

CORROSION AND BIODEGRADABILITY EVALUATION OF STRONTIUM SUBSTITUTED HYDROXYAPATITE COATING ON SURFACE TREATED AZ91 Mg ALLOY FOR BIOMEDICAL APPLICATION

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ABSTRACT

Magnesium alloy has attracted great attention as an orthopedic biodegradable implant material due to its close mechanical properties to natural bone and perfect biocompatibility. But the corrosion of magnesium alloy (AZ91 Mg alloy) in physiological solution limits their biomedical application. In the present work, surface treatment of AZ91 Mg alloy was performed in the mixed acid solution and bioactive strontium substituted hydroxyapatite (Sr-HAP) was electrodeposited on the surface treated AZ91 Mg alloy. The Sr-HAP coating was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray analysis (EDX) and adhesion strength. The corrosion resistance of the electrodeposited Sr-HAP on the AZ91 Mg alloy in simulated body fluid (SBF) was evaluated using potentiodynamic polarization studies. Hence, the Sr-HAP coated on surface treated AZ91Mg alloy is predicted to be the most suitable coating material for orthopedic implants.

KEY WORDS

AZ91 Mg alloy; surface treatment; corrosion resistance; orthopedic implants.

1. Introduction

Magnesium and its alloys have been attracted great attention as orthopaedic implant materials due to its biocompatibility, biodegradability and the mechanical properties that is close to the natural bone and teeth [1]. However, magnesium and its alloys are highly susceptible to corrosion in physiological conditions especially human body fluid or blood plasma solution [2]. Hence, surface treatments are needed to improve the bio-corrosion resistance of magnesium and its alloys. Hydroxyapatite, (HAP $[(Ca_{10}(PO_4)_6(OH)_2])$) is the currently used bio-ceramic and biomedical coating material due to its excellent biocompatibility, bioactivity, and structural similarities close to the minerals of tooth and bone minerals [3]. The biological performance of the HAP based bio-ceramic materials might be

improved by the addition of bio-active ions which has stimulated a number of studies on ion substituted HAP coating [4]. Among these, the beneficial effect of strontium is known to be one of the most critical cations in bone activity to promote the growth of osteoblasts and prevent bone resorption [5]. *In vivo* and *in vitro* studies exhibited the good biocompatibility, osteoconductivity and bone bonding strength of Sr-HAP coating [6,7]. Among various techniques [8-11] electrochemical deposition is one of the most promising methods that has unique advantages due to its capability of forming a uniform coating on a porous substrate or one with complex shape controllability to the thickness, its low deposition temperature and low cost of equipment [12].

The aim of our work was to electrochemically fabricate porous Sr^{2+} substituted HAP coating (Sr-HAP) on Mg alloy. Sr-HAP porous microstructure can be favourable for the growth of cells and rapid adhesion, resulting in a critical stronger bond to the parent tissue [13]. But porous coating of Sr-HAP on Mg alloy decreases the corrosion resistance of Mg alloy [14]. To overcome these problems it is suggested that surface treatments may be used to improve the corrosion resistance and bone bonding ability of Mg alloy. Many surface modification techniques have been established to improve the corrosion resistance of the implant. But there are no reports on the surface treatment of Mg alloy by the mixture of acid which has attracted much attention due to its simplicity, cost effectiveness, bone bonding ability and its applicability to implants with complicated shapes. Thus, based on all the above stated issues, the present work is involved in the development of Sr-HAP coating on surface treated Mg alloy. The Sr-HAP coating on surface treated Mg alloy will serve as a promising candidate with improved bio-corrosion resistance, bioactivity and mechanical property.

2. Experimental

2.1 Mg alloy surface preparation

The AZ91 Mg alloy specimens (Elemental composition wt%: 0.59% Zn, 0.17% Mn, 8.63% Al, <0.05% Cu, <0.05% Fe and balance Mg) of dimensions $10 \times 10 \times 5 \text{ mm}^3$ embedded in epoxy resin leaving areas of 1 cm^2 were used as the substrate material. Before the deposition, surface of all the samples was ground from 800 to 1200 silicon carbide papers (SiC) to ensure uniform surface roughness. After polishing the alloy substrates were subsequently cleaned ultrasonically by deionized water and acetone for 15 min and then used for further experiments.

2.2 Surface treatment of AZ91 Mg alloy

The entire sample surface was subjected to surface treatments by complete immersion in volume concentration of 10% H_2SO_4 , CH_3COOH and 10% HNO_3 , at room temperature for 10 min. After that the surface treated samples were washed with acetone and rinsed by deionized water and then specimens were ultrasonically cleaned with acetone and dried in air.

