zn-Y-Nd alloy. Dopamine and tris-hydrochloric acid (tris-HCl) bath treatments followed by Mg alloy immersion in HF bath. The coating is made up of two layers, each of which is roughly 100 nm thick: a PDA outside layer and a MgF<sub>2</sub> inner layer.

## 2.2. IONIC CONVERSION COATING

Ionic fluids (ILs) are molten organic salts formed entirely of ions at normal temperature [48]. Because of the combination of a charge delocalized anion and a big cation, the salts are defined by weak interaction. ILs have been classified as ecologically friendly or biocompatible compounds in the past. Mg alloys can stay stable over longer periods time without corroding due to the absence of free H<sup>+</sup> or even other metal cations in ILs, providing ideal environment for active metal film development control [49]. One of the research groups created an IL film on the basis of interaction of ILs with highly pure Mg [50], which led to the use of ILs in the creation of Mg alloy composite films. Various ILs conversion coatings have been proposed in the past [51-54]. Because of their biocompatibility, phosphonate derivative-containing coatings have been investigated as a new chemical for Mg alloy corrosion protection. To decrease deterioration in the human body, it been recommended that the AZ31 Mg alloy be surface treated in compatible phosphate-based ionic fluids [55]. IL coating's corrosion resistance and cytotoxicity were investigated, and it was observed that treatment times have a considerable impact on corrosion resistance. A more homogenous IL film was generated when the ZE41 Mg alloy was exposed to the IL of

trihexyl phosphonium diphenyl phosphate at a potential of 200 mV [52]. Because of the protic ammonium-phosphate and trihexyl tetradecyl phosphonium cation mixed with organophosphate, it was suggested that ILs, or  $(CF_3SO_2)_2N^-$  anions, might reacting with Mg alloy surface to develop an excellent corrosion protection coating [50,56,57]. The metal phosphates, metal oxides, and carbonaceous compounds in the IL 300°C conversion coating have a double layer structure having 70-80 nm thickness and outstanding passivation performance in a 1 wt. percent NaCl. Deep eutectic solvents (DESs), are another type of ecologically friendly IL [58]. Because they are non-reactive with water, DESs are easier to synthesise in a pure condition than conventional ILs. Most of them seem to be biodegradable, and the component's toxicological qualities are well known [58]. One of the research groups [59] focused on the creation of DES-based Mg alloy conversion coatings. At 160 degrees Celsius, the interaction of a  $ChCl$ -urea mixture-based DES with the AZ31B Mg alloy was proposed as a new ionothermal method for generating a corrosion resistant layer. Mg alloy and DES reacted to produce a  $MgH_2$  and  $MgCO_3$  conversion coating that replaced a dangerous process. The conversion coating was also found to be superhydrophobic after additional reaction with stearic acid. According to electrochemical polarisation experiments [59], the Mg alloy's corrosion resistance could be increased by the DESs conversion coating. An electric field was also used by the same research group to induce the disintegration of DES, which aided the reactivity of the DES/Mg alloy interface [49]. Surprisingly, the proposed anodic treatment in DESs produced conversion films on Mg alloy substrates with different nanostructures. It was discovered that a more corrosion-resistant conversion coating can be created by increasing anodic current density. On the resulting conversion layer, superhydrophobic and sliding surfaces can be made to even further improve corrosion resistance [49]. Excellent conversion coatings with double capacity of superhydrophobicity and self-healing may also be produced on the AZ31B Mg alloy in DES-based media [60]. Using varied external fields at the IL/substrate contact to build more effective coatings on Mg alloy could be promising.

### 2.3. BIOMIMETIC COATINGS

Phases of CaP are precipitated out of solution and developed on the necessary sample in simulated bodily fluids (SBF) under close physiological conditions in biomimetic techniques for CaP coating deposition [62,63]. CaP coatings made with this approach can be seen in SEM images of a biomimetically synthesised hydroxyapatite coating on a Mg-alloys at higher and lower magnification. The technique offers an affordable option to coat a large number of specimens at once with a uniform coating and is easy to set up and operate. When compared to CaP coatings made using non-physiological pH, composition, and temperature, coatings created in physiological circumstances are expected to produce CaP crystalline structures that are more similar to bone minerals [64]. According to ongoing research [65], altering the coating solution's pH and temperature can help some CaP phases form more quickly than others. Furthermore, it was discovered that the geometry of the specimen to be coated has an impact on the CaP phases that form on sample

