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Electrodeposition of manganese substituted hydroxyapatite/zinc oxide duplex-layer on AZ91 magnesium alloy for orthopaedic applications

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Abstract : AZ91 Magnesium alloy (AZ91 Mg alloy) has been developed as a biodegradable implant material because of its outstanding biodegradability and mechanical properties. But the poor corrosion resistance of AZ91 Mg alloy in physiological solution limits its biomedical applications. In order to improve the corrosion resistance and biological performance of AZ91 Mg alloy, we have fabricated a manganese-substituted porous hydroxyapatite (Mn-HAP)/zinc oxide (ZnO) duplex layer on AZ91 Mg alloy by electrodeposition. The porous Mn-HAP/ZnO duplex-layer coating on AZ91 Mg alloy was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy and energy dispersive X-ray analysis (FESEM-EDAX). Also, the mechanical properties of the duplex-layer coatings were evaluated using adhesion and Vickers micro-hardness tests. The effects of the duplex-layer coating on the corrosion behavior of AZ91 Mg alloy were also investigated in simulated body fluid using electrochemical studies. The potentiodynamic polarization results indicated that the corrosion resistance of AZ91 Mg alloy was significantly improved by the duplex-layer coating. Hence, from the obtained results we believe that the duplex-layer made of ZnO together with porous Mn-HAP on AZ91 Mg alloy could provide effective corrosion protection and enhanced bioactivity. Thus, duplex-layer coated AZ91 Mg alloy can serve as a promising candidate for orthopaedic applications.

Keywords: AZ91 Mg alloy, corrosion resistance, biodegradable implant, orthopaedic applications.

1. Introduction

Magnesium and its alloys have been considered as innovative orthopaedic implant material because of its biocompatibility, biodegradability and mechanical properties closer to natural bone. However, Mg alloys exhibit a poor corrosion resistance due to their high chemical reactivity, which critically restricted their widespread use in the clinical applications.[1,2,3] Hydroxyapatite [HAP, $(Ca_{10})(PO_4)_6(OH)_2$] bioceramics have

attracted special attention as orthopaedic implant biomaterials because its ability to promote cellular functions and good affinity to living bone tissues. Modification of HAP through various ionic substitutions is an attractive topic by considering the major components of biological tissues, such as bone, teeth and some of the invertebrate skeletons. Hence, researchers focus on modifying the HAP by substitution of various ions such as magnesium (Mg^{2+}), strontium (Sr^{2+}), manganese (Mn^{2+}), zinc (Zn^{2+}), etc. The metal ion substituted HAP has drawn much scientific interest since substituted HAP coating have shown to improve both the bioactivity and mechanical properties of implants.[4,5] Among various divalent metal ions, Mn^{2+} has been determined as a potential element for bone resorption and bone metabolism. Manganese has been substituted in HAP coatings to improve the corrosion resistance, biocompatibility and osteoblast differentiation of bone.[6, 7] Several coating techniques have been reported for the development of bioceramic material onto the metallic substrate. Among the different coating techniques, electrochemical deposition method has unique advantages due to its relatively low deposition temperature, process simplicity, the capability of forming a uniform coating on a porous substrate and the availability and low cost of equipment[8].

The objective of our work was to electrochemically fabricate porous Mn-HAP coating on AZ91 Mg alloy. Although this kind of porous microstructure of Mn-HAP may be favourable for the growth of cells and rapid adhesion, resulting in an essential stronger bond to the parent tissue will result in a low adhesion coating and also decrease in corrosion resistance of the porous coating on AZ91 Mg alloy[9]. To overcome these problems, surface modification techniques like coating of oxide is used to improve the corrosion resistance of AZ91Mg alloy. Zinc oxide (ZnO) is a novel multi-functional inorganic material with stable chemical and physical properties, has extensive potential applications in various research areas. ZnO plays an essential role in bone formation and in the improvement of corrosion resistance and the bioactivity property of AZ91 Mg alloy. In the present work, ZnO was coated onto AZ91 Mg alloy for improving the corrosion resistance and also the bioactivity of the substrate[10].

