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Ce-doped MgO films on AZ31 alloy substrate for biomedical applications: preparation, characterization and testing

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Abstract

Magnesium ions, MgO nanoparticles and thin films, magnesium alloys and cerium compounds are materials intensively studied due to their corrosion protection, antibacterial and pharmacological properties. In this work, we have designed, prepared and investigated, novel thin films of MgO doped with cerium, deposited on Mg alloy (AZ31) for temporary implants, in order to enhance their life time. More precisely, we report on microstructure and corrosion behavior of MgO pure and doped with 0.1 at % Ce films, fabricated by sol–gel route coupled with spin-coating technique, on AZ31 alloy substrate. A modified sol–gel method that start from magnesium acetylacetonate, cerium nitrate and 2–methoxyethanol (as a stabilizer for the sol) was been used successfully for cerium doped MgO sol precursor preparation. The structure and morphology of the surface of the coatings, before and after immersion for 7–30 d in Hank's solution at 37 ◦C, were characterized by x-ray diffraction (XRD), scanning electron microscopy, high-resolution transmission electron microscope, x-ray photoelectron spectroscopy and Fourier infrared transmittance spectrum (FT–IR). A comparison between the corrosion protection of undoped MgO and MgO doped with 0.1 at % Ce coatings on the AZ31 alloy substrate is performed by electrochemical tests and immersion tests using open circuit potential and electrochemical impedance spectroscopy in Hank's solution, at 37 ◦C. The electrochemical results showed that the protection of the AZ31 alloy substrate against corrosion was better with the doped with 0.1 at % Ce MgO film deposited than with pure MgO coting. The investigations of the films after immersion in Hank's solution, at 37 ◦C, for 7, 21 and 30 d indicated that the grown layer on the film is bone like apatite that suggests a good bioactivity of 0.1 at % Ce–doped MgO coating. Our work demonstrates that the performance corrosion protection of the biodegradable magnesium alloys used for orthopedic applications, in simulated physiological environments (Hank and Ringer) can be enhanced through coating with Ce^{3+} doped MgO sol–gel thin film.

