Tantalum nitride films for corrosion protection of biomedical Mg-Y-RE alloy

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ABSTRACT

Based on their natural degradation in the human body, magnesium-based alloys are attractive for temporary implants such as cardiovascular stents and bone fixation devices. Unfortunately, rapid degradation of magnesium-based alloys in the physiological environment is a major obstacle limiting wider application. Herein, the WE43 Mg alloy deposited with tantalum nitride films by reactive magnetron sputtering shows enhanced corrosion resistance. The modified WE43 exhibits a 95-fold decrease in the corrosion current density and 100-fold initial increase in the charge transfer resistance in simulated body fluids (SBF). The ion concentration and pH of the soaking solution show that corrosion of the modified WE43 is remarkably retarded during a long-term immersion in SBF for 30 days. The corrosion propagation mechanism of the untreated and modified WE43 during long-term immersion in SBF is investigated.

1. Introduction

Magnesium (Mg) and its alloys have been extensively investigated for potential applications to temporary implants such as cardiovascular stents, bone fixation plates, screws, pins, and nails [1,2]. The main driving force to develop Mg-based implants is their natural degradation under physiological conditions thereby eliminating follow-up surgeries to remove the implants after sufficient tissue healing [3]. Among the various Mg-based alloys, the ones alloyed with rare-earth elements such as WE43 do not contain aluminum with neurotoxicity and also possess high strength and ductility, thereby making them attractive to biomedical applications such as temporary implants [4]. Unfortunately, a major concern of Mg-based implants is rapid degradation in the chloride-containing physiological system. The accompanying drawbacks include premature loss of the mechanical integrity during tissue healing, excessive hydrogen evolution, and local alkalinity which may cause implant failure [5]. As a result, degradation of Mg and its alloys must be controlled prior to clinical acceptance of the temporary implants.

Tantalum (Ta) is a refractory transition metal commonly used in capacitors in electronics. Owing to the good biocompatibility, Ta has also been used as components in primary and revision total hip arthroplasty and clinical studies support further investigation of porous Ta as an alternative to traditional implant materials [6]. The excellent bioactivity has also been confirmed [7-9]. Ta has good inertness in many aggressive environments due to the formation of a stable, compact, and adherent Ta2O5 film on the surface [10,11]. Xu et al. [12] and Díaz et al. [13] observed that Ti-6Al-4V alloy and steel with a Ta2O5 nanocoating barrier prepared by double glow discharge plasma technique and low-temperature atomic layer deposition as well as filtered cathodic arc deposition, respectively had enhanced anticorrosion ability. In comparison, modification of Mg alloys with Ta has seldom been reported. In our recent study, Ta oxide fabricated by reactive magnetron sputtering enhanced both the early-stage corrosion resistance and in vitro biocompatibility of Mg alloy [14]. Wang et al. revealed that Ta ion implantation improved the corrosion resistance of AZ31 Mg alloys and suggested that formation of a dense MgO layer and protective Ta2Al barrier rather than Ta2O5 formation was responsible for the improvement [15,16].
Cu-incorporated Ta nitride nanocomposite thin films have been observed to have anti-bacteria and anti-wear properties [17]. Choe et al. [18] and Alishahi et al. [19] found that Ta nitride coatings produced by different methods retarded corrosion of 316L stainless steels in a 0.05 M H2SO4 solution. The surface morphology was observed by SEM and the binding energies were calibrated referenced to the C 1s line at 284.8 eV. All the XPS spectra were collected after sputtering by Ar for 50 nm are depicted in Fig. 1a. The peaks of Ta, N, and O are presented in Fig. 1b and Fig. S2. As shown in Fig. 1b, the high-resolution XPS Ta 4f spectrum is resolved into three sets of 4f7/2 and 4f5/2 doublets with a spin-orbit splitting of 2.03 eV. The Ta-N bond energy overlaps the peak of Ta 4p3/2 and the strong peak at 397.5 eV for N 1s, while the binding energies were calibrated referenced to the C 1s line at 284.8 eV. All the XPS spectra were collected after sputtering by Ar for 50 nm, which was based on a SiO2 reference. The phase and structure were determined by grazing-incidence X-ray diffraction (GIXRD, SmartLab X-ray Diffractometer, Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation. The diffractometer was operated at 40 kV and 30 mA with an incident angle of 1°. The XRD spectra were recorded over a wide range from 15° to 80° at a rate of 0.02° s⁻¹. The film thickness and elemental maps of the cross-sectional sample were determined by scanning electron microscopy (SEM, JSM-820, JEOL Ltd., Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS, INCAx-sight, Oxford Instruments, Abingdon, Oxfordshire, UK). The surface morphology was observed by SEM with a field emission source (JSM-6335F, JEOL Ltd., Tokyo, Japan).