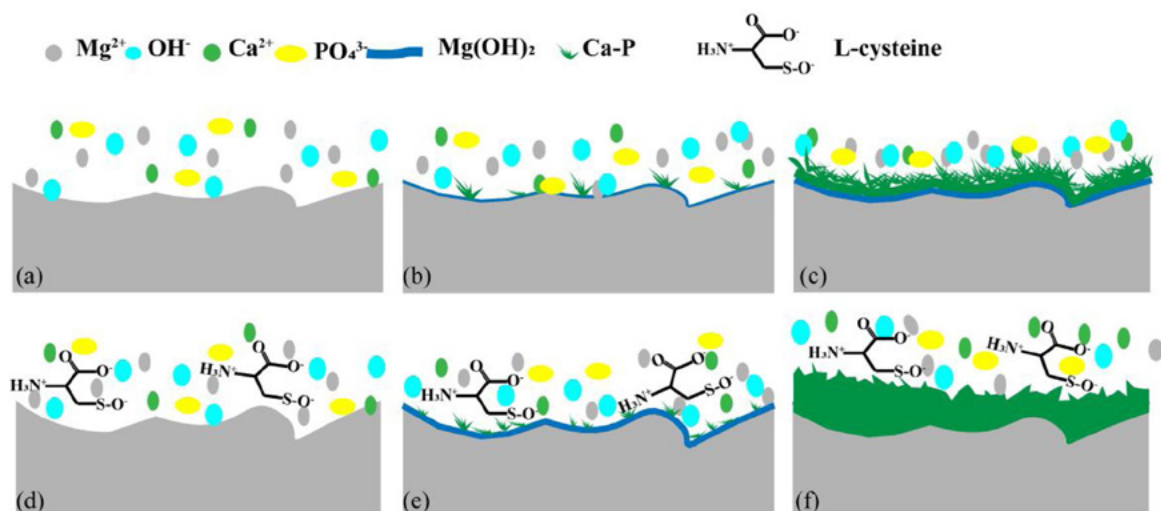
surface [66]. Although the concentration of the SBF used in the publications is typically concentrated, it can range from 1 to 10 SBF [63,67-69]. Additionally, immersion times fluctuate significantly between established protocols, and can be somewhere around 2 h to 20 days [68,70-73]. While using a biomimetic technique, pH and temperature appear to have been explored consistently, staying within physiological range, to be specific at 37 °C and 7.4, respectively. Pre-treatment is typically necessary in this process to affect the coating properties, the Mg reactivity, and the coated specimen's surface reactivity. To achieve this, most studies utilise an alkaline solution, such as NaOH, at various concentrations [74,75], or an acidic solution, such as HCl [77] or HF [76], at various concentrations. In biomimetic norms, however, many investigations have focused on temperature pre-medicines [76,78], or acidic or soluble post-medicines [79]. Covering magnesium and similar alloys using biomimetic technologies has shown to be a successful solution. Some researchers have raised concerns about biomimetic coatings on non-biodegradable substrates like titanium, however they haven't considered the influence of the SBF immersion period on substrate degradation. Previous research has demonstrated that very lengthy immersion in SBF can result in thick coating development if phosphate and calcium ions are abundant [73]. Researchers discovered that a second immersion in a new SBF solution is effective in these circumstances [73]. Numerous researchers have found that it is beneficial to modify the biomimetic convention for biodegradable specimens like Mg and its alloys, by shortening the period spent incubating in SBF, hence minimising the possibility of coating disintegration [80]. Furthermore, as indicated by horizontal CaP crystal binding across the coating, biomimetic CaP coatings on Ti have been labelled as thick, comprehensive, homogenous, and non-porous [81]. According to one of the studies [82], coating formation took place around hydrogen bubbles that were developed on magnesium surface while submerge, resulting in irregular and porous CaP coatings on Mg samples. The non-uniform and porous CaP coating on Mg alloy, according to several studies, is caused by the specimen's non-uniform shape [77] and the presence of Mg<sup>2+</sup> ions, which prevent crystal formation [83]. Porosity production on degradable metals like Mg is another key disadvantage of a biomimetic coating method. Until now, no modification or variation of this procedure has been successful in achieving strong cohesiveness between the specimen and the CaP coating. For biomedical applications, such as orthopaedic applications, it is critical to develop an extremely strong adhesive covering with a long-life span and the ability to endure surgeries.