Introduction

Magnesium based alloys have become as a new generation of medical metallic materials. With or without surface modification, these alloys have attracted much attention due to their biodegradability by corrosion in physiological environment, their nontoxicity and ability to regulate osteoblasts and stimulate the growth of new tissue [1, 2]. Magnesium is essential to human metabolism and is found in bone tissue [3]. To ensure the success of magnesium based materials for temporary implants, the corrosion rate must be reduced and controlled. The repair of damaged hard tissue usually requires that implanted materials remain at least 12 weeks [4]. However, a Mg alloy implant completely dissolved after 6 weeks [5]. The naturally formed MgO and Mg(OH)2 films are not good protective layers because they dissolve easily with existing chloride or sulphate in the body fluid [6]. The surface modification by deposition of protective coatings is the most effective solution that can remarkably enhance the corrosion resistance and control the degradation rate of the metals. Many studies have been reported the use of the magnesium oxide layer as protective coating for the magnesium alloys [7–9]. Magnesium oxide (MgO) has several properties like high chemical stability, and electrical insulating properties [10]. Antibacterial activities of MgO nanoparticles against various pathogens have also been reported [11–13]. The MgO films can be prepared by different coating technologies using: pulsed laser deposition [14], electron beam evaporation [15], magnetron sputtering [16], chemical vapor deposition [17], spray pyrolysis of Mg(2,4–pentanedionate)2 [18], micro-arc oxidation [19], electrodeposition [7, 8] and sol–gel methods [20]. Among the various techniques, the sol–gel method is one of the most widely used to produce high quality coatings due to the possibility to control the stoichiometry and homogeneity of the resulting material. The sol–gel technique provides excellent adhesion between the metallic substrate and the topcoat by low process temperature. There are a few reports on the preparation of MgO thin film via sol–gel route, which differ by the starting materials, the use or not of stabilizers, the deposition method of the precursor sol (spin coating or dip coating) and the type of deposition substrate. MgO thin films preparation by sol–gel method involve the use of alkoxide as precursors [21]. Menon and Bullard [21], prepare precursor of MgO from magnesium ethoxide (Mg(OCH2CH3)2, dispersed in absolute ethanol and refluxed by adding acetic acid (molar ratio 27:3:1 of EtOH:AcOH:Mg(OEt)2. The acetic acid acts as stabilizer of the sol precursor against formation of Mg(OH)2. Precursor solution was spin-cast onto a boron-doped Si (111) wafer. Chakrabarti et al [22], fabricated magnesium oxide films deposited onto soda lime glass substrates by sol–gel technique from magnesium acetate in ethanol and glacial acetic acid; the sol compositions were: Mg acetate/acetic acid/dry ethanol = 1:1–3:29 (molar ratio). A H2O2-assisted sol–gel method for the preparation of precursors for formation of thin films of MgO is described in the report [23]. Sols with Mg to H2O2 ratios of 1:1 and 1:10 were prepared by addition of Mg(OCH3)2 to methanolic H2O2. These sols were deposited by spin coating technique on Si(100) substrate. Yoon and Kim [24], prepared (111) oriented MgO film on Si substrate by spin-coating sol–gel method, using magnesium ethoxide as the starting material. Ho et al [25], prepared polycrystalline MgO thin films with (111) and (100) preferential orientations by dip-coating sol–gel technique on (100)Si substrate in a nitrogen atmosphere, using magnesium methoxide as the starting material. Bazhan et al [26], prepared MgO thin films on glass substrate by dip-coating sol–gel route starting from Mg-acetate tetrahydrate (CH3COO)2 Mg·4H2O), methanol and acid nitric, without and with acetylacetone as stabilizer. In this paper, we report on the cerium-doped magnesium oxide film deposited on AZ31 magnesium alloy substrate by spin coating technique of sol precursor prepared from magnesium acetylacetonate, cerium nitrate hexahydrate and 2– methoxyethanol. To the best of our knowledge, this work presents for the first time the use of magnesium acetylacetonate as a reagent for the sol–gel synthesis of MgO film. In this case, cerium is used as a corrosion inhibitor thanks to its ability to precipitate as insoluble hydroxide on cathode sites, hindering or even completely blocking the corrosion activity in the areas where the oxide coating has suffered damage (self-healing effect) [27–33]. Although the selfhealing effect provided by cerium has been confirmed by numerous studies [28, 30, 33]. This phenomenon can extend the service life of the coating [28, 31]. As dopant, Cerium can also improve the biological and antibacterial proprieties of the

MgO coating in physiological media [34, 35]. It exhibited significant antibacterial activity against S. aureus and E. coli bacterial strains. Moreover, several cerium salts including chloride, nitrate and stearate were known for their antibacterial activity [36, 37]. Zhou et al [38] showed that the promoted osteoblasts by cerium (III) exhibited an enhanced bone resorption capability. Based on the above arguments, the purpose of the present work is to evaluate the effect of cerium dopant on the physicochemical and anticorrosive features of MgO doped with cerium sol–gel coatings deposited on the AZ31 magnesium alloy.

2. Experimental

2.1. Material synthesis. MgO doped with 0.1 at % Ce thin film was prepared by sol–gel route and spin coating deposition technique, starting from magnesium acetylacetonate anhydrous ($Mg(CH_3COCHCOCH_3)_2$, 98%), cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%), and 2—methoxyethanol anhydrous ($C_3H_8O_2$, 99.8%). All reagents provided by Sigma–Aldrich. Magnesium acetylacetonate was dissolved in 2– methoxyethanol, at 65 °C under continuous magnetic stirring. 2–methoxyethanol was used both as solvent and as stabilizer for the as- prepared solution. The required amount of cerium nitrate hexahydrate for preparation of 0.1 at % cerium–doped MgO, was dissolved in distilled water under magnetic stirring. Then, the resulted solution was added to the solution of magnesium acetylacetonate, in order to obtain the sol precursor of 1 at % cerium–doped MgO with a concentration of 2 M. The sol was stirred at 65 °C, for another 2 h to achieve a good homogenization. Magnesium alloy AZ31 square tiles with dimensions of 15 × 15 × 3 mm and, chemical composition (analyzed by energy dispersive spectroscopy (EDS)) of 95 at % Mg, 3 at % Al, 1 at % Zn and 1 at % (Mn, Si, Fe, Ca), were used as substrates to deposit Ce–doped MgO sol precursor via spin-coating technique. In order to increase the adhesion of the sol to the substrate, the surface of AZ31 substrate was polished with Si–C abrasive papers type P1200. Then, ultrasonically cleaned successively with acetone and absolute ethanol. A spin coater Model KW–4 A was used for spin-coating deposition of Ce doped MgO precursor sol on AZ31 magnesium alloy. The film was deposited from fresh sol through spin coating at 1700 rpm for 20 s. After each spin-coating, the layer was heated at 180 °C for 3 min in order to evaporate the solvent and increasing the adhesion of the next layer. The Ce– doped MgO film was obtained by repeating several times the deposition and heating cycle. The coated substrate with deposited film was finally annealed in nitrogen at 550 °C, 3 h, using a rate of heating of 8 °C min^{-1} in order to prevent the formation of cracks in the as-deposited film and, for crystallization of the Ce–doped MgO film. In addition, undoped MgO film was prepared by the same experimental procedure.