2.2. Electrochemical tests

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were performed in simulated body fluids (SBF) at 37 °C on an electrochemical workstation (Zennium, Zahner, Kansas City, Missouri, USA) using a three-electrode cell system. The saturated calomel electrode (SCE), platinum sheet, and specimens were the reference electrode, counter electrode, and working electrode, respectively. Unless specifically specified, the potentials were referred to SCE. The SBF solution was prepared by dissolving reagent grade chemicals (8.035 g NaCl, 0.355 g NaHCO3, 0.225 g KCl, 0.231 g K2HPO4, 3H2O, 0.311 g MgCl2·6H2O, 1.0 M HCl (39 mL), 0.292 g CaCl2, and 0.072 g Na2SO4) in 1000 mL of deionized water. The SBF solution was buffered at pH 7.4 with 6.118 g L⁻¹ tris-hydroxymethyl aminomethane and 10.0 M HCl. The ion concentrations in the SBF solution were 142.0 Na⁺, 5.0 K⁺, 1.5 Mg²⁺, 2.5 Ca²⁺, 147.8 Cl⁻, 4.2 HCO₃⁻, 10 HPO₄⁻, and 0.5 SO₄²⁻ mm, which are close to those of human blood plasma [22]. The bottom and sides of the specimens were sealed with silica gel and the area of the working electrode exposed to the electrolyte was 1 cm² during the electrochemical measurements. EIS was conducted with a 10 mV alternating signal from 100 kHz to 100 mHz at the open circuit potential (OCP) after immersion in SBF for 1, 24, 48, 72, 96, and 120 h. The samples were immersed in the solution for 15 min and the polarization curves were collected at a scanning rate of 1 mV s⁻¹ from –300 mV and 500 mV with respect to OCP.

2.3. Long-term immersion tests

To monitor degradation of the WE43 Mg alloy before and after surface modification, long-term immersion tests were carried out in SBF. According to ASTM-G31-72 [23], the specimens were immersed in SBF and maintained at 37 °C for 30 days. At different immersion time of 1, 3, 7, 15, and 30 days, the concentrations of leached Mg from the samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, PE Optima 2100DV, Perkin Elmer, Waltham, MA, USA). The pH of the corresponding SBF was recorded. The cross sectional and surface morphologies as well as elemental information were acquired by SEM and EDS (INCAx-sight, Oxford Instruments, Abingdon, Oxfordshire, UK) from the uncoated and coated WE43 samples after immersion in SBF for 7, 15, and 21 days.

