Improved corrosion resistance of Mg-Y-RE alloy coated with niobium nitride

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**A B S T R A C T**

Biodegradable magnesium alloys have attracted much attention in recent years due to their potential applications in cardiovascular stents and bone implants. However, their inadequate corrosion resistance in the physiological environment is a major obstacle limiting wider application. In this work, a niobium nitride (NbN) film is deposited on Mg-Y-RE alloy (WE43) by reactive magnetron sputtering to improve the corrosion resistance. The structure of the nitride film is determined by grazing incidence X-ray diffraction and X-ray photoelectron spectroscopy. The corrosion behavior of the uncoated and NbN-coated WE43 is evaluated in simulated body fluids by electrochemical impedance spectroscopy, polarization tests, and immersion tests. The surface morphology of the samples before and after the immersion tests is examined by scanning electron microscopy to assess the degree of corrosion. Our results indicate that the corrosion resistance is improved by the corrosion-resistant nitride film and the reasons are discussed.

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1. Introduction

Magnesium alloys are attractive for biomedical implants such as cardiovascular stents [1–4] and bone implants [5–8] due to their natural degradation [9] and Young’s modulus (41–45 GPa) resembling that of natural bone (3–20 GPa) [10]. Hence, there is no need for a follow-up surgery to remove the implants after tissue healing and the stress shielding effects at the interface between the bone and implant can also be reduced. Mg-Y-RE alloy (WE43) is a promising biodegradable magnesium alloy [11] but its corrosion resistance in the physiological environment is relatively poor [12,13] compared to other materials such as stainless steels, titanium alloys, and cobalt–chromium alloys. Rapid surface corrosion further leads to loss of mechanical strength and excessive production of hydrogen causing deleterious effects in tissues. It is thus crucial to control corrosion on magnesium alloys. Surface modification techniques such as deposition of conversion coatings [14,15], anodization [16,17], electrodeposition [18,19], physical vapor deposition [20–22], and ion implantation [23–25] have been proposed to improve the corrosion resistance. In particular, reactive magnetron sputtering is one of the common and effective techniques to produce high-quality compound films such as oxides, nitrides, and carbides with reproducible stoichiometry and composition on a large scale [26].

Nitrides typically possess good corrosion resistance even in a hostile environment [27,28]. Moreover, niobium and niobium oxide have good biocompatibility [29–31] and niobium nitride films have been shown to mitigate corrosion on stainless steels [32,33]. However, there has been little work conducted on the effects of niobium nitride films on the corrosion resistance of magnesium alloys. In this work, niobium nitride (NbN) films were deposited on WE43 magnesium alloys and a series of experiments were performed to investigate and compare the surface corrosion resistance of the uncoated and coated WE43 alloys under simulated physiological conditions.

2. Experimental details

As-cast WE43 (Mg, 4.01 wt.%; Y, 2.45 wt.%; Nd, 1.47 wt.% Zr) samples with dimensions of 10 mm × 10 mm × 5 mm and silicon were used as substrates in this study. The WE43 samples were ground with SiC abrasive paper of different grades, cleaned with ethanol in an ultrasonic bath, and dried in air. The NbN films were deposited by direct current reactive magnetron sputtering using Nb as the sputtering target, argon as the sputtering gas, and nitrogen as the reactive gas. The base pressure in the vacuum chamber was 4.7 × 10⁻⁶ Pa and working pressure was 0.43 Pa. The flow rates of Ar and N₂ were 3 sccm and 9 sccm, respectively. The power was 100 W and deposition time was 2 h. The cross-section of the NbN film deposited on silicon was examined by field-emission scanning electron microscopy (FE-SEM). Grazing incidence X-ray diffraction (GIXRD) was conducted at an incident angle of 2° to determine the crystalline structure of the coating. The chemical states were determined by X-ray photoelectron spectroscopy (XPS) with Al Kα irradiation. The sputtering rate was estimated to be approximately 7 nm min⁻¹ based on similar sputtering experiments conducted on a SiO₂ reference. Water contact angle measurements were performed by the sessile drop method on a contact angle goniometer.
at room temperature and five measurements were conducted and averaged for each specimen.