2.2. Characterization methods. The crystallographic structure of the undoped and Ce–doped MgO thin films were examined by using a Bruker–AXS tip D8 ADVANCE diffractometer. CuKα radiation (wavelength 1.5406 Å) with a grassing incidence configuration and, LiF crystal monochromator and Bragg–Brentano diffraction geometry were employed. x-ray diffraction (XRD) data were acquired at 25 °C with a step–scan interval of 0.02° and a step time of 10 s. The microstructure of the thin films was qualitative and quantitative analyzed using a FEI QUANTA INSPECT F SEM, equipped with a field emission gun (EDS) and a JEOL JEM- ARM200F high-resolution transmission electron microscope (HR-TEM) operated at 200 kV. Xray photoelectron spectroscopy (XPS) was used to examine the chemical composition of the MgO doped with 0.1 at % Ce film surface after immersion in Hank's solution, at 37 °C for 7 d, 21 d and 30 d. The measurements were carried out in an analysis chamber equipped with a 150 mm hemispherical electron energy analyzer (Phoibos), a dual-anode (Mg/Al Kα) x-ray source, and a monochromatized (Al Kα/Ag Lα) x-ray source, which formed part of a complex surface science cluster (Specs). Monochromatized Al Kα1 (1486.74 eV) radiation was used to extract electrons from the sample, whereas the analyzer was operated in fixed–transmission mode with a pass energy of 20 eV and an estimated total resolution of about 0.75 eV. The base pressure during the measurements was about 10−9 Pa. Sample neutralization was achieved using an electron flood gun operated at energy of 1 eV and an electron current of 100 mA. The energy scale was calibrated to the standard value of C 1 s (284.6 eV). The Fourier infrared transmittance spectrum (FT–IR, Agilent 5500), recorded at room temperature, was used in order to analyze the composition of the grown layer on Ce—doped MgO film, after immersion in Hank's solution, at 37 ◦C, for 7 d, 21 d and 30 d. To evaluate the anticorrosion performance of Ce–doped MgO films coatings, electrochemical impedance spectroscopy (EIS) tests were performed at open circuit potential after 24 h of immersion in Hank's solution at 37 ◦C using a potentiostat/galvanostat VoltaLab (PGZ 301, Dynamic-EISVoltammetry) from Radiometer Analytical (France) coupled by the VoltaMaster 4 software. The measurements were carried-out on three electrodes cylindrical cell [39, 40]. The samples of coated AZ31 alloy used are active surface plates 0.196 cm2 as working electrode. A silver/silver chloride electrode (Ag/AgCl) and a large platinum plate were used as reference and counter electrodes, respectively. All the EIS results were processed by Voltamaster 4 software by applying an amplitude perturbation of 10 mV and a scanning frequency ranging from 105 Hz to 10−2 Hz with 5 points per decade. Furthermore, the experimental spectra were fitted to equivalent circuit functions using a simple procedure by means of Zsimpwin software. The corresponding program was described elsewhere [40–42].