3. Results and discussion

3.1. Surface characterization

Fig. 2a shows the optical microstructure of the WE43 Mg alloy. The alloy is composed of the Mg matrix and a distribution of second phases which seem to be crystallized along the grain boundaries as well as in the matrix. The XPS full spectrum of the coated WE43 after sputtering for 50 nm are depicted in Fig. 1a. The peaks of Ta, N, and O are observed from the XPS full spectrum in Fig. 1a. Oxygen arises from natural oxidation/adsorption and/or residual H₂O or O₂ in the deposition chamber. The high-resolution XPS spectra of Ta 4f, N 1s, and O 1s are presented in Fig. 1b and Fig. S2. As shown in Fig. 1b, the high-resolution XPS Ta 4f spectrum is resolved into three sets of 4f⁷/₂ and 4f⁵/₂ doublets with a spin-orbit splitting of 1.9 eV and intensity ratio of 4:3. The peaks at 22.8 eV for Ta 4f⁷/₂ and 24.7 eV for Ta 4f⁵/₂ are in good agreement with the chemical state of Ta in TaN [24]. Two more sets of Ta 4f peaks appear at higher binding energies of 23.3 eV/25.2 eV and 24.6 eV/26.5 eV attributed to Ta suboxide in the film [24–26]. Fig. S2a shows that the N 1s peak overlaps the peak of Ta 4f⁷/₂ and the strong peak at 397.5 eV for N 1s corresponds to the formation of TaN. With regard to the O 1s in Fig. 2b, the peaks at 530.4 eV and 531.0 eV are associated with Ta suboxides and that at 531.9 eV arises from –OH due to air exposure [27]. Therefore, a surface layer composed of TaN and Ta suboxide (TAN) is formed on the WE43 Mg alloy by reactive magnetron sputtering. Fig. 1c presents the GLXRD spectrum of the deposited film on silicon. The peak at 34° is assigned to the (110) reflection of TaN [JCPDS No. 71–0259]. A broad peak in the range of 42°–60° also emerges from the deposited film in accordance with those observed previously from amorphous oxidized Ta films [16] and by Kulisch et al. [28]. Consequently, the sputtered film has a mixed structure of crystalline TaN and amorphous Ta suboxide. Fig. 2a and b shows the cross-sectional SEM image of the TAN-coated WE43.
(TAN-WE43) sample and corresponding EDS elemental maps of Ta and Mg. The thickness of the deposited TAN film is 621 ± 4 nm. Fig. 2c and d presents two representative regions of surface morphology of the TAN-WE43 sample observed by SEM. Fig. 2c depicts a continuous and dense TAN film formed on the WE43 Mg alloy. However, as shown in Fig. 2d there are some defects such as large particles (indicated by arrows), which are not closely connected with the uniform parts of the film forming some large gaps. This may be caused by low substrate temperature during film deposition or incomplete removal of contaminants from the substrate surface during sample preparation.

3.2. Electrochemical studies

Fig. 3 presents the electrochemical potentiodynamic polarization curves of WE43 and TAN-WE43 after immersion in SBF for 15 min. The corrosion potential $E_{corr}$, corrosion current density $I_{corr}$ and cathodic Tafel slope $\beta_c$ are calculated from the cathodic polarization curves according to the method described previously [29] and the values are listed in Table 1. The corrosion potential of the modified WE43 in SBF shifts to $-1767.4 \pm 18.2$ mV, which is slightly more positive than that of the bare WE43. No clear positive shift was also reported by Jia et al. from SiP-coated Mg–1Ca alloy [30]. The corrosion rate depends on the corrosion current density, which is an important parameter in corrosion resistance characterization and a smaller corrosion current density corresponds to a lower corrosion rate. The corrosion current density of TAN-WE43 decreases to $6.2 \pm 1.4 \mu$A cm$^{-2}$, which is approximately two orders smaller than that of the bare WE43 sample, thus providing evidence that the TaN film notably retards the corrosion of WE43 Mg alloy in SBF. Fig. 4 shows the OCP of WE43 and TAN-WE43 during immersion in SBF for 120 h. The OCP of the untreated WE43 increases rapidly during the initial 24 h, rises slowly in the next 24 h, and stabilizes thereafter. The initial OCP increase is caused by the formation of corrosion products and the surface is covered uniformly by the corrosion products after immersion for 48 h. The OCP of the TAN-WE43 rises gradually in the first 48 h and then stabilizes. This phenomenon is common due to continuous plugging of the microspores of the TaN film by the corrosion products in the initial stage.