Biomimetically developed apatite coating on a pure Mg specimen to improve corrosion protection were explored by one researcher [73]. In SBF, they used either single-coated or double-coated substrates, with pure Mg as a control. Other investigations found that coating Mg alloys AZ91D and AZ31 with this method before doing in vitro immersion testing, electrochemical [84] and SBF solution [85] provided similar corrosion resistance. Recent investigations on biomimetic CaP-coated pure Mg, on the other hand, have shown corrosion protection and enhanced cell adhesion [75,79]. The biomimetic method has most likely been studied as a viable strategy for employing CaP on Mg specimens, as previously indicated. Given this, and as reported

in the literature, further refinement of these methods is required if they are to be used as a viable CaP coating approach on magnesium and its alloys.

## 2.4. HYDROTHERMAL COATING

The uncoated Mg alloy's outer layer lacks adsorption sites associated with Ca-P crystal formation. In the absence of a chelating specialist in hydrothermal coatings method, high-temperature corrosion would produce a significant number of  $Mg^{2+}$  ions, leading to the creation of  $Mg(OH)_2$  and aggressive absorption of a  $Ca^{2+}$  ions. Similarly, coating a Mg alloy with a very pure Ca-P coating is difficult, because the binding strength between the specimen and the coating is poor, reducing the implant's mechanical stability in the body. Several conjugates, polymers, and chemicals are utilised as precursors or inducers to ramp up the formation of calcium phosphate in attempt to optimise phase purity, bonding strength, and density of Ca-P coatings [86-88]. EDTA is an organic compound that promotes HA nanocrystal nucleation and growth by binding to divalent metallic cation and reacting with calcium ion. On the other hand, MEA is an aminol that speeds up the synthesis of hydroxyapatite crystal and increases the solvency of reactants in hydrothermal reactions [89,90]. Because it contains  $-NH_2$ ,  $-COOH$ , and  $-SH$ , L-cysteine was discovered to get a decent capacity to suppress metallic corrosion. Using a hydrothermal technique, one of the researchers [91] created an L-cysteine CaP coatings on AZ31 which is bioinspired. Addition of L-cysteine increased corrosion resistance, illustrated in Fig.3, which depicts the Ca-PL-Cys-coating development mechanism. A hydrothermal technique was used to coat the exterior layer of Mg alloy with HA, with in the centre, PDA acts as a glue. PDA's catechol functional group is very sensitive to metal iron absorption, which helps generate the HA coating by binding  $Ca^{2+}$  ions and subsequently drawing  $PO_4^{3-}$  to develop hydroxyapatite nuclei, allowing for cross-connection with hydroxyapatite. The interactions of the polyhydroxyl unit of glucose with  $Ca^{2+}$  ions in fluid solution may enable the formation of Ca-P crystals on the pure magnesium surface [92].



**Figure 3.** Ca-P coating formation mechanism (a-c) and Ca-PL-Cys coating creation technique (d-f) [92]

According to one of the researchers [93], glucose can be used as a catalyst to convert gluconic acid into a carboxyl group under hydrothermal treatment, creating a negative charged magnesium surface that draws in  $\text{Ca}^{2+}$  ions and advancing the creation of a corrosion protective Ca-P coatings while also significantly reducing the Mg substrate's anodic dynamics in Hank's solution. The glucose-initiated compound coating of Mg  $(\text{OH})_2$  and Ca-P provoked by hydrothermal treatment of pure Mg is depicted schematically in Fig. 3. Table 2 lists the characteristics, structure, and composition of chelating agents utilised in the recent creation of Ca-P coatings on Mg alloy surfaces using the hydrothermal process.