The present work deals with the development of Mn-HAP coating on ZnO coated AZ91 Mg alloy for the improved adhesion strength, corrosion resistance and biological properties. Here, the first layer (i.e.,) ZnO coated AZ91 Mg alloy improves the corrosion resistance.

The second layer Mn-HAP coating which is porous in nature with good bioactivity will certainly pave the way for the development of bone tissues through pores in between them.

Thus, the duplex-layer coated Mg alloy is believed to be the promising candidate for orthopaedic applications.

2. Experimental

2.1. Mg alloy surface preparation

AZ91 Mg alloy (elemental composition (wt%): 0.59% Zn, 0.17% Mn, 8.63% Al, <0.05% Cu, <0.05% Fe and balance Mg) with dimensions of 10×10×5 mm^3 was used as the substrate material. Before the deposition process, all the specimens were mechanically ground with various silicon carbide (SiC) abrasive sheets (800, 1000 upto 2000 grit) to obtain homogeneous roughness, then ultrasonically cleaned with ethanol, and acetone for 10 min to remove AZ91 Mg alloy surface residues, and then finally dried at room temperature and then used for further studies.

2.2. Preparation of electrolyte

The electrolyte solution for Mn-HAP deposition was prepared by dissolving the analytical grade calcium nitrate dihydrate ($Ca(NO_3)_2.2H_2O$), manganese nitrate ($Mn(NO_3)_2.6H_2O$) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) in deionised water. The pH was adjusted to 4.7 using dilute NH_4OH (or) HCl. Similarly, the electrolyte for ZnO coating is adopted from the method followed by [11]. All the chemicals were of analytical grade used without further purification and deionized water was used throughout their experiments

2.3. Electrochemical deposition

2.3.1. Electrodeposition of ZnO on AZ91Mg alloy

Electrodeposition of ZnO on AZ91 Mg alloy was carried out in a three electrode cell arrangement by galvanostatic method using an electrochemical workstation (CHI 760C(CH Instruments, USA)). The electrodeposition of ZnO was carried out in 0.05 M $Zn(NO_3)_2.6H_2O$ solution at the current densities of 1 mA

cm^{-2}. The deposition was carried out for 30 min at the room temperature. After the deposition, the ZnO coated AZ91 Mg alloy surface was washed with deionized water to remove residual electrolyte, and then dried for 24 h.

2.3.2. Mn-HAP coating on ZnO coated AZ91 Mg alloy

The electrolytic deposition of Mn-HAP coating on AZ91 Mg alloy has been carried out at current densities of 9 mA cm^{-2}. An aqueous solution containing 0.4 M $Ca(NO_3)_2.2H_2O$, 0.1 M $Mn(NO_3)_2.6H_2O$ and 0.3 M $(NH_4)_2HPO_4$, was subjected to magnetic stirring at room temperature for 2 h. The electrolyte solution is taken in the appropriate molar ratio (Ca + Mn)/P of 1.67. The electrodeposition was performed for 30 min and the coatings were gently rinsed with deionized water and then dried for 24 h.

2.4. Characterization of the duplex-layer (Mn -HAP/ZnO) coatings

Fourier transform-infrared spectroscopy (FT-IR, Impact 400 D Nicholet Spectrometer) was utilized to identify and confirm the functional groups of the as-formed coatings in the frequency range from 4000 cm^{-1} to 400 cm^{-1}. Phase compositions of the as-formed coatings were analyzed by X-ray diffraction (XRD, Seifert, X-ray diffractometer Siemens D500 Spectrometer)

The morphological features and the elemental composition of the as-deposited coatings were observed after gold sputtering using a high resolution scanning electron microscopy (HRSEM, JEOL JSM-6400, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS).

2.5. Mechanical properties of the duplex-layer (Mn-HAP/ZnO) coatings

2.5.1. Adhesion test

The Adhesion strength of Mn-HAP, ZnO and Mn-HAP/ZnO coated AZ91 Mg alloy specimens were examined by pull-out test with at least five measurements for each experiment. All the experiment samples were subjected to pull-out test using a universal testing machine (Model 5569, Instron) at a crosshead speed of 1 mm min^{-1}.

2.5.2. Hardness tests

Vickers micro-hardness tests were performed on the Mn-HAP, ZnO and Mn-HAP/ZnO duplex-layer coated AZ91 Mg alloy samples using Akashi AAV-500 series hardness tester. Each sample was subjected to at least six measurements under the hardness testing.