As one of the useful techniques to investigate the corrosion processes at the electrode/electrolyte interface and evaluate the corrosion resistance, EIS is conducted after immersion in SBF for different periods of time up to 120 h. Fig. 5 shows the Nyquist plots and fitted curves of the WE43 and TAN-WE43 samples and the corresponding experimental and fitted Bode impedance and phase angle plots are given in Figs. 6 and 7. As shown in Fig. 5a and b, the Nyquist plot of the untreated WE43 during the entire immersion time shows two arcs corresponding to two time constants. The two loops of the bare WE43 show a larger radius with soaking time.
Ascencio et al. reported a similar behavior of WE43 Mg alloy in modified-SBF [31]. In the beginning, the two arcs are clearly separated and integrated after immersion for 72 h. The initial separation is also indicated by the reduced slope in the middle frequency range of the Bode impedance plots (Fig. 6a) and the two split phase angle maxima (Fig. 7a) [32]. When the immersion time is increased to 72 h, the change in the slope in the middle frequency becomes blurred and the two phase angle maxima also merge into each other (Figs. 6b and 7b) suggesting two integrated arcs. An equivalent circuit model with two time constants, \( R_s(CPE_{dl}\text{R}_{ct})(CPE_{diff}\text{R}_{diff}) \), as shown in Fig. 8a is adopted to fit the EIS data of the WE43 Mg alloy. \( R_s \) is the resistance of the electrolyte between the working electrode and reference electrode, \( CPE_{dl} \),
represents the capacitance of the double layer at the electrolyte/metal interface, and $R_{ct}$ is the relevant charge transfer resistance. $CPE_{diff}$ and $R_{diff}$ are related to the capacitance and relevant resistance induced by the diffusion process in a finite region. The same equivalent circuit has been implemented by Wu et al. [33] to simulate the EIS data of the Mg-Nd-Zn-Zr alloy in the 0.9 wt% NaCl solution. As shown in Fig. 8a, the high-frequency arc in the impedance diagram is assigned to the effect of the charge transfer resistance and double layer capacitance, whereas the low-frequency arc is related to the diffusion process, which is also implied by the upward curve rather than horizontal line at low frequencies in the Bode impedance plot [32]. Even though corrosion products cover the substrate surface during immersion, only one arc emerges at high frequencies. The resistance of the corrosion products layer with a loose structure (confirmed by the following SEM images of the samples after immersed in SBF) is so small in comparison with the charge transfer resistance that the corresponding arc of the corrosion layer is virtually undetectable in the impedance diagram [34].

With respect to TAN-WE43, the Bode phase diagrams in Figs. 6c, d and 7c, d shows three arcs as it is a very sensitive method to identify the number of time constants. During the 120-h immersion period, the second loop and third loop are clearly separated, while the first two loops are also separated according to the phase angle vs frequency diagram, even though the first loop is too small and cannot be clearly observed from the Nyquist diagram. As shown in Fig. 5c and d, as the immersion time is increased, two apparent loops in the medium and low frequency ranges of the TAN-WE43 sample become smaller and a similar phenomenon has been reported by Ishizaki et al. for the AZ31 Mg alloy coated with super-hydrophobic films [35]. This is also confirmed by the fitted EIS results and the reasons will be discussed in that part. A parallel combination of $CPE_f R_f$ is introduced to construct an equivalent circuit model with three time constants, $R_s (CPE_f R_f)(CPE_{dl} R_{ct}) (CPE_{diff} R_{diff})$ in Fig. 8b to fit the EIS data. $CPE_f$ is ascribed to the capacitance of the deposited film and $R_f$ is the pore resistance resulting from the formation of ionically conductive paths across the film. The three loops of TAN-WE43 at high, middle, and low frequencies are associated with the surface film, charge transfer process, and diffusion process, respectively. The equivalent circuit for TAN-WE43 is different but similar to that proposed for polypropylene-coated mild steel [36] and polymer-coated Mg-Gd-Y alloy [37]. As shown in Figs. 5–7, the Nyquist and Bode plots of TAN-WE43 are fitted well, so the equivalent circuit in Fig. 8b can be used to analyze the EIS data of TAN-WE43.

The fitted values of $R_{ct}$ and $R_{diff}$ of WE43 and $R_f$, $R_{ct}$, and $R_{diff}$ of TAN-WE43 are shown in Fig. 9. For the untreated WE43 Mg alloy, prolonged exposure to SBF increases both $R_{ct}$ and $R_{diff}$. The charge transfer resistance, $R_{ct}$, is considered the most appropriate parameter to monitor the protective properties of the film because it reflects the corrosion rate of the metal substrate [38]. $R_{ct}$ of WE43 increases from $87 \Omega \text{cm}^2$ at 1 h to $432 \Omega \text{cm}^2$ at 120 h and so the
corrosion rate of the uncoated WE43 decreases with immersion time. This is ascribed to the continuous formation of the corrosion products layer on the WE43 Mg alloy and the corrosion products can serve as a barrier layer for the WE43 substrate against further corrosion to some extent. The decreased dissolution rate comes from the increased thickness of the corrosion layer with better protective ability. However, very limited protection is provided if the corrosion products layer has a loose structure (confirmed by SEM). Hence, \( R_{ct} \) of the untreated WE43 Mg alloy does not reach a very large value. Meanwhile, when diffusion occurs, it cannot be ignored because the corrosion process can be affected by the movement of chemical species. When the immersion time is increased to 120 h, \( R_{diff} \) of the WE43 sample increases to 659 \( \Omega \) cm\(^2\). For the uncoated WE43, \( R_{diff} \) represents the resistance against diffusion of the produced Mg\(^{2+}\) through the corrosion layer away from the Mg substrate. Transportation of the produced species is more difficult when the corrosion products layer becomes thicker.