2.3 Preparation of electrolyte

The electrolyte for the deposition was prepared by dissolving analytical grade calcium nitrate dihydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$). The amount of the reactants was calculated based on the Ca/P target molar ratio 1.67. The pH was adjusted to 4.5 using dilute NH_4OH or HCl .

2.4 Electrochemical deposition of Sr-HAP

Electrodeposition of Sr-HAP on AZ91 Mg alloy was carried out in a regular three electrode cell arrangement by galvanostatic method using an electrochemical workstation (CHI 760C (CH Instruments, USA)) in which the platinum electrode served as the counter electrode, AZ91Mg alloy and saturated calomel electrode (SCE) as the working and reference electrodes, respectively. The electrodeposition of Sr-HAP was carried out in an aqueous solution containing 0.4 M $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.1 M $\text{Sr}(\text{NO}_3)_2$ and 0.3 M $(\text{NH}_4)_2\text{HPO}_4$ under the magnetic stirring at room temperature ($28 \pm 1^\circ\text{C}$) and the pH was maintained at 4.5 at a current densities of 9 mA cm^{-2} for the duration of 30 min. After the deposition, the Sr-HAP coated AZ91 Mg alloy surface was washed with deionized water to remove residual electrolyte, and then naturally dried for 24 h.

2.5 Mechanical characterization

2.5.1 Adhesion strength

The adhesion strength of the Sr-HAP, on the bare and surface treated AZ91 Mg alloy samples were studied by pull-out test according to the American Society for Testing Materials (ASTM) international standard F1044 were subjected each sample at least five measurements quick set epoxy adhesive. After heating in an oven at 100°C for 60 min the fixtures were subjected to pull-out test. The cross-head speed of 1 mm/min , using a universal testing machine (Model 5569, Instron).

2.5 Surface Characterization of the coatings

The functional groups of the coatings was characterized by Fourier transform infrared spectroscopy (Impact 400D Nicolet Spectrometer), in the over frequency range from 4000 to 400 cm^{-1} . The surface morphology and micro structure of the coating was observed using high resolution scanning electron microscopy (JEOL JSM-6400, Japan). The phase compositions of the coatings were identified by X-ray diffraction (XRD) (bruker & advance diffractometer). The scanning angle is ranged from 20° to 60° with a scan

rate of 0.02°. The chemical composition of the samples were investigated by energy dispersive X-ray spectroscopy (EDS).

2.6 Electrochemical investigation of the coatings

The corrosion resistance of the uncoated, and Sr-HAP, coated on untreated and surface treated Mg alloy in stimulated body fluid solution (SBF) was evaluated from Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The electrochemical measurements were carried out using three electrode cell arrangement using (CHI 760 electrochemical workstation (USA). The saturated calomel electrode served as the reference electrode, The working and counter electrodes were AZ91 Mg alloy and platinum, respectively. The potentiodynamic polarization studies were recorded with a sweep rate of 1 mV the electrochemical impedance studies were recorded with a frequency range 10 Hz–100 kHz.

3. Results and discussion

3.1 Surface characterization of the surface treated Sr-HAP coating

3.1.1 FT-IR analysis

Fig 1. Shows the FT-IR spectra of the Sr-HAP coating on acid treated AZ91 Mg alloy. The characterized peaks appeared at 3589 cm⁻¹ and 1639 cm⁻¹ are attributed to the stretching and bending mode of water molecule. The peaks corresponding to phosphate group of Sr-HAP acid treated at 1017 cm⁻¹ (v3) and 590 cm⁻¹ & 559 cm⁻¹ (v4) as well as the peaks observed at 1080 cm⁻¹ (v3) and 945 cm⁻¹ (v1). While the, absorption bands at 3448 cm⁻¹ and 636 cm⁻¹ are assigned to the stretching and bending vibration of OH⁻ groups of Sr-HAP. All these peaks confirm the formation of Sr-HAP coating on acid treated AZ91 Mg alloy.

