



Fabrication and characterisation of novel ZnO/MWCNT duplex coating deposited on Mg alloy by PVD coupled with dip-coating techniques



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ABSTRACT

Zinc oxide (ZnO)/multi-walled carbon nanotube (MWCNT) duplex coating was synthesized on Mg-0.8Ca-3Zn alloy by physical vapour deposition (PVD) combined with dip coating. The ZnO inner layer was 1.1 μm thick and consisted of spherical nanoparticles. The outer layer of the MWCNTs was 10.2 μm thick, the diameter of the raw MWCNTs was approximately 42 nm, and their lengths were around a few microns. The ZnO/MWCNT duplex coating showed higher compressive strength than the single-layer coated ZnO and bare Mg alloy after immersion in simulated body fluid (SBF) solution. Polarisation and electrochemical impedance spectroscopy tests revealed that the ZnO/MWCNT duplex coating has lower corrosion current ($i_{\text{corr}} = 7.2 \mu\text{A}/\text{cm}^2$) and higher charge transfer resistance ($R_t = 5250 \Omega \text{cm}^2$) than the ZnO single-layer coated ($R_t = 3420 \Omega \text{cm}^2$; $i_{\text{corr}} = 42.3 \mu\text{A}/\text{cm}^2$) and bare Mg alloy ($R_t = 1720 \Omega \text{cm}^2$; $i_{\text{corr}} = 205.4 \mu\text{A}/\text{cm}^2$). In the immersion test, the ZnO/MWCNT duplex coating protected the substrate effectively in the SBF solution, while moderate to serious damage in this electrolyte was observed on the surface of the ZnO-coated and bare samples, respectively. The results indicated that the deposition of MWCNTs as the outer layer and ZnO as the inner layer on the surface of bare Mg alloy sample is a promising technique to enhance its corrosion resistance.

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1. Introduction

Magnesium (Mg) alloys as temporary implants have received great consideration as a result of their comparable mechanical properties with natural bones and good biocompatibility, along with their biodegradability in implant applications, which resulted in the prevention of additional surgery for implant removal [1–3]. In addition, Mg will be able to control bone proliferation and remodelling due to its engagement in the bone mineral surface reaction [4]. Yamasaki et al. [5] demonstrated that Mg^{2+} in apatite crystals may increase the speed of osteoblast adhesion and enhance

bone formation. However, the fast degradation rate of Mg alloys in corrosive atmospheres decreases the mechanical integrity of the implants ahead of time and generates hydrogen gas and corrosion products [6]. These products could generate regional inflammation and restrict the possible medical applications of Mg alloys [7,8].

In order to improve the corrosion resistance of Mg alloys in the physiological environment, an appropriate coating on Mg alloy is typically applied [4]. Among surface modifications, physical vapour deposition (PVD) and dip-coating were applied for nano zinc oxide (ZnO; inner layer) and carbon nanotube (outer layer) coatings, respectively. Furthermore, ZnO is one of the essential materials used in several products such as ceramics, cement, glass, and composites. Moreover, ZnO is used in medical products since Zn is a crucial micronutrient, providing essential functions in human and animal growth, health, and well-being [9,10]. Likewise, ZnO belongs in the rank of attractive inorganic materials possessing outstanding

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properties such as low cost, high photo and chemical biocompatibility, stability, abundance, non-toxicity, and biodegradability [11,12]. It was reported [13] that the Mg-rich epoxy containing zinc oxide particles demonstrated higher corrosion resistance compared to the Mg-rich epoxy-coated AZ91D alloy. Furthermore, Qing et al. [14] showed that fluorinated polysiloxane/ZnO nanocomposite-coated steel demonstrated superhydrophobic properties and high corrosion resistance.

Another study [15] demonstrated that poly(*o*-toluidine) containing nano-ZnO had a lower corrosion rate compared to the poly(*o*-toluidine), which is attributed to the creation of a homogeneous protective layer on the steel surface. However, the ZnO PVD coating suffers from a great number of porosities, voids, and cracks, which resulted in increased penetration of the solution in the Mg alloy substrate [16,17]. Hence, MWCNTs were prepared as an outer layer to seal the porosities of the ZnO plasma-coated sample and improve the corrosion properties of the Mg alloy substrate. It was demonstrated [18] that the addition of the carbon nanotube (CNT) as an additive to the bioactive coating materials can promote the proliferation of the osteoblast cells through the nano pore walls. In addition, a coating of MWCNTs on the metal surface improves the mechanical properties of the substrate [18]. Carbon nanotubes have distinctive electrical, optical, and mechanical characteristics as well as excellent chemical stability, which has led to substantial scientific study to add MWCNTs as reinforcement to amplify the mechanical and corrosion characteristics of the matrix [19]. In this context, incorporation of MWCNTs into nickel matrix coatings can reduce the corrosion rate of the composite coatings [20,21]. Another study [22] revealed that the addition of CNTs to the Ni–P coatings can increase the corrosion resistance of the composite coating due to the formation of the passive film. In addition, higher corrosion resistance of Ni–CNT composite coated compared to the Ni coating on Ti–6Al–4 V alloy was reported by Lee et al. [23]. However, there is no study regarding the preparation of nano-structure ZnO/MWCNT duplex coating on Mg alloy via PVD coupled with dip coating. Thus, the primary purpose of the present research is the synthesis and characterisation of a novel ZnO/MWCNT composite coating on Mg alloy.