With regard to the WE43 Mg alloy with the TaN film, the trends of \( R_{ct} \) and \( R_{diff} \) are different and another parameter \( R_f \) is discussed. As shown in the inset image in Fig. 9, after immersion for 1 h, TAN-WE43 shows a small \( R_f \) suggesting that after a short time, the electrolyte absorbs and reaches the metallic substrate through the latent defects or discontinuities, which provide the pathways for the solution to reach the substrate/film interface and have a detrimental effect on the corrosion performance [39]. The increase in \( R_f \) at 24 h may be due to plugging of pores by the corrosion products [40]. \( R_f \) decreases subsequently due to increased penetration of the electrolyte through the existing and newly formed defects in the film. A small \( R_f \) has been also observed by Wu et al. from the Mg–3.0Nd–0.22Zn–0.4Zr alloy modified by a diamond-like carbon film fabricated by plasma immersion ion implantation and deposition after immersion in 0.9% NaCl for 30 min arising from random defects in the diamond-like carbon film [33]. Therefore, it is important to design effective strategies to reduce defects in the film, for example, by optimizing the deposition conditions and pretreatment. \( R_{ct} \) of TAN-WE43 Mg decreases rapidly during immersion for 24 h and then decreases gradually afterwards. This means that the metal substrate underneath the film continues to dissolve and the corrosion rate of the TAN-WE43 Mg alloy in SBF is quite large in early immersion but decreases after 24 h. Compared to the untreated WE43, the modified WE43 shows a larger \( R_{ct} \) at each time point during the immersion period of 120 h, especially in the initial stage. \( R_{ct} \) of TAN-WE43 reaches 8850 \( \Omega \) cm\(^2\), which is 101 times that of the WE43 substrate after immersion for 1 h. Even after 120 h, \( R_f \) of TAN-WE43 is 1281 \( \Omega \) cm\(^2\), which is much larger than 432 \( \Omega \) cm\(^2\) of WE43. These results prove that the dissolution rate of the WE43 Mg alloy underneath the TaN film is notably smaller over the 120 h immersion period. Meanwhile, as degradation of the Mg substrate under the TaN film only occurs in defective areas, diffusion of the produced Mg\(^{2+}\) species though the accumulated corrosion products away from the metal surface is much more difficult under the TaN film. In the beginning, the deposited film has limited imperfections and diffusion of the produced species is strongly impeded, resulting in a large \( R_{diff} \). As
immersion proceeds, the corrosion process at the film/metal interface produces more defects in the film making it easier for the produced species to diffuse resulting in $R_{\text{diff}}$ reduction. After immersion in SBF for 1–120 h, the diffusion resistance of TAN-WE43 reaches $8578 - 1748 \ \Omega \text{cm}^2$, whereas that of the bare WE43 is only 23–659 $\Omega \text{cm}^2$. Consequently, the EIS results shown above show that the TaN film provides protection and retards dissolution of the WE43 Mg alloy in SBF.

