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Improvement of Biodegradable Magnesium-Based Alloys Properties by Ca-P Based Bioceramics Biomimetic Deposition

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Abstract
Bioactive ceramic coatings based on calcium phosphate (Ca-P) are commonly used to modify implant material surfaces and to create new surfaces with completely distinct characteristics from the substrate. Several coating methods are often used to coat metal implants. In the present study, an attempt was made to develop a Ca-P coating biomimetically on magnesium alloy substrates (AZ31) by immersing them in a supersaturated calcification solution (SCS). The Ca-P deposit thus formed has been then evaluated according to the physicochemical and mechanical characteristics. Calcium phosphate deposits (Ca-P) were considered using an optical microscope (OM), scanning electron microscope (SEM), X-ray dispersive analysis (EDX), and X-ray diffraction (XRD). Whereas, the Ca-P deposits adhesive nature on untreated and treated surfaces was determined by scratch analysis. The biomimetic deposition of calcium phosphate (Ca-P) is an easy and cost-effective method that preserves the substrate's mechanical properties and provides good adherence.

Keywords: Magnesium Alloy, Ca-P Coating, Biomimetic, Adhesion, Supersaturated Calcification Solution (SCS).

Introduction

The materials currently used as orthopedic implants for bone replacement such as total hip and knee replacement consist of metals and metal alloys [1]. As implant materials, a variety of metallic biomaterials such as titanium alloys, stainless steels, and cobalt-chromium-based alloys have been widely used [2]. Traditional metallic biomaterials (316L stainless steel, titanium alloys and cobalt-based alloys) have been used due to their excellent mechanical and anti-corrosion properties but they release toxic elements (traces of nickel, etc.) such as corrosion product and friction debris in the human body. On the contrary to traditional metallic biomaterials, Mg alloys have an elastic modulus similar to that of human bone, inhibiting the stress shielding effect [3]. Because of their mechanical properties, which are similar to natural bone, magnesium (Mg) alloys are gaining traction as attractive biodegradable materials for orthopedic applications [4, 5]. Magnesium (Mg) and several of its alloys are hence attractive alternatives for biodegradable implant applications. Mg is non-toxic and can even aid in the repair of hard tissue after implantation in the human body [4]. It is necessary for the human body's biological activities to function properly. In the researches of biodegradable magnesium alloys, the main disadvantage of magnesium alloys is their high rate of corrosion in electrolytic aqueous environments which can cause severe interactions with human organisms [6-9]. As a consequence, improving the corrosion resistance of magnesium alloys is critical for their prospective biomedical uses. Some study has recently been conducted to inhibit the biodegradation rate of magnesium alloys [10]. Surface modification is one of the most effective ways to minimize the biodegradation rate of magnesium alloys [11, 12].

A surface coating is also an effective technique to promote the surface bioactivity of biomaterials [13]. As a result, by selecting the appropriate surface modification, it is feasible to lower the rate of biodegradation of magnesium alloys and improve surface bioactivity [14]. Surface treatment of magnesium alloys will increase biocompatibility by lowering biodegradation rates and resulting in improved bone-implant interactions [15]. Has used a phosphate treatment to coat calcium phosphate on a magnesium alloy in order to increase the surface bioactivity of the magnesium alloy [12]. Coatings on implants can be created in a variety of ways. Processing techniques by spraying, techniques by wet process, and techniques by plasma spraying are the three primary groups [16, 17].

To assist industrial development, processing methods for depositing calcium phosphates on magnesium implants must preserve the substrate's mechanical qualities, ensure good coating adherence, and be simple and inexpensive. Various research projects are focused on the development of novel thin coatings production techniques that are promoted as a viable alternative. For its simplicity, the biomimetic technique was chosen for this investigation [18].