2.6. Electrochemical investigation of the duplex-layer (Mn-HAP/ZnO) coatings

Potentiodynamic polarisation studies was carried out in SBF solution to evaluate the corrosion resistance of bare AZ91 Mg alloy, HAP, Mn-HAP, ZnO and Mn-HAP/ZnO coated AZ91 Mg alloy samples, respectively. The electrochemical experiments were carried out in a 50 ml SBF solution at a generally accepted human body temperature of 37 ± 1 ºC.

3. Results and discussion

3.1. Surface characterization of the duplex-layer (Mn-HAP/ZnO)coatings

3.1.1. FT-IR analysis

The FT-IR analysis of the duplex-layer (Mn-HAP/ZnO) coated AZ91 Mg alloy was carried out and the corresponding spectrum is shown in Fig. 1. The formation of Mn-HAP/ZnO duplex-layer exhibited the following peaks:

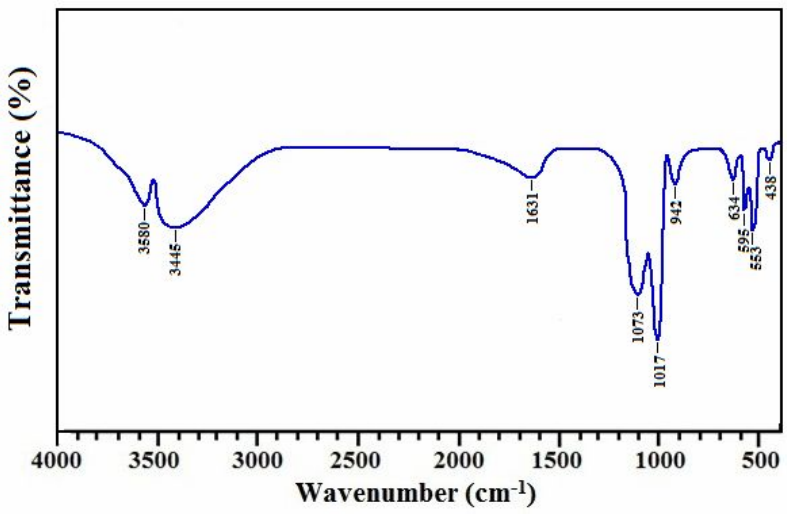

Fig. 1. FT-IR spectrum of Mn-HAP/ZnO duplex-layer coating.

The broad peaks at 3445 cm^{-1} and 1631 cm^{-1} are attributed to the stretching and a bending mode of water molecule. The characteristic peaks located at 1017 cm^{-1} (ν_3) and 595 cm^{-1} & 553 cm^{-1} (ν_4) as well as the peaks observed at 1073 cm^{-1} (ν_3) and 942 cm^{-1} (ν_1) were assigned to the phosphate groups in Mn-HAP. Moreover, absorption bands at 3580 cm^{-1} and 634 cm^{-1} are due to the stretching and bending vibration of OH groups of Mn -HAP, respectively. Apart from these, the peak at the region of 438 cm^{-1} is attributed to the Zn-O stretching and also a broad absorption band at 3440 cm^{-1} confirms the -OH groups on the surface of ZnO coating. All these peaks confirm the formation of Mn-HAP/ZnO duplex-layer coating on AZ91 Mg alloy.

3.1.2. XRD analysis

The XRD pattern of Mn-HAP/ZnO duplex-layer coated AZ91 Mg alloy is shown in Fig. 2. The main diffraction peaks identified for Mn-HAP are in good agreement with the standard data for HAP (ICDD card No. 09-0432).