**Table 2.** Recent investigations on chelating compounds, related active groups, and coating characteristics.

Chelating agent	Specimen	Conditions of hydrothermal reaction	Coordination ion	Active group	Coating composition	Properties of coating	Ref
Glucose	pure Mg	500 mM glucose, 250 mM $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 250 mM $\text{KH}_2\text{PO}_4$ , 120 °C, 24 h, pH = 10	$\text{Ca}^{2+}$ ion	Carboxyl group transformed from aldehyde group	Mg $(\text{OH})_2$ DCPA HA CDPA	Corrosion protection is enhanced by a denser coating morphology that uses several large single particles as its building blocks.	93
L-cysteine	Mg alloy AZ31	0.15 g/L L-cysteine, 0.25 M of $\text{CaCl}_2$ and $\text{KH}_2\text{PO}_4$ , 60°C, 30min	$\text{Ca}^{2+}$ ion	sulfenyl)-SH(amin o)- $\text{NH}_2$ (carboxyl )- $\text{COOH}$	Ca $(10-x)$ $(\text{HPO}_4)_x$ $(\text{PO}_4)_{(6-x)}$ $(\text{OH})_{2-x}$ $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ , Ca $_{10}$ $(\text{PO}_4)_6(\text{OH})_2$	The morphology of the coating has been greatly enhanced in terms of uniformity and integrity. Coating thickness twice that of the control group; enhanced corrosion resistance.	92

Polydopamine (PDA)	Mg alloy AZ31	5 M NaOH 60 °C 3 h 2 mg/mL dopamine hydrochloride 14 mM Ca(NO <sub>3</sub> ) <sub>2</sub> 8.4mM NaH <sub>2</sub> PO <sub>4</sub> 4 mM NaHCO <sub>3</sub> 3,93K 4 h	Ca 2+ ion	Catechol	PDA/HAp	Increased adhesion, proliferation, and dispersion of osteoblasts; Denser coating structure; Lower corrosion rate	126
Deoxyribonucleic acid (DNA)	Mg alloy AZ31	1g/L DNA, 14 mM Ca(NO <sub>3</sub> ) <sub>2</sub> 8.4mM NaH <sub>2</sub> PO <sub>4</sub> 4 mM, NaHCO <sub>3</sub> 150 °C, 4h	Ca 2+ ion	Base pair and deoxyribose double helix	tricalcium phosphate (TCP), dicalcium phosphate anhydrous (DCPA) and calcium-deficient hydroxyapatite (CDHA)	By fine-tuning the coating grain, researchers can increase bonding with sample. Improve the resistance to corrosion	127
Polyacrylic acid (PAA)	Mg alloy AZ31	1 M NaOH 60 °C for 1h, 14 mM Ca(NO <sub>3</sub> ) <sub>2</sub> 8.4mM NaH <sub>2</sub> PO <sub>4</sub> 4 mM NaHCO <sub>3</sub> 90 °C, 4 h	Ca 2+ ion	COO-	Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ; (Ca, Mg) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ; and HA	Good corrosion resistance; denser stereoscopic blade structure; 10.69 N adhesive force	128

Phytic acid (PA)	Mg alloy AZ31	0.70 wt. % phytic acid, 4.90 wt. % Ca(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O and 0.89 wt.% P <sub>2</sub> O <sub>5</sub> at 40 C for 40 min, pH = 4.5	Ca 2+ ion	COO-	Phytic acid/HA	24.3 ± 1.7 MPa bonding strength; good corrosion resistance	129
Ciprofloxacin hydrochloride (CIP)/ Polyacrylamide hydrochloride (PAH)	Mg alloy AZ31	5 M NaOH 30 min 14 mM Ca(NO <sub>3</sub> ) <sub>2</sub> , 8.4 mM NaH <sub>2</sub> PO <sub>4</sub> , 4 mM NaHCO <sub>3</sub> , 150 °C, 240 min	Ca 2+ ion	COO-	CIP/PAH/HA; composite coating	Excellent corrosion protections; CIP discharge that may be controlled; Antibacteria I activity is excellent, and cytocompatibility is adequate.	130