Were the first to develop biomimetic calcium phosphate coatings in 1990. The objectives of this paper is to evaluate the corrosion rate and behaviours of magnesium alloys during the biodegradation process, as assessed by in-vitro assays. The second step was to develop a Ca-P based biomimetic deposit on magnesium alloy substrates by immersing them in a supersaturated calcification solution (SCS). Therefore, formation of a protective layer based on Ca-P, in order to improve the corrosion resistance of magnesium alloys.

Materials and Method

Substrate Material

A commercial magnesium alloy sheet, such as rolled, 5.0 mm thick was used in this study. The substrate material was AZ31 magnesium alloy with an elemental composition of (% by weight): 2.53% Al, 0.962% Zn, 0.346% Mn, 0.0271% Si, <0.002% Cu, <0.0002 % Ni, 0.0039% Fe and 96.1% Mg) is identified using the Energy Dispersive Spectrum (EDS), has been widely characterised in some researches [19-21]. The surface of the 20mm × 20mm × 5mm samples was polished with 800 # and 1000 # SiC paper, respectively (to ensure the same surface roughness) and ultrasonically washed with deionized water and ethanol for 10 min. After cleaning, the substrates were cold air dried and stored for later use.

Alkaline Surface Treatment

Before the deposition to modify the corrosion resistance, the chemical composition and the morphology of the Mg surface an alkaline treatment was applied by soaking the samples in a solution of 5 M NaOH for 24 h at the temperature 60 °C to passivate surfaces. The purpose of soaking in 5 M NaOH is to activate the surface by improving the deposition process.

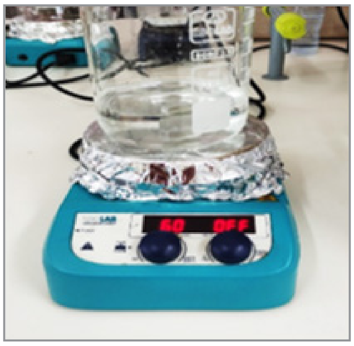

Figure 1: Sample Treated With

Deposit Solution

Supersaturated calcification solution (SCS) was prepared by successively dissolving the reagent grade chemicals $CaCl_2$, NaH_3PO_4 and $NaHCO_3$ in distilled water [22]. The different ion concentrations are shown in Table 1.

Table 1: SCS Solution Composition

Mass of salts in a liter of SCS (mg/l)			
Components	$CaCl_2$	NaH_3PO_4	$NaHCO_3$
SCS	555	300	126

Biomimetic Deposition Protocol

The biomimetic deposition was carried out as follows: the samples (untreated and treated with NaOH) were immersed in beakers SCS solution. Then the beakers were placed on a hotplate at 37 °C with stirring for 4 h, 3 days with a stirring speed of 140 rpm. Finally, the samples were taken after the immersion times and rinsed thoroughly with demineralized water and then dried in an oven at 60 °C for 2 h.

Figure 2: Biomimetic Deposition

Characterization Techniques

The surface changes morphology of the samples before and after tests were characterized by scanning electron microscopy (FE-SEM, Quanta 250), equipped with an energy dispersive spectrometer (EDS). X-ray diffractometer (XRD, Rigaku Ultima IV. Ltd. Tokyo, Japan, λ= 0.154681 Å) with CuKα radiation with large angles of 2θ from 10 ° to 90 °, the test voltage is 40 kV and the step is 0.02 ° has been used. The Vickers hardness was performed on the INNOVATES type digital microhardness tester. The Vickers microhardness (HV) measurements were carried out using a load of 200 g for 10 s. The determination of the solution's pH to be tested was accomplished at a temperature of 37 °C, using a model pH meter produced by Hanna Instruments. The adhesion tests by scratch test of the Ca-P deposit was carried out at room temperature with an SCM Revetest scratch test device (CSM Instruments) using a conical diamond tip of Rockwell C type with radius 200 µm and angle 120 °. The data acquisition frequency was 5 kHz. The tests were realized by increasing the load from 1N to 50N (load rate: 49N / min) with a displacement speed of 5 mm.min-1 over a distance of 5 mm. The nature of the scratch was examined for its different types of defects (chipping, buckling, delamination), cracking by an optical microscope (OM). A two-dimensional scanning profilometer (Cyber Technology CT100 laser source) has been used to measure surface roughness.