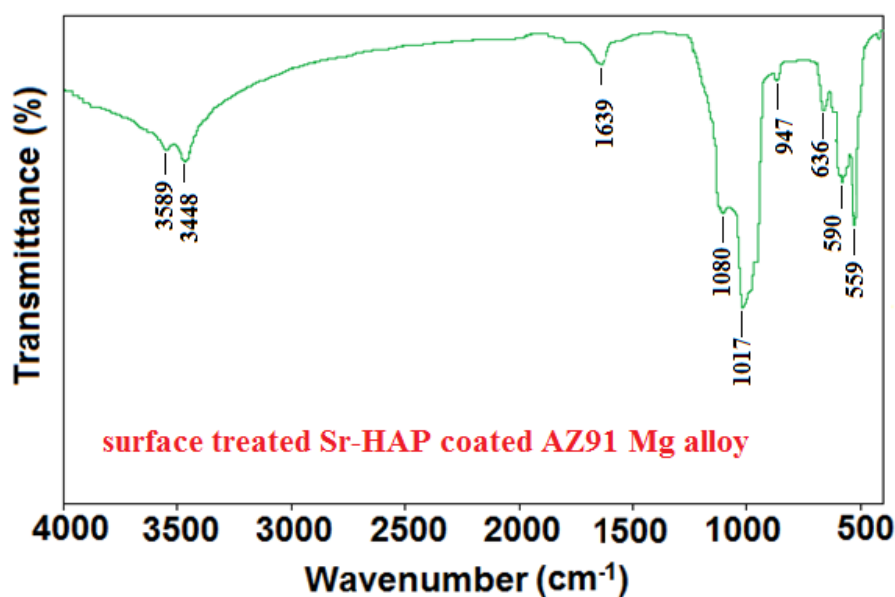


Fig: 1 The FT-IR spectra of surface treated Sr-HAP coated AZ91 Mg alloy

3.1.2 XRD analysis

Fig. 2 shows the XRD patterns of the coating on Sr-HAP coating on acid treated AZ91 Mg alloy. The main diffraction peaks of 2θ values of 25.8°, 31.7°, 32.4° and 32.6° was supports for the formation of Sr-HAP on acid treated Mg alloy. The characterized peak positions shifted towards the lower 2θ values from the standard

XRD patterns for HAP, indicating the substitution of Sr into the HAP lattices as reported by Gopi *et.al.*⁶¹ All these peaks confirm the present of HAP which are well evident from the ICDD card No: 09-0432 these results is good agreement for Sr-HAP coating on AZ91 Mg alloy.

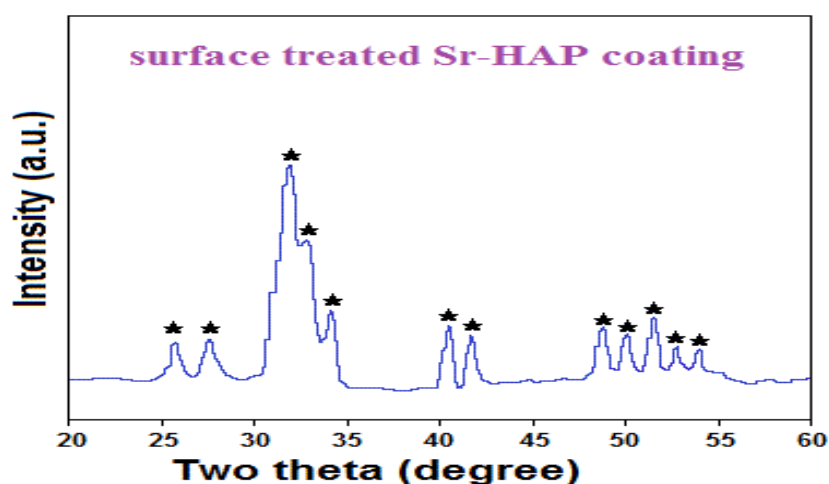


Fig: 2 The XRD pattern of surface treated Sr-HAP coated AZ91 Mg alloy

3.1.3. SEM and EDS analysis

Fig. 3(a-c) shows the HRSEM microstructure information of the Sr-HAP coating on untreated AZ91 Mg alloy & acid treated AZ91 Mg alloy. The surface morphology of Sr-HAP, coating on mg alloy at current densities of 6 mA cm⁻² for the duration of 30 min. Fig. 3(b) shows the porous

and uniform microstructure structure on surface treated mg alloy sample surface.

Fig. 3(d) shows the EDS spectrum results indicates the presence of Ca, Sr, O and P element in the Sr-HAP, coating on the surface of AZ91 Mg alloy.