3. Results and discussion

3.1. Structural and morphological characterization of the MgO films Figure 1 shows the XRD pattern of pure and doped with 0.1 at % Ce MgO films, obtained by annealing at 550 ◦C, 3 h in N2. As can be seen in figure 1, there are peaks of the cubic phase of MgO (space group: Fm–3 m, JCPDS card No. 04–013-2090 [43]) and, peaks assigned to Mg hexagonal phase (space group P63/mmc, Pattern: 04−015−2580 [44]) and to cubic phase of Mg0.63Al0.37 (space group: I–43 m, JCPDS: 01– 081–2919 [45]) which belongs to the AZ31 substrate. The program package Powder Cell 2.4 [46] was used to refinement of the MgO specific peaks observed at 2θ of 42.86◦ and 62.06◦ , indexed to (200) and (220) crystal planes of the face-centered cubic phase of Ce−doped MgO film. The values of the crystallographic parameter 'a', volume of cell (Vol), and crystallite size (d) of the undoped and 0.1 at % Ce–doped MgO films are listed in table 1

As can be seen in table 1, the values of crystallographic features (a andVol) of undoped MgO increase by incorporating of cerium (Ce3+) in the lattice of MgO film. The Ce3+ ions substitute Mg2+ ions, that produces an expansion of the crystalline cell, due to the higher ionic radius of Ce3+ (1.02 Å) compared with the one of Mg2+ (0.65 Å) [47]. Figure 2 shows the results of scanning electron microscopy (SEM) investigations on the microstructure of 0.1 at % Ce−doped MgO films deposited on AZ31 substrate and annealed at 550 ◦C, 3h in N2 . The SEM micrographs of Ce–doped MgO film show a granular structure, specific to the films deposited from precursor sols. The surface of the film shown nanometric grains with an average grain size of 12.5 nm, which forms submicronic agglomerates, as shown in figure 2(a). In order to determine the thickness of the Ce–doped MgO film, SEM images were recorded in backscattered electrons mode on the fresh cross section of this film together with corresponding chemical elements map (see figures 2(b)–(e)). An average thickness of 2.5 μm was found for the MgO doped with 0.1 at % Ce film. Figure 3 shows the transmission electron microscopy images of the cross section surface for MgO doped with 0.1 at % Ce film, deposited on AZ31 alloy substrate and annealed at 550 ◦C, 3h in N2 . The HR-TEM image (figure 3(a)) show the lattice fringes of polycrystalline nanoparticles with d = 1.57 Å and 2.22 Å, corresponding to the (220) and (200) crystallographic planes of the cubic phase of MgO (JCPDS card No. 04-006-0699 [43]). The selected-area electron diffraction (SAED) pattern of Ce–doped MgO film (figure 3(c)) shows diffraction spots of crystalline phase indicating different crystallographic directions. The rings correspond to cubic phase of MgO [43]. HRTEM and SAED analyses confirm the XRD results.

3.2. Anti-corrosion performances

3.2.1. open circuit potential (OCP) measurements In order to investigate the corrosion behavior of the magnesium oxide (MgO) with and without cerium dopant coated AZ31 electrodes, the OCP and the EIS measurements were recorded after an immersion period of 24 h in Hank’s solution, at 37 ◦C. Figure 4 shows the OCP curves of AZ31 magnesium alloys substrate coated by undoped and 0.1 at % Ce−doped MgO, after 24 h immersion in Hank’s solution, at pH = 7.4 and 37 ◦C. The OCP measurments show the evolution of the potentials values by the presence of cerium in the MgO coating compared with undoped one. As can be seen on figure 4, the values of cerium-free MgO coating potentials increase to a stable value of approximately −1.595 V/Ag/AgCl, close to that of uncoated AZ31 alloy, reflecting a low resistance corrosion in simulated physiological environment. This behavior can be correlated to film cracking. On the other hand, the potential of cerium-doped MgO coatings show a slow increase to almost steady values of −1.421 V/Ag/AgCl. According to these results, the corrosion potential of the AZ31 alloy coated by MgO doped with cerium is nobler than that of the undoped coating deposited on Mg alloy. In addition, a potential margin of 170 mV/Ag/AgCl was marked between the system not doped and that doped with cerium. This observation highlights the inhibitor effect of cerium as a healing/cicatrizing agent for the magnesium oxide film, same comparative results were found by Hassen et al using protective magnesium coating electroplated then doped with cerium using chemical conversion method [48, 49]. Compared with undoped MgO film, the cerium-doped MgO coating is more resistant to electrolyte infiltration, generally indicating that this system is more stable thermodynamically [50, 51]. To confirm this interpretation, an EIS investigation of the same samples was conducted after each OCP measurement.