3.3. Long-term degradation behavior

To monitor the long-term degradation behavior, release of Mg ions and pH value change of the immersed solution are monitored for up to 30 days. Fig. 10 depicts the concentrations of released Mg
ions from WE43 and TAN-WE43 after immersion in SBF for 1, 3, 7, 15, and 30 days and the corresponding pH values of the immersed solution. As shown in Fig. 10a, WE43 shows fast release of Mg ions in the first 7 days. Compared to the untreated WE43 sample, TAN-WE43 shows much less leaching of Mg ions during the whole immersion process. The concentrations of released Mg from the untreated and treated WE43 are 206.1–941.7 μg mL\(^{-1}\) and 32.7–536.1 μg mL\(^{-1}\), respectively, during the 30-day immersion period. With increasing soaking time in SBF, OH\(^{-}\) is released from both WE43 and TAN-WE43 to raise the pH. Release of OH\(^{-}\) in the second phase with a relatively notable potential as a cathode is proportional to the cathodic reaction and reflects the overall corrosion rate. As shown in Fig. 10b, the pH of the solutions of the untreated and coated WE43 Mg alloy increases rapidly in the initial 7 days and gradually afterwards. After 1 day, the pH of the solution of the bare Mg alloy rises to 8.25 ± 0.19 and that of TAN-WE43 is only 7.51 ± 0.01, which is only slightly larger than that of the SBF of 7.4. The solution of TAN-WE43 exhibits lower alkalinity than that of WE43 at each immersion time point. After 30 days, the solution of TAN-WE43 is 8.39 ± 0.14, which is much smaller than that of the untreated WE43 of 9.3 ± 0.13. The trend of Mg leaching is similar to that of the pH and the results confirm that degradation of the WE43 Mg alloy is effectively mitigated by the TaN film.

To further investigate corrosion propagation along the longitudinal and lateral directions, SEM images and EDS line scans are acquired from WE43 and TAN-WE43 after immersion for 7, 15, and 21 days. Since the longitudinal corrosion propagation of the bare and coated Mg alloy is not uniform, it is better to monitor different regions to monitor the actual corrosion conditions. As shown in Figs. 11–13 and Figs. S3–S8, two representative regions including a slightly corroded region and severely corroded region are present. Fig. 11a and b shows that all the regions on WE43 are covered by the corrosion products and the maximum thickness of the corrosion layer on the untreated WE43 is 91.5 μm after 7 days. Fig. 11a and b also reveal that the corrosion layer has a loose structure with many cracks providing channels for SBF and limited protection. As shown in Fig. S3, Mg, P, Ca, and O are detected from the corrosion layer on the untreated WE43 due to the formation of MgO, Mg(OH)\(_2\), phosphate, and carbonate during immersion [31]. The former three heavy elements are determined by EDS [29] and the line scan is acquired from up to down along the red line across the resin, corrosion layer, and Mg substrate. The top layer of the corrosion products on the uncoated WE43 shows stronger P and Ca signals and weaker Mg signal and the P and Ca signals weaken and Mg signal strengthens towards the Mg substrate. The Mg, P, and Ca signals cannot be observed at some cracks.

After immersion for 7 days, TAN-WE43 shows less corrosion as shown in Fig. 11c–f. It can be seen that the maximum thickness of the corrosion products on the TaN film is 44.4 μm, which is much smaller than that observed from the bare WE43. The slightly- and severely-corroded surfaces show three different structures: A – intact region, B – slightly corroded region with blisters, and C – severely corroded region with ruptured film. The corrosion layer beneath the TaN film has a loose structure with some cracks resulting in regions B and C. Fig. S4 show Ta at the top of the corrosion layer although the signal is weak. Mg, P, and Ca are also detected from the film region because the loose corrosion products may slip to the film side during sample preparation. The P and Ca concentrations decrease from the top to inner layers of the corrosion products of TAN-WE43 and the Mg content exhibits a reverse tendency.

After exposure to SBF for 15 and 21 days, corrosion of the untreated WE43 extends to deeper locations and the corrosion penetration depths are 136.2 μm and 163.4 μm as shown in Fig. 12a and b as well as Fig. 13a and b. The untreated WE43 also shows rapid penetration in the first 7 days and it slows after 15 days. The
thickness of TAN-WE43 Mg alloy reaches 99.2 µm and 119.9 µm after immersion in SBF for 7 and 15 days (Figs. 12c–f and 13c–f), which are obviously smaller than those of the untreated substrate.