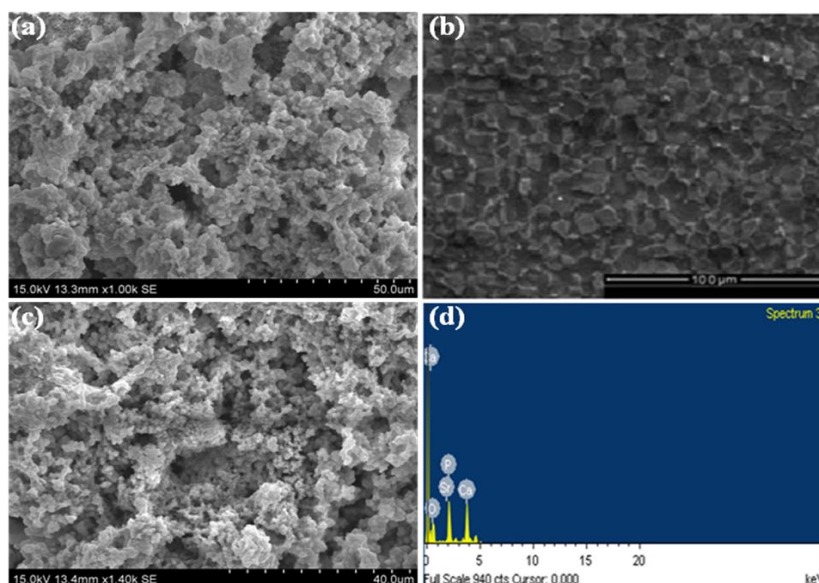


Fig: 3 HRSEM images of (a) Sr-HAP coated (b) surface treated (c) surface treated Sr-HAP coating on AZ91 Mg alloy (d) EDAX spectrum of surface treated Sr-HAP coating on AZ91 Mg alloy

3.2 Mechanical properties of surface treated Sr-HAP coating

3.2.1 Adhesion tests

The adhesion strength of the Sr-HAP coating on untreated and surface treated AZ91 Mg alloy samples were studied by pull-out test. The adhesion strength of Sr-HAP coating on surface treated Mg alloy was found higher (11.3 ± 0.3) than the Sr-HAP coating that

was obtained on untreated Mg alloy (9.1 ± 0.2) this shows that surface treated Mg alloy helps in improve the adhesion strength of Sr-HAP coating to the implant.

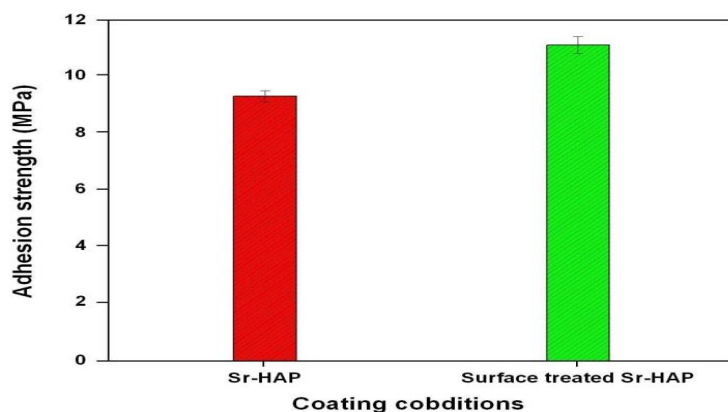


Fig. 4. (a) Adhesion strength of Sr-HAP, surface treated Sr-HAP coated AZ91 Mg Alloy Specimens.

3.3. Electrochemical characterization

Corrosion is one of the most important problems for orthopedic applications. corrosion resistance of AZ91

Mg alloy Sr-HAP coated surface treated and untreated, were investigated in SBF solution.