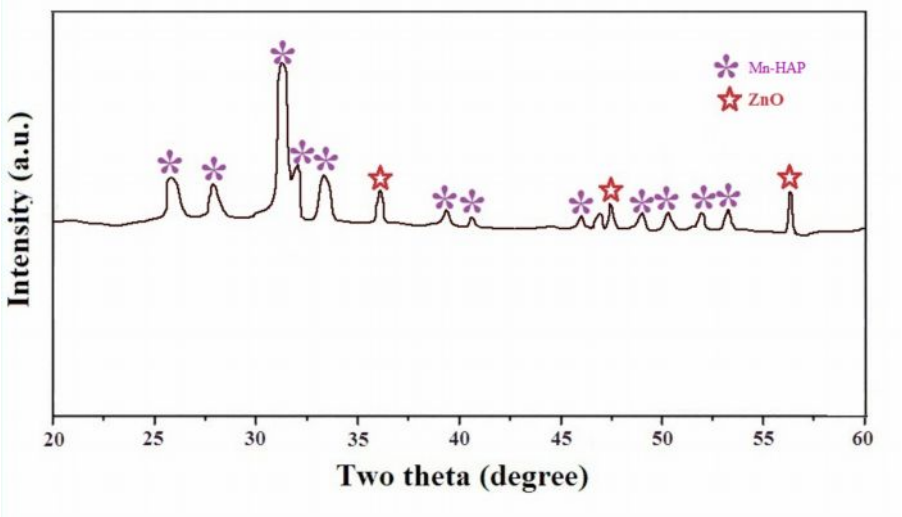

Fig. 2. XRD patterns of Mn -HAP/ZnO duplex-layer coated AZ91 Mg alloy.

The major intense peaks (Fig. 2) are observed at 2θ values of 25.6°, 31.9°, 32.3° and 32.5° corresponds to Mn-HAP and no other secondary peaks were found. Similarly, the diffraction peaks of ZnO are located at 2θ values of 36.2°, 47.4° and 56.5° which are well evident from the ICDD card No. 89-0511. It indicates that the duplex-layer coating contains the Mn-HAP and ZnO crystalline phases.

3.1.3. SEM and EDS analysis

Figure 3 reveals the HRSEM microstructure information of ZnO and Mn- HAP/ ZnO duplex-layer coating on AZ91 Mg alloy and the EDS spectrum of duplex-layer coated AZ91 Mg-alloy.