The increasing rate of the maximum thickness of the corrosion products on TAN-WE43 is smaller than the coated one especially in the initial stage. With respect to TAN-WE43 after immersion for 15 days, regions without corrosion are still found as shown in Fig. 12c. Region C exhibits more blistering and delamination allows easier transportation of the produced species to accelerate the reaction with Mg. As shown in Fig. 13d and f, after 21 days, parts of the TaN
film detach from region D (severely corroded region with film delamination). The condition in this region is similar to that of the corroded WE43 without treatment. Dissolution of the Mg substrate in this region is easier than that of the other three regions and the TaN film in regions A and B provides a relatively good barrier against corrosion. The corresponding EDS line scans in Figs. S5–S8 demonstrate that the P and Ca contents tend to decrease except at the crack and fall-off regions from the top to inner layers of the corrosion products of WE43 and TAN-WE43, whereas the Mg signal exhibits a reverse phenomenon similar to that observed after immersion in SBF for 7 days. The results indicate with penetration of SBF, Mg in the outer layer continues to react with Ca and P species and Mg in the inner layer is gradually consumed to begin to combine with P and Ca species to form products. Some different phenomena are also observed during the late immersion stage. The EDS line scans in Fig. S5b do not show Mg, P, and Ca in some regions due to the large cracks or fall-off of the looser corrosion products during sample preparation. The volcano-like precipitates in Figs. S7a, S8d illustrate that the volcano-like precipitates have a larger Ca ratio consistent with the observation by Ascencio et al. from corroded WE43 Mg alloy immersed in modified SBF [31].

Fig. 14 depicts the surface morphology of WE43 and TAN-WE43 after immersion in SBF for 7, 15, and 21 days. Even though the samples are coated with carbon, some areas shown in Fig. 14a–c still appear white due to charging of the thick insulating corrosion products. As shown in Fig. 14a–c, a severely corroded surface with many large cracks is observed from the bare WE43 Mg alloy after the 7, 15, and 21 days. The volcano-like precipitates also emerge from the corroded WE43 surface after 7 days. The SEM images further confirm regions A, B, C, and D. Parts of the TaN film rupture after immersion for 7 days, while most of the surface is intact or just blisters. When the immersion time is increased to 15 days, the area of region C increases and those of regions A and B decrease. After 21 days, the TaN film delaminates as shown in region D, which may result from the hydrogen gas and corrosion products produced during corrosion [41,42].

Corrosion of Mg-based alloys in aqueous environments often involves microgalvanic coupling between the cathodic regions such as the second phase and anodic regions namely the Mg matrix since the second phase has a nobler potential and is less reactive than the Mg matrix. The overall reaction for the corrosion of Mg is expressed as:

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2$$

(1)

The overall reaction may be the sum of several partial reactions including the anodic production of Mg$^{2+}$ (Equation (2)), cathodic hydrogen production (Equation (3)), and product formation (Equation (4)) as follows:

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$$

(2)

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$

(3)

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2$$

(4)

For the untreated WE43 Mg alloy, the Mg(OH)$_2$ layer forms gradually on the surface during immersion in SBF. The fitted EIS results (Fig. 9) show that this corrosion products layer can provide protection to some extent to the WE43 substrate against further corrosion and better protective ability is achieved by a thicker corrosion layer up to an exposure time of 120 h. The cross-sectional and surface SEM views of the corroded WE43 at 7, 15, and 21 days (Figs. 11a, b and 12a, b, as well as Fig. 13a and b) disclose that the corrosion layer has a loose structure with many cracks offering limited protection. For the WE43 Mg alloy with the TaN film, after
immersion for 1 h, a small \( R_f \) value is obtained (Fig. 9), implying that the electrolyte has traversed through the imperfections onto the Mg substrate after a short time. Compared to the untreated WE43, TAN-WE43 has a larger charge transfer resistance \( R_{ct} \) at each time point during the 120 h immersion period and \( R_{ct} \) of TAN-WE43 is 101 times that of the WE43 substrate after 1 h (Fig. 9). The larger \( R_{ct} \) leads to a smaller dissolution rate of the WE43 Mg alloy under the TaN film. After immersion in SBF for 1–120 h, the diffusion resistance \( R_{diff} \) of TAN-WE43 reaches 8578–1748 \( \Omega \) cm\(^2\), which is much larger than 23–659 \( \Omega \) cm\(^2\) of the bare WE43 (Fig. 9). Diffusion of the produced species though the accumulated corrosion products away from the Mg surface becomes more difficult under the TaN film and the large charge transfer resistance and diffusion resistance mitigate corrosion in SBF. The surface SEM images of the immersed samples (Fig. 14) reveal that the WE43 surface is fully covered by corrosion products after 7 days, whereas the coated WE43 Mg alloy shows less local corrosion even after immersion for 21 days. The cross-sectional SEM images of the immersed samples (Fig. 11–13) show that TAN-WE43 experiences less corrosion penetration and lateral propagation than the untreated WE43 during 21-day immersion. The excellent corrosion resistance of the TaN film is also demonstrated by the smaller corrosion current density (Fig. 3), Mg leaching (Equation [2]), as well as pH variation (Equation [3]) in the 30-day study (Fig. 10). Both the cross section and surface SEM images of the corroded TAN-WE43 immersed for 7 and 15 days (Figs. 11c–f, 12c–f, and 14d and e) confirm the three regions: \( A \) – intact region, \( B \) – slightly corroded region with blisters, and \( C \) – severely corroded region with ruptured film. As the immersion time is increased, the area of regions A and B decreases and those of regions C and D increase (Fig. 13c–f, and Fig. 14f). As degradation of the Mg substrate under the TaN film occurs, more and larger imperfect areas are produced to expedite dissolution of Mg. When the exposure time is long enough, film rupturing and delamination occur. In summary, the TaN film deposited on the WE43 Mg alloy mitigates the corrosion of the WE43 Mg alloy.