3.2.2. EIS measurements

The surface resistance of uncoated and coated AZ31 alloy substrate in Hank’s solution was investigated using EIS techniques. The electrochemical impedance curves of undoped and doped MgO/AZ31 system, recorded after a stabilization period of 24 h on the OCP using continuous and pulsed currents were illustrated in figure 5. The electrochemical impedance data are represented graphical by complex-impedance-plane plots, often called Nyquist plots (figure 5(a)), and ohmic resistance corrected Bode plots (figure 5(b)). The ohmic resistance corrected Bode plots was adopted because it is useful when the solution resistance is not negligible [52]. As well known, Hank’s solution contains many salts with different concentration. The Nyquist plots of the coated with undoped and doped with 0.1 at % cerium MgO film consist of one visible capacitive loop. The diameter of the doped coating loop is bigger compared to that of the undoped system. As consequence, this confirms that the incorporation of cerium improves the corrosion resistance of the coated AZ31 alloy substrate in Hank’s solution [27]. The corrected Bode plots (figure 5(b)) indicate an increase of the magnitude of the impedance modulus |Z| as well as the phase angle (-φ) with the addition of the doping Ce cations. The value of impedance modulus recorded onto the undoped system at 0.01 Hz (|Z|0.01 Hz) after 24 h of immersion was 26 451.7 Ω cm2. The final |Z|0.01 Hz of the 0.1 at % Ce-doped system was ∼117 809.6 Ω cm2 , four orders higher than that of the undoped coated MgO/AZ31 alloy. This is in good agreement with the interpretation of Nyquist diagrams. Regarding the Bode phase diagram of the undoped coating (figure 5(b)), after 24 h in Hank’s solution, it was noticed the presence of two times constant. The first constant, at higher frequency, correspond to the MgO film associated with the corrosion resistance of the sol–gel system [53], and another at middle frequencies, possibly attributed to the charge transfer processes of the corrosion film formed on the coating. However, the time constant associated with the resistance of the sol gel coating, initially showed a maximum absolute value of phase angle significantly higher (∼68◦) than that observed for the undoped coating (55◦). A low value of this parameter is usually indirectly related to the existence of constituent defects in the coating, such as porosity and/or cracks, meaning that the cerium containing coating exhibited better barrier performance [54]. A suitable equivalent electrical circuit model was used to fit the experimental electrochemical impedance results for the undoped and doped MgO coatings deposited on the AZ31 alloy (see inset in figure 5(a)). The equivalent circuit of the AZ31 alloy coated by pure MgO and 0.1 at % Ce-doped MgO (inset in figure 5(a)), is constituted by: RS that represents the electrolyte resistance, Rf represents the coating resistance, CPEf (or Qf) is the sol–gel film capacitance, Rox is the corrosion layer resistance. Rct is the charge transfer (or corrosion) resistance. Qdl is the constant phase element (CPEdl) which is related to the nonhomogeneity of the double layer surface (the double layer capacitance) which they are at the origin of the frequency dispersion [53]. The impedance of the capacitor (ZCPE) can be expressed as:

where, Q is the capacitance (the CPE constant), n is a constant ranging from 0 to 1; $n = 1$ for a capacitor, 0.5 for a Warburg element and, when $n = -1$, an inductance. $n = \alpha/(\pi/2)$, α being the phase angle of the CPE (radians). The exponent n defines the deviation from the ideal behavior ($\phi = 90^\circ$) and is related to the angle θ as:

where θ is the phase deviation from the ideal case ($\theta = 90^\circ$). For $n = 1$, equation (1) equals quation (3):