## 2.5. ALKALI-HEAT TREATED CONVERSION COATING

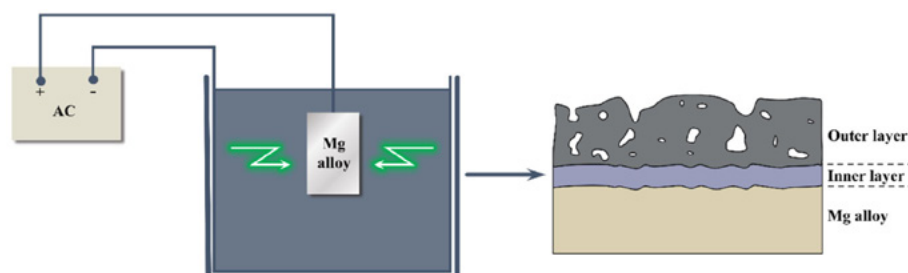
To remove oil and other impurities from Mg and Mg alloy alkali heat treatment is an important step. Coatings are typically used as a pre-treatment to improve corrosion resistance of adjacent layer to strengthen the bond between outer layer and the sample. The sample was submerged in an extremely saturated solution of NaHCO<sub>3</sub> - MgCO<sub>3</sub> having a pH of 9.3 for 24 hours before being heated at 500 °C for 10 hours for alkali-heat treatments [94]. The coating in SBF has a high level of corrosion resistance. Simultaneously, in an early cytotoxicity investigation, it shows no cytotoxicity by cell development, with no morphological changes on cells or inhibitory effect. One of the researchers [95] used alkali heat pre-treatment to create LbL assembled coatings, which boosted the binding force between the sample and LbL layer and improved corrosion protection. The benefits of alkali heat treatment coating are its good biocompatibility and excellent corrosion resistance. In any event, the coatings are exceedingly thinner and therefore could not be utilised as a topcoat, or even as a primer.

## 3. MAO COATING

Plasma Electrolytic Oxidation is another name for micro arc oxidation (MAO) (PEO), is a greener alternative to anodization [96,97]. MAO has lately been popular



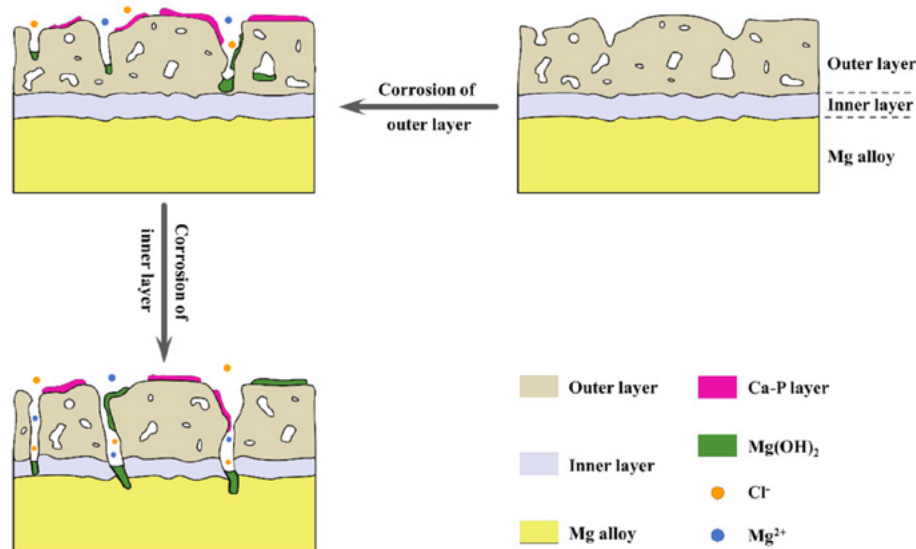
for covering magnesium alloys with oxide-ceramic coatings [98]. In the PEO technique, the cathode is a cylindrical SS container, and the anode is a Mg alloy. Due to the higher temperature induced by the high voltage, an oxide coating developed on the outer layer of the Mg alloy at first, and vigorous gas development could be seen. The voltage then continues to rise, although at a slower rate, and the oxide film is broken at the weaker portion, with the thickness of the coating gradually increasing. Due to exceptionally powerful discharges on the surface of the specimen [99], discharge channels emerged, and the electrolyte fused into these channels. A combination of high voltage and high temperature in the discharge channel converts a few of the Mg on the specimen external layer and an electrolyte within channels to plasma, which is subsequently transformed to plasma through a plasma chemical process. Metallic ions generated by the magnesium alloy are expelled and moved away from it, whereas oxygen ion moved in reverse direction. The oxide is subsequently deposited on the outer layer [100] as a result of an interaction between magnesium metallic ions and oxygen ions. The applied electric field pushes anions from the MAO electrolyte, such as  $\text{SiO}_3^{2-}$  or  $\text{PO}_4^{3-}$ , toward the anode, where they reacting with  $\text{Mg}^{2+}$  ions from the discharge channels of Mg specimen [101]. A ceramics-like covering with better corrosion resistance, bonding strength and wear resistance is formed by MAO process. Fig. 4 depicts the MAO coatings on Mg alloy production procedure and structure. At the start of the MAO process, a dense and thin coating is applied to magnesium alloy. Because of this, the MAO coatings have a two-layered microstructure with a thick inside layer and a porous outside layer [102].