2. Experimental

The cast Mg-0.8Ca-3Zn alloy was prepared under a protective gas atmosphere containing 60% argon and 40% carbon dioxide in an induction furnace according to the previous study [24]. For the PVD coating of Mg alloy samples, a hybrid ion beam deposition system (HVC Penta Vacuum), which is composed of a linear ion source and magnetron sputtering source with a ZnO (99.99%) target, was used. The parameters of the PVD coating are presented in Table 1. For the MWCNT coating, the isopropyl alcohol (IPA) based zwitterionic surfactant solution with a concentration of 1.0 wt% MWCNTs was prepared according to Umeda et al. [25]. The Mg-0.8Ca-3Zn alloy specimens were dipped into the solution and then annealed at 500 °C for 30 min in a furnace under protective gas atmosphere [25]. This step was replicated to increase the loading of MWCNTs on

the Mg alloy surface.

Fig. 1a shows the schematic diagram of the setup for ZnO/MWCNTs duplex coating. Fig. 1b shows the transmission electron microscopy (TEM) images of the as-received MWCNTs (>95% purity) with the lengths of 0.5–2 μm. The histogram of MWCNTs diameter was estimated by ImageJ software and the results shows that the diameter of the MWCNTs was in the range of 12–46 nm. The cylindrical specimens were 10 mm (diameter) × 20 mm (height) and were prepared for compression test (Instron-5569 universal) with a displacement rate of 0.5 mm/min at room temperature. The bare Mg alloy and coated alloys were immersed in SBF for 10 days and eventually cleaned with chromium trioxide (CrO₃) to eliminate the corrosion products from the specimen surface.

For conducting electrochemical measurements by PARSTAT 2263 potentiostat/galvanostat (Princeton Applied Research), the bare Mg alloy and Mg coated samples with a surface area of 1 cm² were prepared and soaked in the cell containing three electrodes and the SBF solution at 37 °C with a pH value of 7.44 according to [24]. The electrochemical impedance spectroscopy (EIS; VersaSTAT 3 machine) was performed in the frequency range of 100 kHz to 0.01 Hz with 10 points per decade and 10 mV. For the immersion test, the same samples were submerged into 200 ml of the SBF solution (pH 7.4) according to ASTM: G1-03 [26]. The change in the pH value of the SBF was recorded during the immersion test at 24 h intervals.

The in-vitro corrosion rates (C_R) were subsequently measured (mm/year) using the weight loss test based on the following equation: $C_R = W/Atd$, where W and A are the weight loss and sample area exposed to the solution, respectively, and t and d are the exposure time and density, respectively. An X-ray diffractometer (XRD; Siemens D5000) was employed to determine the phase component using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) generated at the acceleration voltage of 35 kV and the filament current of 3025 mA over the diffraction angles (2θ) of 20–80° with 0.04 increments. Microstructures of the bare Mg alloy and Mg alloy-coated samples were studied using scanning electron microscopy (SEM; JEOL JSM-6380LA) coupled with energy-dispersive X-ray spectroscopy (EDX; JEOL Inc., Tokyo, Japan) and TEM (HT7700 Hitachi).

3. Results and discussion

3.1. Characterisation of the uncoated and coated Mg alloy samples

SEM micrographs of the uncoated Mg-0.8Ca-3Zn alloy reveal the evolution of eutectic structure along the grain boundaries (Fig. 2a). The EDX analysis indicated that this structure consists of Ca₂Mg₆Zn₃ and α -Mg (Fig. 2b). The XRD patterns of the bare Mg alloy showed the reflections of Ca₂Mg₆Zn₃ with low intensity and α -Mg with high intensity (Fig. 3a). In the case of the ZnO coating, bubble-like structures with uniform distribution as well as some defects such as micro-pores and micro-cracks were observed on the PVD film (Fig. 2c). It was reported [17,27] that the existence of such cracks can be due to the presence of compressive intrinsic stress in the coatings prepared via sputtering. The presence of these defects leads to further penetration of the physiological solution into the PVD coating and initiation of electrochemical reaction between the coating and substrate, which results in the debonding of the coating/substrate interface.

The EDX analysis exhibited the presence of Zn, O, Mg, and a trace amount of Ca in the PVD film, implying the formation of a ZnO layer on the Mg alloy substrate (Fig. 2 d). The diffraction pattern of the PVD film (Fig. 3b) was further confirmed by the presence of ZnO at $2\theta = 31.7^\circ, 36.2^\circ, 47.5^\circ, \text{ and } 62.8^\circ$, which were indexed to the (100), (002), (102), and (103) planes (JSPC card number 01-075-0576).

Table 1
Deposition parameters of PVD coating.

| Parameters | Quantity |
|------------------------------|--------------------------|
| Ar flow rate | 175 sccm |
| Base pressure of the chamber | 2.55×10^{-3} Pa |
| Sputtering pressure | 0.24 Pa |
| RF sputtering power | 200 W |
| Deposition time | 90 min |
| Bias voltage | –150 V |

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