($Q_o = Q_{dl}$) indicating that CPE behaves as an ideal capacitor. For $n = 0$, equation (1) is written

as: $Z_{CPE} = Q_o^{-1}$ indicating that in this case the CPE behaves as a resistor. Finally, for $n = 0.5$, equation (1)

can be written as $(\omega) = 1/Q_o j\omega$, that is, is equivalent to the Warburg impedance (ZW). ω is the radial frequency. The values obtained for each component of the circuits are shown in table 2. For the doped coated MgO/AZ31 alloy, Rf marked higher values with comparing to those of undoped system. This implies that the corrosion of the Ce−doped coated MgO/AZ31 is more limited compared than without doping cations [27, 49, 55]. Further, the Rs and Rct of the doped coating are considerably greater, which indicates that the presence of cerium within the composition of the corrosion film provides additional protection to the metallic surface. This fact supplies an explanation about the best overall corrosion performance of the doped coatings during the electrochemical test, in which Rf values were maintained higher than those the undoped coating (31 360 Ω cm2 vs 5,10.106 Ω cm2 after 24 h of immersion). Furthermore, Qdl decreases while Qf increased signifying the formation of a more protective and thicker oxides layer. This difference was often attributed to the presence of corrosion product layer that processing a certain electronic conductive character [56]. From the values of CPE(dl,f), (nf and ndl), listed in table 2, we can observed that when we add the cerium to the MgO, the value of nf increases while the value of ndl remains almost constant at the unit. This confirms that the coating surface has a capacitive electrochemical behavior.

3.3. In vitro bioactivity investigation of Ce−doped MgO coating

3.3.1. Surface analysis by SEM-EDS of Ce doped MgO film after immersion in Hank's solution In order to investigate the chemical modifications occurring on the surface of the MgO coating doped with 0.1 at % Ce after immersion in Hank's solution over the long term, and thus to evaluate its bioactivity in vitro and its corrosion resistance, immersion tests were performed. Figure 6 display the SEM micrographs and corresponding EDS spectrum of 0.1 at % Ce−doped MgO coating surface after immersion in Hank's solution, at 37 ◦C for 7, 21 and 30 d. This figure characterizes the morphology and chemical composition of the doped MgO coating after immersion in Hank's solution for 7, 21 and 30 d. After immersion for 7, 21 and 30 d, the coating of Ce−doped MgO was covered with a white layer, which is due to the interaction of existing chemical elements in the simulated physiological medium with magnesium oxide from the film. This suggests that this white layer was the result of the nucleation and grows of the apatite on the Ce–doped MgO film [57]. To verify this assumption, the chemical composition of this layer formed in vitro was analyzed by EDS method which indicated the presence of carbon (C), calcium (Ca), chlorine (Cl) and phosphorus (P) together with magnesium (Mg), oxygen (O) and cerium (Ce), which mainly form the solution and the studied coating. The chloride, detected by EDS on the surface of the film immersed for 7, 21 and 30 d in Hank's solution, comes from the simulated physiological environment and represents a source of corrosion for both the coating and the substrate. According to the EDS results (table 3), the atomic percentage of calcium and phosphorus increases with the extension of the immersion time in Hank's solution from 7 d to 30 d, which confirms the evolution of the layer thickness deposited on the MgO film. As it is indicated in the literature [49, 58], the layer formed on the surface of the cerium-doped MgO film is a calcium phosphorus (Ca–P) based layer. These two chemical elements are the main constituents of bone apatite. It in nutshell, the growth of bone-like apatite helps to improve the corrosion resistance of the Ce– doped MgO coating and promotes the osteointegration of the Mg alloy-based implant.

3.3.2. Surface analysis by FTIR of Ce–doped MgO film

after immersion in Hank's solution The FT–IR spectrum of 0.1 at % Ce–doped MgO coating after immersion in Hank's solution for 21 d is shown in figure 7. The FT–IR spectrum indicate that the sample contains some the functional groups of apatite (chemical formula: $Ca_5(PO_4)_3(F,Cl,OH)$), after being soaked in simulated physiological solution. As can be seen in figure 7, the sharp band in the domain 3300–3600 cm−1 corresponds to OH and H_2O bands of apatite [59]. The band centered at 3700 cm–1 is the characteristic frequency of the O–H stretching vibration of $Mg(OH)_2$. Absorption bands at 2030, 1400 and 865 cm−1 are ascribed to CO_3^{2-} anion of carbonates. The bands at 2165, 1000 and 568 cm–1 indicate the presence of PO_4^{3-} group [60, 61]. The results of FT-IR confirm that the grown layer on Ce–doped MgO coating deposited on AZ31 substrate is bone like apatite.