4. Conclusion

A coating consisting of TaN and Ta suboxide is deposited on the WE43 Mg alloy by reactive magnetron sputtering and the anticorrosion properties are investigated by electrochemical tests and immersion tests for up to 30 days. The corrosion current density of TAN-WE43 in SBF is approximately two orders less than that of the bare WE43 substrate translating into a smaller dissolution rate. During extended exposure to SBF, the charge transfer resistance \( R_{ct} \) and diffusion resistance \( R_{diff} \) of WE43 tends to increase whereas those of TAN-WE43 increase. The modified WE43 exhibits larger \( R_{ct} \) and \( R_{diff} \) during 120-h immersion in SBF, especially in the initial stage, suggesting the effective corrosion protection by the TaN film. The untreated WE43 Mg alloy shows rapid corrosion propagation in both the longitudinal and lateral directions during immersion because the loose corrosion layer formed provides limited protection. The corrosion layer on TAN-WE43 is thicker larger than that on the untreated WE43 after exposure for 7 days because the TaN film acts as an effective barrier to protect the WE43 substrate from the SBF. As degradation of the Mg substrate under the TaN film occurs finally, more and larger imperfect areas are produced to expedite dissolution of Mg. When the exposure time is long enough, film rupturing and delamination occur. In summary, the TaN film deposited on the WE43 Mg mitigates the corrosion of the WE43 Mg alloy.

Acknowledgments

This work was supported by City University of Hong Kong Research Grants Council (RGC) General Research Funds (GRF) Nos. CityU 11301215 and 11205617.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jallcom.2018.06.151.

References

Supporting Information

Tantalum nitride films for corrosion protection of biomedical Mg-Y-RE alloy

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Fig. S1: Optical microstructure of the WE43 Mg alloy.
Fig. S2: High-resolution XPS spectra of (a) N 1s and (b) O 1s acquired from the TaN film on WE43 after sputtering for 50 nm.
**Fig. S3:** EDS line scans of the (a) slightly corroded region and (b) severely corroded region of WE43 after immersion in SBF for 7 days. The scans start from the top of the red line drawn in the corresponding SEM cross-sectional images.
Fig. S4: EDS line scans of the (a) slightly corroded region and (b) severely corroded region of TAN-WE43 after immersion in SBF for 7 days. The scans start from the top of the red line drawn in the corresponding SEM cross-sectional images.
**Fig. S5:** EDS line scans of the (a) slightly corroded region and (b) severely corroded region of WE43 after immersion in SBF for 15 days. The scans start from the top of the red line drawn in the corresponding SEM cross-sectional images.
Fig. S6: EDS line scans of the (a) slightly corroded region and (b) severely corroded region of TAN-WE43 after immersion in SBF for 15 days. The scans start from the top of the red line drawn in the corresponding SEM cross-sectional images.
Fig. S7: EDS line scans of the (a) slightly corroded region and (b) severely corroded region of WE43 after immersion in SBF for 21 days. The scans start from the top of the red line drawn in the corresponding SEM cross-sectional images.
Fig. S8: EDS line scans of the (a) slightly corroded region and (b) severely corroded region of TAN-WE43 after immersion in SBF for 21 days. The scans start from the top of the red line drawn in the corresponding SEM cross-sectional images.