Results and Discussion

Morphology and Microstructure of Deposits Analysis

From Figure 3, it can be seen that the morphology of the deposit on the pretreated surface has a certain architecture with a porosity. The Ca-P coating formed on the sample alkaline treatments (NaOH) showed the most uniform, dense, and think surface. It is provide good protection for the Mg substrate. It is well-known that the surface pre-treatments favor Ca-P depositions [23]. The EDS spectrum of the deposits Ca-P showed the presence of Ca, P, O as well as Mg, and C. Major peaks due to Ca, P, and O, confirming the presence of Ca-P [24]. Peak C can come from the carbon required during sample preparation. Analysis also revealed that Mg incorporated into the apatitic Ca-P coating. The Mg peak appeared with high intensity in the XRD diffractograms due to the very thin Ca-P layer as shown in a prior study [25].

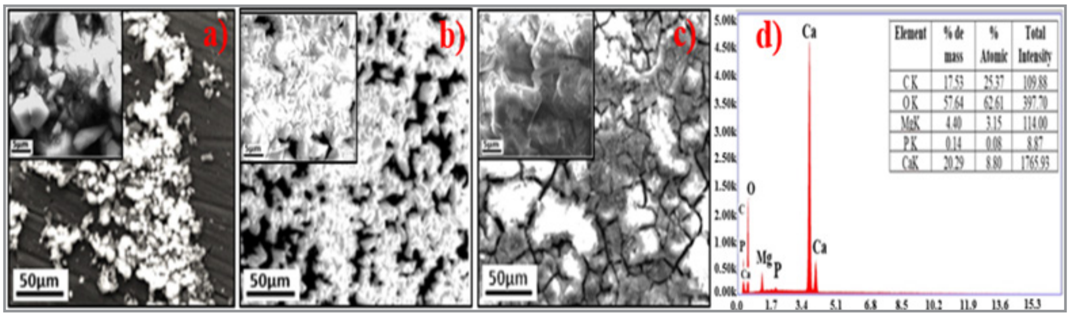

Figure 3: Morphology of Ca-P deposits of CSC solution a) Untreated surface /4 h, b) Untreated surface /3d, C) Treated surface NaOH / 3d, and d) EDS analysis of the Ca-P deposit of pretreated AZ31

Micro-hardness of Ca-P Deposits

Figure 4 shows the micro-hardness evolution of AZ31 alloy compared with that of the deposits Ca-P. A significant evolution is observed in the microhardness of the deposit on the surface pretreated with NaOH compared with the substrate and the deposits on the untreated surface.

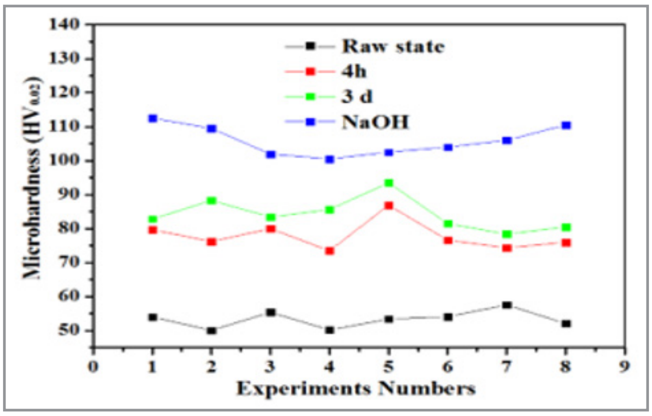

Figure 4: Microhardness Evolution of Ca-P Deposits

Adhesion Analysis

The load at which total peeling-off of the coating from the substrate occurs is referred to as the critical load[26, 27]. The adhesion analysis for Ca-P deposits (with and without surface treatment) was performed by scratch test, is shown in Figure 5. The Ca-P deposition on the untreated substrate (AZ31) displayed harsh spallation behavior due to poor adhesion of the coating to the surface. The peel force LC3 = 10.13 N for the deposit on the surface pretreated with NaOH greater than that recorded for the other two deposits. This proves that this deposit has better adhesion compared to other deposits. The surface pretreated with NaOH process improve the adhesion strength between a Ca-P coating and the AZ31 substrate.