3.3.3. Surface analysis by XPS of Ce-doped MgO film after immersion in Hank's solution XPS method was used in order to investigate the presence and the valence states of the chemical elements of hydroxyapatite, formed on the MgO doped with 0.1 at % Ce film surface during immersion in Hank's solution. Figure 8 shows the XPS spectra obtained by analyzing the surface of 0.1 at % Ce doped MgO coating after immersion for 30 d in Hank's solution, at 37 ◦C. For the film immersed for 7, 21 and 30 d, practically the same spectra were obtained, only the atomic percentages of the chemicals elements detected on sample surfaces changed (table 4). The general XPS spectrum of the MgO–Ce coating after 30 d in Hank's solution at 37 ◦C is shown in figure 8(a), in the range of chemical binding energies 0–1400 eV. The binding energy of the peaks of the various chemical elements present on the surface of the sample was calibrated using the binding energy of C 1 s (285.0 eV). The general spectrum of the analyzed film (figure 8(a)) indicates peaks of C 1 s, O 1 s, Mg 2p, Ca 2p, Cl 2p, P 2p, Ce 3d and other unlabeled peaks belonging to Zn 2p1/2. The chemical bond energy are: Zn 2p3/2 at 1028.66 eV, Ca 2 s (439.0 eV, in $CaHPO_4$, [62]), Mg 1 s (1304.80 eV, in $MgCl_2·6H_2O$, [63]), etc. The chemical elements such as Mg, O and Ce were derived from the cerium–doped MgO film deposited on the surface of the AZ31 substrate. The source of other chemical elements, such as C, O, Ca, P and Cl is Hank's solution in which the sample was immersed. In order to identify the nature of the chemical bonds of these elements (C, O, Ca, Cl, P, Mg and Ce) present on the surface of the films, the deconvolution of the XPS spectra was carried out. Figure 8(b) shows the high resolution XPS spectrum for the carbon peak (C 1 s). This peak was deconvoluted into four peaks corresponding to binding energies of: 284.80 eV;