Electrochemical measurements were conducted on a Zahnerr Zenium electrochemical workstation with the three-electrode configuration. A saturated calomel electrode (SCE) was used as the reference electrode, a platinum sheet served as the counter electrode, and the sample constituted the working electrode. Unless otherwise stated, the potential was referenced to SCE. All the electrochemical experiments were conducted in simulated body fluids (SBF) [34] at 37 °C. The area exposed to the solution was 1 cm² during the electrochemical measurements. After immersion in the solution for 10 min, electrochemical impedance spectroscopy (EIS) was performed from 100 kHz to 100 mHz with a 10 mV disturbing signal at open circuit potential (OCP). The polarization curves were acquired at a scanning rate of 1 mV s⁻¹ between −250 mV and 350 mV versus OCP. In addition, immersion tests were performed to evaluate the corrosion resistance of the coated samples. The uncoated and NbN-coated samples were immersed in SBF for 3 h and then the surface morphologies of the samples before and after the immersion tests were examined by SEM.

3. Results and discussion

The NbN film was deposited on silicon so that the film’s thickness could be determined accurately. As shown in Fig. 1, which depicts the SEM image of the cross-section of the NbN film, the film thickness is about 280 nm. The cross-section image shows a uniform and dense film as well as a good interface between the fabricated film and the substrate. At the same time, no obvious pinhole and micro-defects were observed. The compactness, uniformity, and adhesion strength to air [40,41]. Niobium oxy-nitride and oxide can be inferred as the outermost layer is removed by sputtering. The Nb 3d spectra at 0 min can be deconvoluted into several peaks. The peaks at 205.6 eV and 208.5 eV are assigned to niobium oxy-nitride caused by diffusion of O into the NbN film [38,39]. The peaks at 207.1 eV and 209.8 eV are associated with Nb₂O₅, a native oxide on Nb compounds after exposure to air [40,41]. Niobium oxy-nitride and oxide can be inferred as the major components on the surface. After sputtering for 4 min and 10 min, the Nb 3d peaks shift to a lower binding energy. The strong peaks at 203.4 eV and 206.2 eV indicate the formation of NbN [42].

Fig. 2 shows the GLXRD spectra of the NbN-coated WE43, NbN-coated silicon, and uncoated WE43 samples. The nitride-coated WE43 sample shows one primary diffraction peak associated with the [2 0 0] orientation of the FCC phase of δ-NbN [33,36]. The Mg phase [37] from the substrate is also detected because the NbN film is more hydrophobic than the detection depth. Another peak related to the [1 1 1] of the δ-NbN phase is detected from the nitride-coated silicon sample thus further proving that the NbN film is produced on the WE43 substrate.

Fig. 3 shows the Nb 3d, N 1 s, and O 1 s XPS spectra of the NbN-coated WE43 Mg alloy at different sputtering times. Oxygen is present in the near surface due to natural oxidation/adsorption as well as residual H₂O or O₂ in the deposition chamber. The peak position and shape shown by the three spectra on the surface are different from those at greater depths, although there is no appreciable difference between sputtering for 4 min and 10 min. This indicates that the chemical states of the elements are consistent and stable through the NbN film after the outermost layer is removed by sputtering. The Nb 3d 3p peaks at 0 min can be deconvoluted into several peaks. The peaks at 205.6 eV and 208.5 eV are assigned to niobium oxy-nitride caused by diffusion of O into the NbN film [38,39]. The peaks at 207.1 eV and 209.8 eV are associated with Nb₂O₅, a native oxide on Nb compounds after exposure to air [40,41]. Niobium oxy-nitride and oxide can be inferred as the major components on the surface. After sputtering for 4 min and 10 min, the Nb 3d peaks shift to a lower binding energy. The strong peaks at 203.4 eV and 206.2 eV indicate the formation of NbN [42].