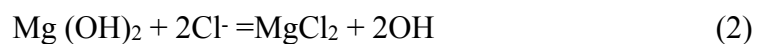
**Figure 4.** Schematic example of MAO coating preparation and structure on Mg alloy [96].

The two-layered structure of MAO coatings can be seen using scanning electron microscopy (SEM). Thermal strains induced by quick solidification of molten oxide in a gradually cooling electrolyte form small pores, whereas miniature fractures are formed by thermal stresses caused by quick solidification of molten oxide in a gradually cooled electrolyte [103]. MAO coating act as physical barriers, successfully isolating the Mg sample from hostile environments and lowering its corrosion resistance [104]. The corrosive  $\text{Cl}^-$  ion penetrates the exterior layer through micropores during the initial phase of submersion in physiological environment. Simultaneously, the coating's main ingredient ( $\text{MgO}$ ) reacts with  $\text{H}_2\text{O}$  to form  $\text{Mg}(\text{OH})_2$  as per Eq. (1) [105]. The hydrated substance partly fills the pores in the coating, whereas the rest settles on the outer layer [106]. Notwithstanding its volatile chemical characteristics,  $\text{Mg}(\text{OH})_2$  could be converted to dissolvable  $\text{MgCl}_2$  through  $\text{Cl}^-$  as per Eq. (2), releasing hydroxyl ions [107]. After then, as per Eq. (3) [105], a Ca-P layer structure arises as the  $\text{OH}^-$  interacts with various chemicals and ions. During this period, the MAO coating's breakdown is slowed by the outside porous layer. The corrosion zone expands as the

submersion duration rises, and the pores get deeper and larger, facilitating electrolyte infusion into the inward dense layer [108]. The innermost thick layer is useful in stopping aggressive medium from reaching and touching magnesium substrate, and if this layer is removed, corrosive medium would penetrate and touch the magnesium substrate. Because of its high inherent corrosion characteristics in aqueous solution, Mg corrosion occurs quickly when the electrolyte meets the substrate [109]. During this time, the MAO coatings' corrosion resistance is primarily dependent on the interior dense layer. The MAO coating's two-layered structure, as illustrated above, can greatly increase the corrosion protection of Mg alloys. Figure 3 depicts the biodegradation process of the MAO coating on Mg alloy.



**Figure 5.** MAO coating on Mg alloy biodegradation process [96]



### 3.1. ANTIBACTERIAL MAO COATINGS ON MG ALLOYS

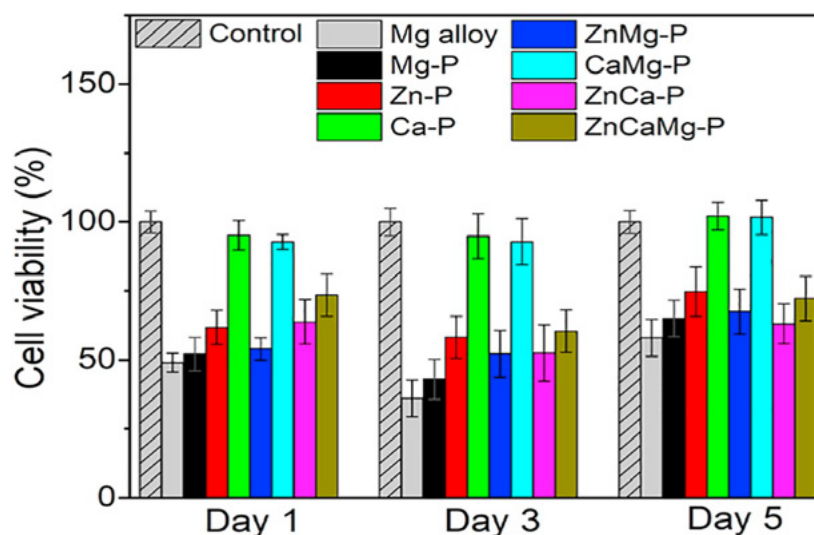
Mg's antibacterial capabilities have been revealed in a number of previous studies [110,110]. The results demonstrated that Mg was effective towards methicillin-resistant *Staphylococcus aureus* when it was injected into rats with implant-related infection (MRSA). One of the researchers used pure Mg, glass slides, and polyurethane stents to grow *Escherichia coli* (*E. coli*). After 16 hours of coculturing with pure Mg, the bacterial cell density was at its lowest, indicating that Mg has a very powerful antibacterial impact. Mg has also been shown to have outstanding antibacterial properties in the past [112]. The alkaline rise caused by Mg's breakdown in solution is responsible for its antibacterial effect [113]. It was observed that AZ31 and pure Mg along with silicon and fluorine coatings created by chemical conversion technique lost their antibacterial activities because of its dense coating on the surface [114]. Coating Mg alloy with antibacterial coatings, in this way, could be a potential methodology for increasing antibacterial effects and corrosion resistance of the magnesium alloy