286.29 eV, 287.78 eV and 289.22 eV. The maximum positioned at 284.80 eV corresponds to C–C or C–H bonds [44, 64, 65]. Boyd et al [66], reported that the peak at 284.80 eV is associated with C–C bonds. The peak around 286 eV is attributed with C–O–C bonds [67]. The maximum at 287.78 eV is attributed to O, O–C–O, C=O bonds while the peak around 290 eV could be associated with C–metal or O–C=O bonds of COOH and COOR [68, 69]. Figure 8(c) shows that high resolution XPS spectrum of the O 1 s peak, detected at the surface of the film, indicates a binding energy of 531.51 eV. This peak was decomposed into three peaks which were attributed to the following bonds: O^{2-}, O–P, O–Ca, O–Mg; (530.35 eV), C=, PO_4^{3-}, −OH (531.41 eV) and C−, H_2O (532.81 eV). For Mg 2p, the XPS spectrum, shown in figure 8(d), indicates that its corresponding peak is located at 49.8 eV and can be broken down into three peaks, binding energies positioned at 49.78 eV and 50.68 eV, respectively. These two peaks are due to the presence of the compounds $Mg(OH)_2$ and MgO, formed on the surface. Cerium (Ce 3d) which is present in the samples does not appear in the XPS spectrum because it is below the detection limit of XPS (∼1 at %) [70]. In addition, it is well known that Ce^{3+} and Ce^{4+} give much lower XPS signals (peaks) compared to other chemical elements. Figure 8(e) shows the high resolution XPS spectra for the Ce 3d of the film surface. The high resolution XPS spectrum for Ca 2p (figure 8(f)) shows peak binding energies of 347.22 eV (2p3/2) and 351.0 eV (2p1/2). These two asymmetric peaks have been broken down into three peaks positioned on the axis of the binding energies as, the first of which is at: 347.13 eV corresponding to the Ca–(PO_4^{3-}) bonds, the second is at 350.68 eV corresponding to the Ca−(OH^-) bonds and the last at 351.61 eV corresponding to the Ca–(PO_4^{3-}) bonds. This last peak at 351.61 eV corresponds at the same time to the Auger peak of Mg. Similar results were obtained by Ortega et al [71]. Figure 8(g) shows the high resolution XPS spectrum for the P 2p peak located at 132.92 eV, which was deconvoluted into two peaks with binding energies located at 132.71 eV (2p3/2) and at 133.61 eV (2p1/2), respectively. The P 2p peaks consist of the 2p3/2 and 2p1/2 doublet separated by an energy difference of about 0.9 eV and with the area ratio = 2/1. The binding energies corresponding to the doublet are specific to phosphates. This result proves that the layer formed by immersion in Hank's solution of AZ31 substrates coated with an MgO film doped with cerium, is of calcium phosphate (Ca–P) specie. Therefore, we can say that the MgO film doped with cerium promotes the growth of hydroxyapatite on the surface of AZ31 alloy substrate. Also a Cl 2p peak was detected; its high resolution XPS spectrum was illustrated in figure 8(h). This peak was deconvolved into two peaks, with binding energies positioned at 198.14 eV and 199.72 eV. The domain of these energies is attributed to metal chlorides ($MgCl_2$ and $CaCl_2$). The chlorine and sodium come from Hank's solution. XPS quantitative analysis allowed us to compare the amounts of material deposited on the surface of samples by immersion in Hank's solution, at 37 ◦C, at different times. Table 4 shows the concentrations of the chemical elements detected by XPS on the surface of the three samples (7, 21 and 30 d). From this table, the atomic percentages of the calcium and phosphorous increase by increasing the immersion time in Hank solution of the MgO film doped with 0.1 at % Ce while the amount of Mg decrease. This suggests the increase of the amount and the thikness of hydroxyapatite ($Ca_5(PO_4)_3(OH)$ or $Ca_{10}(PO_4)_6(OH)_2$) formed on the film surface, in good agreement with the results of EDS analysis. The corrosion products founded on the pure magnesium sample and AZ31 alloy in Hank's solution [41] (not shown here) are brucite $Mg(OH)_2$, calcite ($CaCO_3$) and calcium phosphate $Ca(HPO_4)_2{\cdot}2H_2O$. Therefore, these coatings promotes the formation of apatite like bone and consequently, enhance the integration of the magnesium alloy based implant into the human body and increase their service life in the same time. Therefore, AZ31 magnesium alloys coated with cerium-doped MgO thin films can be used in areas where uncoated Mg alloys are used. Types of biodegradable medical implants based on magnesium alloys are: plates for mandibular reconstruction, cervical spines, bone screws and rods implants into the hip bone, femurs, tibias, intramedullary nails, clips, intravascular stents, scaffolds, etc [72–76].

4. Conclusions

We have developed an effective strategy to corrosion protection of the AZ31 alloy within physiological environment by coating with undoped and doped with cerium MgO films. These protective coatings have been successfully prepared using sol–gel route and spin-coating deposition technique. The relationship between the microstructural properties and the anticorrosion performance of the undoped and Ce−doped MgO coatings deposited on AZ31 alloy substrate were careful investigated using electrochemical techniques (OCP, EIS) and surface analysis methods (XRD, SEM/EDS and XPS). Detailed structure and microstructure analysis highlighted that the undoped and 0.1 at % Ce–doped MgO compounds are formed into coatings, characterized by a good adhesion with AZ31 alloy substrate, homogeneous morphology of surface and cross-section of the films, uniform repartition of the chemical element in these coating films. Apatite layers containing calcium phosphate (Ca–P) specie are grown on the pure MgO and 0.1 at % Ce–doped MgO coatings after immersion test in Hank's solution at 37 ◦C, for 7, 21 and 30 d, which indicates an excellent bioactivity of the Ce−doped MgO coatings. In summary, the coating of 0.1 at % Ce–doped MgO strengthen the integration of the magnesium alloy as AZ31 alloy into the human body and increase their service life as a biomedical implant with good osseointegration property.

Data availability statement

No new data were created or analysed in this study.

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Conflict of interest

The authors declare no conflict of interest.

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