Fig. 4 displays the water contact angles of the uncoated and NbN-coated WE43. The average contact angle of the SS304 sample is 39.4°, while the NbN-coated SS304 sample shows a larger average contact angle of 64.8°. This implies that the NbN-coated surface is more hydrophobic than the substrate. The more hydrophobic surface is relatively stable and the amount of reactive magnesium in the near surface is reduced, thereby giving rise to better corrosion resistance [43,44].

Fig. 5 shows the polarization curves acquired from the uncoated and NbN-coated WE43 samples in SBF. The cathodic and anodic polarization curves represent cathodic hydrogen evolution and anodic dissolution of the samples, respectively. The use of both the anodic and cathodic Tafel regions is preferred over that of only one Tafel region in the Tafel extrapolation method. The corrosion rate can also be determined by Tafel extrapolation of the cathodic polarization curve when the anodic polarization curve does not display an extensive Tafel region [45]. The proper Tafel methods should be chosen for different materials. Magnesium alloys have an abnormal polarization behavior and their polarization curves do not follow the traditional Tafel equation [46].

Fig. 5 shows a non-symmetrical polarization curve between the anodic and cathodic branches, and the cathodic curve produces a better Tafel region. Zhao et al. [47], Wu et al. [48], Zhao et al. [49], and James et al. [25] have applied the cathodic Tafel method to the determination of the corrosion rate. Therefore, the corrosion potential and corrosion current density are determined from the cathodic Tafel region in this work. The corrosion potential of the NbN-coated WE43 shifts toward the positive direction from −1.991 V to −1.805 V, indicating that the sample experiences less corrosion than the untreated WE43 in SBF. According to the cathodic extrapolation, the uncoated WE43 has a corrosion current density of 5.593 × 10⁻⁸ A cm⁻² in SBF but that of the NbN-coated WE43 diminishes significantly to 3.817 × 10⁻⁸ A cm⁻². The smaller corrosion current density corresponds to a smaller
corrosion rate and better corrosion resistance is achieved on the NbN-coated sample. Fig. 6 displays the equivalent circuits as well as experimental and fitted Nyquist plots of the untreated and NbN-coated WE43 samples in SBF. The untreated and NbN-coated WE43 samples display two capacitive loops, although the second capacitive loop at low frequencies is not obvious in the WE43 sample. As shown in Fig. 5(a), an equivalent circuit with two time constants is used to fit the experimental data of the Nyquist plots. \( R_s \) represents the solution resistance between the working electrode and reference electrode. As a constant phase element, CPE\(_1\) is the capacitance of the surface film or corrosion product layer and \( R_1 \) is the pore electrical resistance to the ionic current through the pores. CPE\(_2\) represents the capacitance of the double layer at the electrolyte/substrate surface and \( R_2 \) represents the electrical charge transfer resistance of the substrate. Jemash et al. [25], Xia et al. [50], and Zhao et al. [49] have used a similar circuit to explain the corrosion behavior of the untreated and/or modified WE43 alloy in NaCl and SBF solutions. As shown in Fig. 6(b), the capacitive loop at high frequencies is generally related to electrolyte penetration whereas the capacitive loop at low frequencies results from electrochemical reactions. The capacitive loops of the NbN-coated WE43 are much larger than those of WE43 disclosing that the NbN-coated WE43 has better corrosion resistance.

The fitted values of the equivalent components are listed in Table 1. As the solution resistance, \( R_s \) has a small value and does not show much...
difference between the untreated WE43 and NbN-coated WE43 samples. Generally, higher resistance and lower capacitance translate into better corrosion resistance. Table 1 shows that the NbN-coated WE43 has smaller CPE1 and CPE2 than the untreated WE43, indicating that the NbN coating renders better corrosion resistance. Moreover, significant improvement in both R1 and R2 can be observed. The larger R1 corresponds to higher resistance to electrolyte transportation through the film or product layer and bigger R2 means larger resistance to magnesium dissolution. This result also shows that the NbN film retards surface corrosion on the WE43 alloy. Therefore, it can be concluded from the Nyquist results that the NbN film significantly improves the corrosion resistance of WE43 and the results are in agreement with the polarization results.