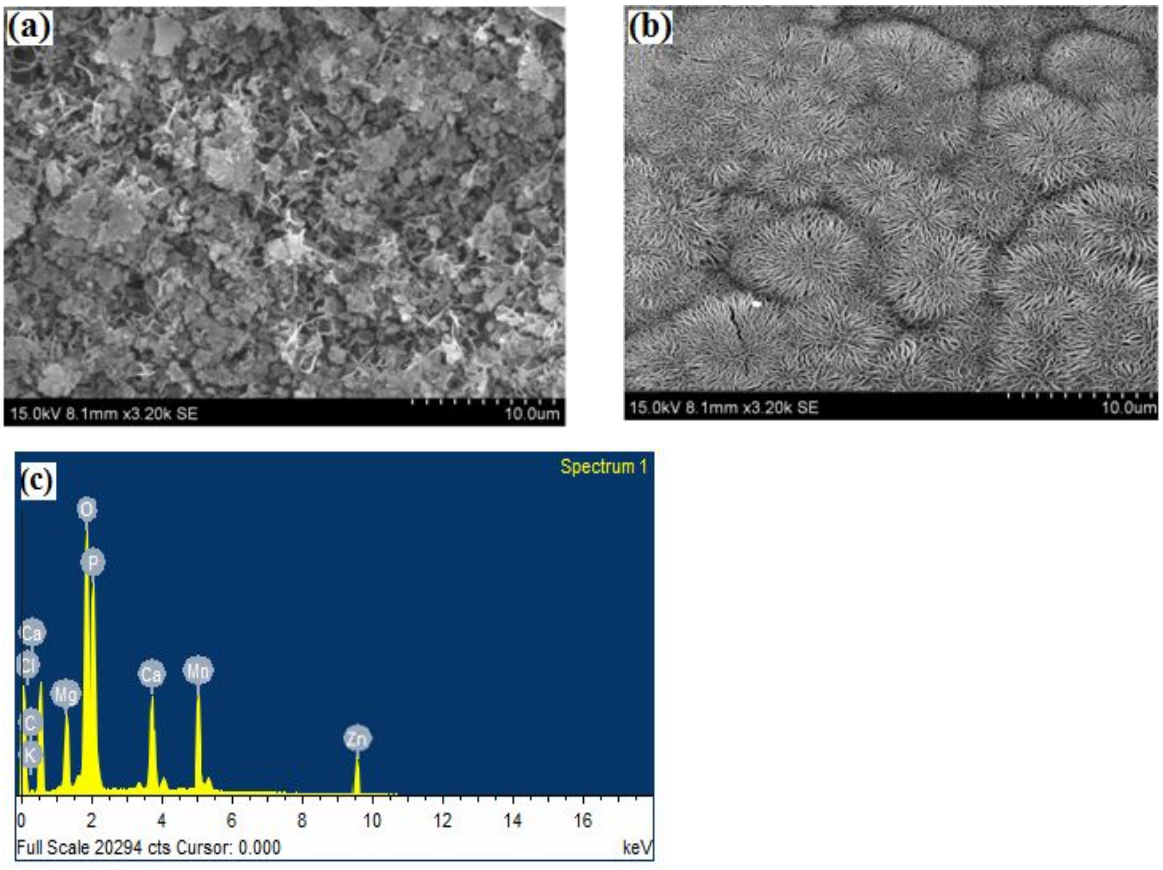

Fig. 3. HRSEM images of (a) ZnO coating (b) Mn-HAP/ZnO duplex-layer coating on AZ91 Mg alloy and (c) EDS spectrum of Mn-HAP/ZnO duplex-layer coating on AZ91 Mg alloy.

The surface morphologies of ZnO coating on AZ91 Mg alloy at current densities 1 mA cm^{-2} for the duration of 30 min is shown in Fig. 3(a). The morphology of the ZnO coating at current density of 1 mA cm^{-2} exhibited uniform distribution of micro flower structure. The Mn-HAP coating on ZnO coated AZ91 Mg alloy (Fig. 3b) composed of uniform, compact and interconnected porous network like microstructure. However, the porous network structure of the coating (Mn-HAP) on AZ91 Mg alloy as well as on ZnO coated AZ91 Mg alloy may be beneficial for the initiation of bone formation, providing abundant site for the growth of osseous tissue. Fig. 3c shows the EDS spectrum of the duplex-layer (Mn-HAP/ZnO) coated AZ91 Mg alloy. This spectrum indicates the presence of Ca, Mn, Zn, O and P there by confirming the existence of Mn-HAP/ZnO duplex-layer coating on the surface of AZ91 Mg alloy.

3.3. Mechanical characterisation of the duplex-layer (Mn-HAP/ZnO) coated AZ91 Mg alloy.

3.3.1 Adhesion strength

The adhesion strength of the Mn-HAP, ZnO and duplex-layer (Mn-HAP/ZnO) coated AZ91 Mg alloy was evaluated. The adhesive strength of the Mn-HAP coating on the ZnO coated AZ91 Mg alloy (12.1 MPa) was higher than that of the individual coating of Mn-HAP (9.8 MPa) and ZnO (13.1 MPa) coated AZ91 Mg alloy. This improved adhesion strength of the as-formed duplex-layer coating will make it suitable for orthopaedic applications.

3.3.2. Hardness

The Vickers hardness (H_v) values for the Mn-HAP, ZnO and duplex-layer Mn-HAP/ZnO coatings on AZ91 Mg alloy samples, were evaluated. For the Mn-HAP and ZnO coated AZ91 Mg alloy specimens, the Vicker's micro-hardness values were found to be 316.2±10.6 and 110.5±13.4, respectively. Whereas, the H_v value obtained for the duplex-layer coated AZ91 Mg alloy was 358.6±11.1, which is higher than that of the Mn-HAP and ZnO coated AZ91 Mg alloy specimens.

3.4. Electrochemical characterisation

3.4.1. Potentiodynamic polarisation studies

Figure 4 reveals the potentiodynamic polarisation curves of HAP, Mn-HAP, ZnO and duplex-layer Mn-HAP/ZnO coated AZ91 Mg alloy samples, respectively in SBF in the potential range of -600 mV to -2200 mV vs. SCE at OCP condition.