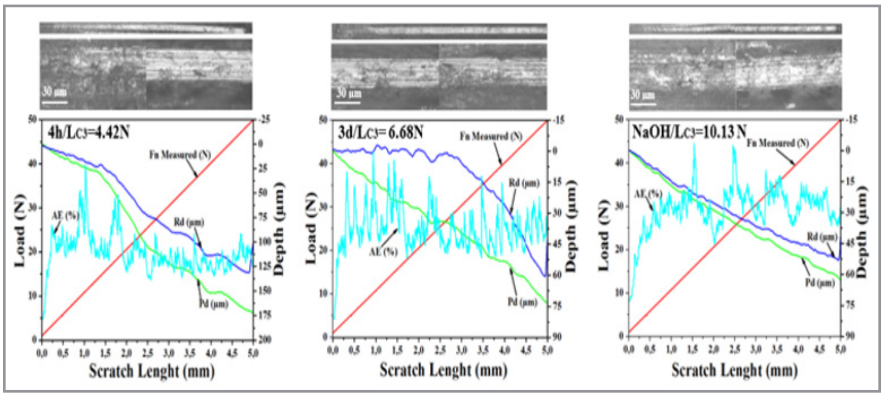

Figure 5: Optical microscope İmage and Evolution of Penetration Depths (Pd), Residual Depths (Rd), and Normal force (Fn) of Deposits (after 4h, 03 days), and Treated with NaOH, Respectively

Roughness Variation

Figure 6 show the evolution of the roughness of Ca-P deposits, it is noted that the roughness of the deposit on the surface pretreated with NaOH is greater than the other two deposits (without surface treatment).

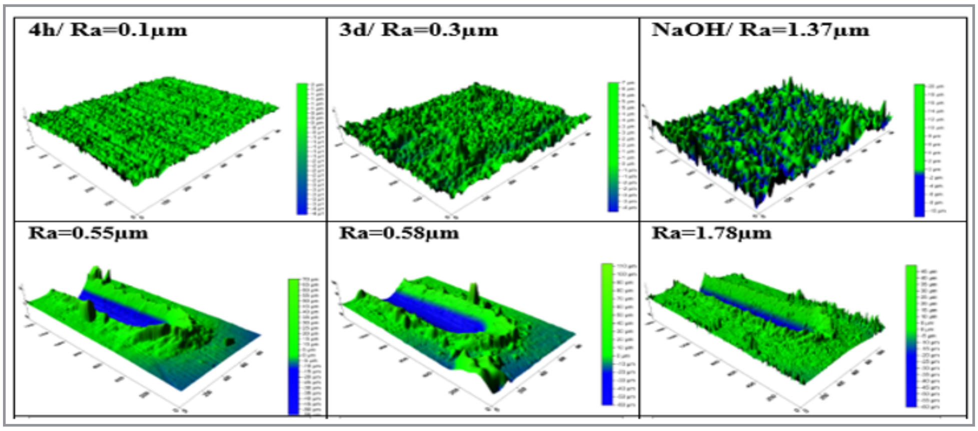

Figure 6: Roughness (Ra) Evolution of Ca-P Deposits and 3D Scratch Test

Conclusion

There are a multitude of surface treatment methods applied to deposit calcium phosphates on metal implants. During this work the biomimetic method was used. It can conclude from the obtained results that:

- The deposit (Ca-P) developed on a pretreated surface (NaOH) of AZ31 present better properties (hardness, adhesion) compared to the untreated surface;
- The biomimetic deposition of Ca-P is simple and economical method, preserves the mechanical properties of the substrate, and provides good adhesion on substrate.

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