concurrently. For development of antibacterial coating on the metal surface MAO technique is effective, economical and extensively used method [115].

The MAO approach produces coatings that are largely made up of substrate oxides, but they also contain electrolyte components [116]. As a result, altering the electrolyte composition can efficiently vary the composition of the MAO coating [117]. Furthermore, significant antimicrobial activity is known for Zn, Cu, and Ag, and these antibacterial metallic components kill bacteria by denaturing proteins, damaging membranes, and generating oxidative stress [118-121]. Antibacterial coatings can be made using this metal complex or by merely putting micro/nanoparticles of these metals to MAO electrolyte [122].

#### 4. BIOCOMPATIBILITY OF CONVERSION COATINGS

CaP type coatings have good biocompatibility, according to the cell survival test findings shown in Fig. 6, which can be attributed to their DCPD content.



**Figure 6.** After 1, 3, and 5 days of incubation, cell feasibility of all treated specimen and bare AZ31 [123].

Because of its outstanding biocompatibility and biodegradability [125], DCPD is an essential biomaterial in the field of bone cement [123,124], and its degradation products can supply vital calcium and phosphorus supplies for bone tissue regeneration. The effects of CaP, ZnP, and MgP coating types on the precipitation of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_3(\text{PO}_4)_2$  have not been thoroughly investigated.

According to the different morphologies of all conversion coating after a 15-day soaking, there are more precipitations on CaP and MgP type conversion coatings than on ZnP type conversion coatings. The divergence of phosphates, magnesium, and calcium precipitation on diverse types of coatings can be explained by two factors:

1. CaP type and MgP type coatings have a higher solubility than ZnP type coatings. As a result, the alkalization of the Hanks' solution near the magnesium complex sample and the precipitation of phosphates magnesium and calcium is accelerated by the breakdown of conversion coatings.

2. The CaP and MgP coatings have the same composition as the phosphate precipitation from Hanks' solution, that minimises the principal factor driving precipitation nucleation and development and, as a result, speeds up precipitation during the immersion test [123].

## 5. CONCLUSION

In vivo corrosion of biomedical magnesium can be controlled by alloying magnesium with by alloying it with biocompatible elements, by changing surface microstructure and applying protective coating to isolate implant and body fluid.

Because of the lower cost and easiness in operation conversion coating can be generally utilized in biomedical fields. Chemical conversion coatings are created by interaction of precipitation and chemical dissolution. Fluoride conversion coating can give safety during the initial phases of implantation due to its thin coating, however it must be employed for long-term applications. Fluoride leak during Mg implants corrosion and its cytotoxicity for tissue are unknown, and it would have a negative impact on bone, necessitating additional investigation. Alkali heat treatment coating has good biocompatibility and excellent corrosion resistance; however, coatings are extremely thin and cannot be used as topcoat.

It was observed that Zn, Cu and Ag have excellent antimicrobial capacity, and these antibacterial metallic components kill microorganisms through protein denature, membrane destroy and oxidative stress. MAO is another technique used for bioactive and antibacterial coating on magnesium and its alloys. Antibacterial coatings can be made by mixing micro/nanoparticles of these metals with MAO electrolyte.

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