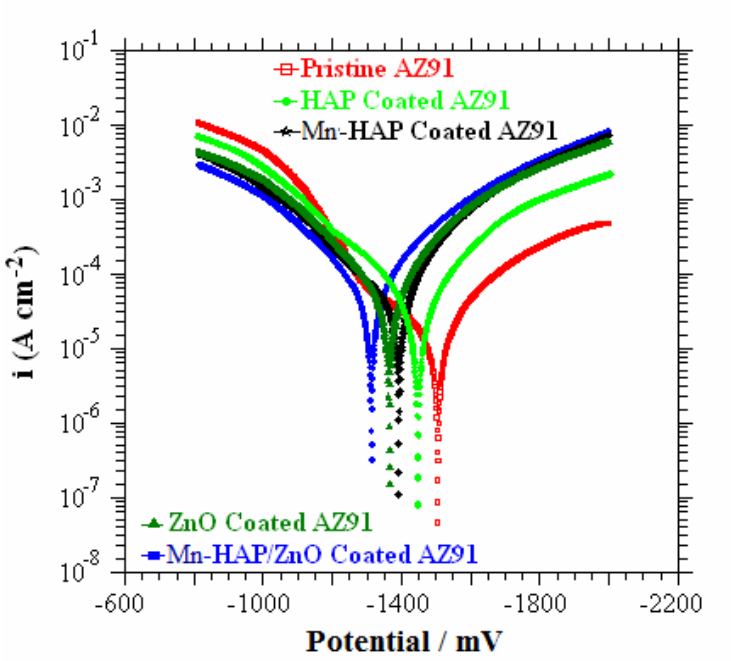

Fig.4. Potentiodynamic polarisation curves of uncoated, HAP, Mn-HAP, ZnO and Mn-HAP/ZnO duplex-layer coated AZ91 Mg alloy specimens in SBF solution.

The potentiodynamic polarization curves obtained reveals that the E_{corr} and i_{corr} values for the uncoated AZ91 Mg alloy specimen were found to be -1510 mV vs. SCE and 9.1 A cm^{-2}, respectively. For the HAP and Mn-HAP coating on AZ91 Mg alloy the E_{corr} and i_{corr} values were -1458 mV vs. SCE and 6.3 A cm^{-2}; -1368 mV vs. SCE and 2.4 A cm^{-2}, respectively. Thus, the polarization values obtained for Mn-HAP coated AZ91 Mg alloy were found to be nobler than that of the HAP coated AZ91 Mg alloy specimen. While the polarisation curve for ZnO coated AZ91 Mg alloy showed E_{corr} and i_{corr} values as -1361 mV vs. SCE and 1.6 A cm^{-2}, respectively. From Fig.4, the ZnO coated AZ91 Mg alloy sample is found to be more protective than the Mn-HAP coated AZ91 Mg alloy specimen. The higher E_{corr} value obtained for ZnO coated AZ91 Mg alloy are due to the formation of compact and uniform microstructure coating. The polarisation curve of the Mn-HAP/ZnO duplex-layer coated AZ91 Mg alloy specimen shows E_{corr} and i_{corr} values of -1320 mV vs. SCE and 1.2 A cm^{-2}, respectively.The shift of E_{corr} and i_{corr} values towards the noble direction is an indication that the Mn-HAP/ZnO duplex-layer coating possessed higher corrosion resistance in SBF solution.

4. Conclusions

In summary, this work recognized the possibility and effectiveness of fabricating the duplex-layer (Mn-HAP/ZnO) coating on AZ91 Mg alloy by electrodeposition for improved corrosion resistance and bioactivity. The surface morphological of duplex-layer coating on AZ91 Mg alloy exhibited the uniform deposition of porous Mn-HAP on ZnO coated AZ91 Mg alloy which indicated that the as-formed coatings could protect

AZ91 Mg alloy more effectively. The duplex-layer (Mn-HAP/ZnO) coatings were uniform and adherent in nature. Having observed and evaluated the corrosion protection performance of all the as-formed coatings, we found that the duplex-layer coatings significantly improved the corrosion resistance of AZ91 Mg alloy. The porous Mn-HAP coating on ZnO coated AZ91 Mg alloy allow for the biological fixation of biodegradable implants to host bone via in growth into the integrated porous microstructure. Thus, the duplex-layer coated AZ91 Mg alloy appears to have promising in orthopedic applications.

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