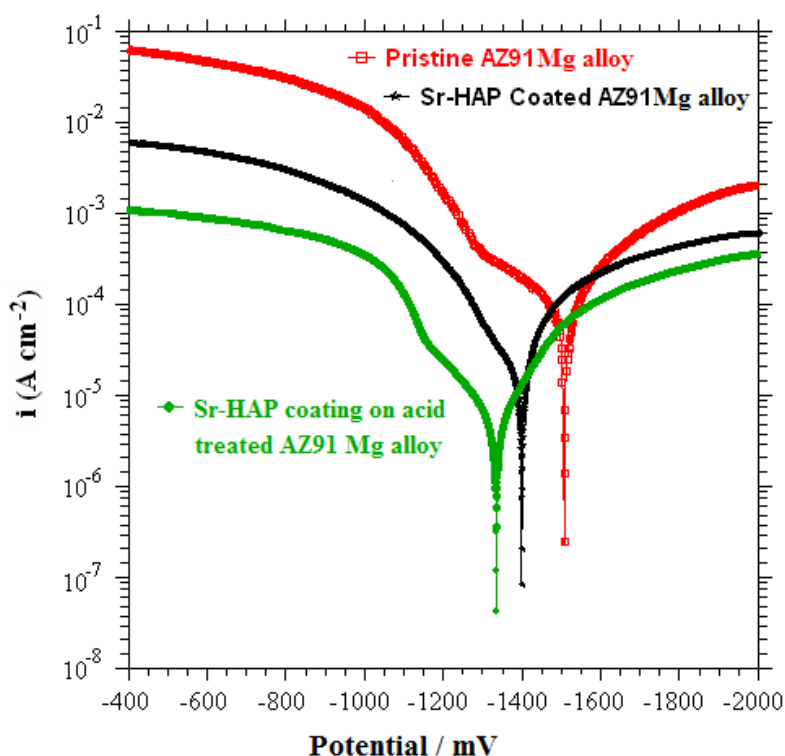


Fig.4. Potentiodynamic polarization curves for uncoated, Sr-HAP, and surface treated Sr-HAP coated AZ91 Mg alloy specimens in SBF solution.

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from the curves shown in Fig. 4. Uncoated mg alloy specimen was found to be (1510&9.1) and, Sr-HAP coating on untreated and treated mg alloy found to be (1390&2.6and 1335&1.4). (E_{corr}) generally shifted to the positive potential side. It was found that the polarization curves for Sr-HAP coated Mg alloy samples showed much positive shift compare to bare Mg alloy. Similarly Sr-HAP coated on surface

treated Mg alloy exhibited highly corrosion resistance compare to bare Mg alloy, Sr-HAP coated Mg alloy samples. Generally the positive side shift of corrosion potentials accompanied by decrease of corrosion current indicates that the tendency to corrosion of coated samples decreases. These Sr-HAP coated on surface treated Mg alloy proved to be better corrosion resistance implant.

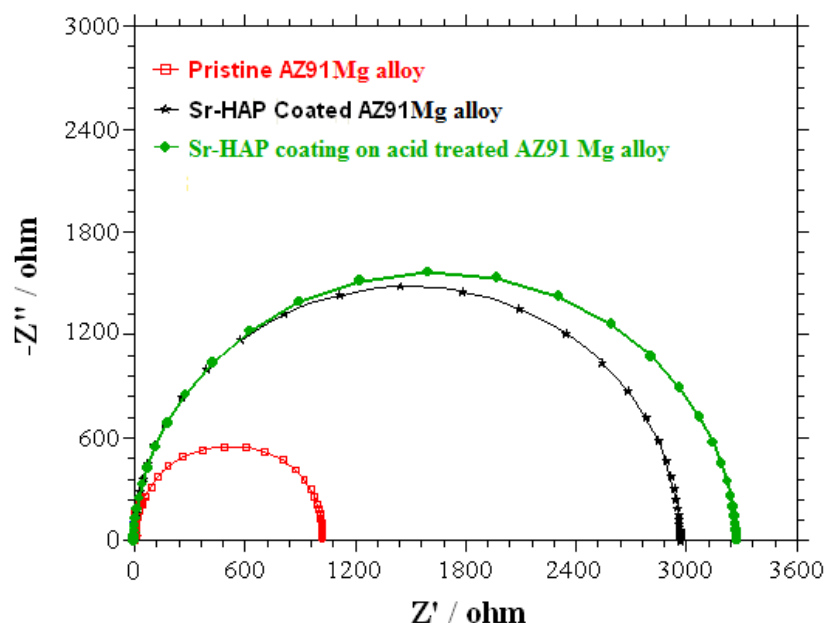


Fig. 5. Nyquist plots for uncoated, Sr-HAP, and surface treated Sr-HAP coated AZ91 Mg alloy specimens in SBF solution.

Fig. 5 shows the Nyquist plots obtained for uncoated Sr-HAP coated, Sr-HAP surface treated coated, were performed in SBF solution were fitted Using equivalent circuits. For the uncoated Mg alloy samples polarization resistance (R_p) values were 1020 and Sr-HAP coated samples these values were found to be 2976. respectively for the Sr-HAP coating on surface treated AZ91 Mg alloy were found to be 3468 which is higher than that of the uncoated, Sr-HAP and Sr-HAP surface treated coating on AZ91 Mg alloy is highly corrosion resistance on Mg alloy surface.

CONCLUSION:

In this study, electrochemical deposition was successfully coating on surface treated Mg alloy for improved corrosion resistance and bioactivity. The surface treated Sr-HAP coating exhibited higher corrosion resistance in SBF solution then pure Sr-HAP coating. Furthermore adhesion strength is improved. These results is demonstrated electrodeposition on surface treated Sr-HAP coatings on Mg alloy for use as bioactive coating materials.

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