To obtain a better understanding of electrochemical corrosion, the Bode plots of the untreated and NbN-coated WE43 samples in SBF are shown in Fig. 7. The NbN-coated WE43 shows larger impedance and phase angle in a wide range of frequencies. At a low frequency of 100 mHz, the impedance of the untreated WE43 is 78.1 Ω, whereas the NbN-coated WE43 shows a much larger impedance of 1,930.5 Ω. This is because the NbN film on the WE43 surface impedes the charge transfer process. Compared to the maximum phase angle of 29.5° observed from the untreated WE43, the maximum angle of the NbN-coated WE43 is 64.4°. This provides evidence about retarded charge transfer as well as good protection rendered by the NbN coating. Again, the Bode plot results are consistent with those inferred from the polarization and Nyquist plots.

Fig. 8 depicts the SEM images of the surface morphology of the uncoated and NbN-coated WE43 samples before and after immersion in SBF. As shown in Fig. 8(a), besides the magnesium matrix, which contains a small amount of dissolved yttrium, the Nd-rich second phase [37] can be observed from the relatively rough surface of the WE43 substrate. Fig. 8(b) shows no gross surface defects on the NbN-coated WE43 and the surface is smoother after deposition. This kind of surface state is beneficial to the improvement of corrosion resistance. Fig. 8(c) shows that nearly the entire surface of the uncoated WE43 sample is covered by corrosion products after immersion and cracks, which allow easy penetration of SBF through the product layer to promote corrosion on the untreated sample. This can also be concluded from the small electrical resistance R1 of the untreated WE43 sample. The energy-dispersive X-ray spectroscopy (EDS) data in Fig. 8(c) shows that the corrosion products are rich in Mg, O, P, and Ca, which may be caused by precipitation of MgO and/or Mg(OH)2, phosphates, and carbonates [49,51]. On the contrary, as shown in Fig. 8(d), no severe corrosion occurs on the NbN-coated WE43 sample and there is only local corrosion, which may be caused by magnesium corrosion from defects in the NbN film. The EDS results in Fig. 8(d) discloses that the corrosion products consist of Mg, O, and P in the local corrosion area similar to those on the uncoated WE43, and only Mg from the substrate and Nb from the film are detected from the smooth area, indicating that the film is protective to the substrate. Therefore, the extent of surface corrosion is much less severe on the NbN-coated WE43 and the corrosion resistance of the WE43 sample is improved by the NbN film.

### 4. Conclusion

NbN films are deposited on WE43 samples by reactive magnetron sputtering to improve corrosion resistance. XPS corroborates the formation of the NbN film on the WE43 substrates. Electrochemical results reveal that as a result of the sturdy NbN film on the WE43 samples, the corrosion resistance in SBF is improved. The surface morphology after the immersion tests in SBF is in agreement with the electrochemical results. Our results suggest that the fabrication of an NbN film is a useful approach to improve the corrosion resistance of WE43 magnesium alloys.

| EIS fitted data of the untreated and NbN-coated WE43 in SBF. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Rs (Ω cm²) | CPE1 (S sⁿ cm⁻²) | n₁ | R1 (Ω cm²) | CPE2 (S sⁿ cm⁻²) | n₂ | R2 (Ω cm²) |
| WE43          | 17.28              | 3.482 × 10⁻⁵   | 0.8545         | 50.2            | 1.215 × 10⁻²   | 0.5934         | 8.997         |
| NbN-coated WE43  | 16.62              | 6.604 × 10⁻⁶   | 0.9347         | 926             | 2.563 × 10⁻⁴   | 0.5802         | 1116          |

Fig. 6. (a) Equivalent circuits and (b) Nyquist plots of the uncoated and NbN-coated WE43 samples in SBF.

Fig. 7. Bode plots of the uncoated and NbN-coated WE43 samples in SBF.
Fig. 8. SEM images of the surface morphology: (a) uncoated WE43 before the immersion test, (b) NbN-coated WE43 samples before the immersion tests, and (c) uncoated WE43 after the immersion test, and (d) NbN-coated WE43 samples after the immersion tests.

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