Plasma enhanced chemical vapor deposited silicon coatings on Mg alloy for biomedical application

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1. Introduction

Magnesium and its alloys have raised great interest in the field of biomedical implant by virtue of their outstanding biological performance and superior mechanical properties [1–3]. However, the high corrosion rate and accumulation of hydrogen gas upon degradation hinders their clinical application [4,5]. Surface modification methods such as PECVD [6], magnetron sputtering [7], alkaline heat treatment [8], micro-arc oxidation [9], electrodeposition [10] and sol–gel method [11], are effective to solve these problems.

It has been reported that silicon film has good biocompatibility, anti-corrosion property and inertness to biological tissues [12–15]. In addition, nanostructured porous silicon can degrade completely in aqueous solutions into non-toxic silicic acid, the major form of silicon in the human body, leaving no non-resorbable or poorly resorbable fragments in the human body [12]. Above all, silicon-based coatings, such as SiC [6], bioglass [16], Si/HA (silicon-substituted hydroxyapatite) [17], SiN [18] have been used in the field of biomedical application. However, to date, no report has been found to enhance the corrosion resistance of WE43 alloy by silicon film.

As PECVD is a commonly used method to deposit silicon-based coatings, therefore, in our present work, we employ this approach to coat WE43 alloy with the aim to slow down the degradation rate. The surface characteristics, in vitro corrosion behavior, biocompatibility and hemocompatibility of the amorphous Si coated WE43 alloys were investigated.

2. Material and methods

2.1. Preparation of the samples

The extruded WE43 Mg alloy (91.35 wt.% Mg, 4.16 wt.% Y, 3.80 wt.% RE, 0.36 wt.% Zr, 0.20 wt.% Zn, 0.13 wt.% Mn) was provided by Changchun Zhong-Ke-Xi-Mei Magnesium Alloy Co. Ltd., China, with an extrapolation ratio of 10. The extruded bar was cut into discs of 10 mm in diameter and 2 mm thick. All the disc samples were mechanically ground down to 2000#. Afterwards, they were cleaned ultrasonically in acetone, alcohol and distilled water for 15 min respectively before conducting the deposition process. Silicon film was prepared by a customized PECVD apparatus with an input 13.56 MHz radio frequency (RF) power of 60 W, silane (SiH₄, 99.999%) gas flow rate of 5 sccm, deposition pressure at 20 Pa, substrate temperature at 250 °C and deposition time of 30 min. Prior to the deposition, Ar⁺ ions were used to sputter-clean the samples to remove the surface contamination.

2.2. Surface microstructure and characterization

The microstructural characteristics of the films were examined by glancing angle X-ray diffraction (GAXRD; D8-Discover, Bruker Co. Ltd.) with an incident angle of 1° and the scanning rate of 4°/min, using CuKα radiation (λ = 1.540598 Å) at 40 kV. The surface elemental composition and valance state of the surface elements were...
identified by X-ray photoelectron spectrum (XPS; AXIS Ultra, Kratos Analytical Ltd.). The surface chemical composition was further analyzed by Auger electron spectroscopy (AES; PHI-700, ULVAC-PHI Inc.) after being sputtered by Ar⁺ for 3 min in order to avoid the effects of surface contaminant.

2.3. Immersion test

The samples were immersed in static regime at 37 ± 0.1 °C (pH = 7.4) in simulated body fluid (SBF) [19] for 10 days according to ASTM G31-1972 standards with a solution volume to specimen surface of 0.2 mL/mm². The pH value and hydrogen evolution volume of the solution were recorded during the immersion test. The surface morphology of the samples before and after the immersion test was observed by scanning electron microscope (SEM, 1910FE, Amray Co. Ltd.) and the composition of the corrosion products was analyzed by the equipped energy-dispersive spectroscopy (EDS). The hydrogen evolution experiment was conducted in accordance to Ref. [20].

2.4. In vitro cytotoxicity and hemocompatibility evaluation

The cytotoxicity of the extracts of the Si coated WE43 alloys was evaluated by MTT test according to a standard procedure described in reference [21] using murine fibroblast cells (L929 cells). The in vitro hemocompatibility evaluation was investigated by hemolysis and blood platelets adhesion test as described previously [22].

3. Results and discussion

3.1. Microstructure and composition of the Si film

Compared with the GAXRD pattern of WE43 substrate (PDF #65-3365), we can conclude that an amorphous silicon film has been successfully fabricated on the surface of WE43 alloy, as indicated by a broad scattering signals around 28° shown in Fig. 1(a). Surface chemical composition was analyzed by survey and high-resolution XPS spectra as shown in Fig. 1(b). An intense peak at a binding energy of 98.9 eV and a relatively weak peak at 102.9 eV are observed in the Si2p spectra, which can be assigned to silicon [23] and silicon dioxide [24], respectively. For the O1s spectra, the peak located at 532.1 eV is ascribed to silicon dioxide [25]. The detected oxygen and carbon appeared in the survey spectra is probably originated from surface contamination and presumably reaction of dangling bond with the atmospheric oxygen. In order to clarify this problem, the surface composition was further analyzed by AES after Ar⁺ sputtered for 3 min to remove the surface contamination. It can be seen that only two typical peaks Si LMM (98 eV) and Si KLL (1621 eV) assigned to Si [26] appear in AES spectra as shown in Fig. 1(c). Combined with the results of XPS and GAXRD, we can conclude that the amorphous silicon film have been well prepared on WE43 alloy by PECVD method.

3.2. Immersion test of the Si coated samples

It can be seen from Fig. 2 that both of the pH value and the hydrogen evolution rate are quite lower than those of the uncoated WE43 alloy (p < 0.01), indicating that silicon film can effectively slow down the corrosion rate and alleviate the local alkalization of the WE43 alloy. Before immersion in SBF, the surface morphology at low magnification for the uncoated (Fig. 3a) and Si (Fig. 3b) coated alloys is compact and uniform. Abrasive scratches resulted from the mechanical polishing and spherical silicon particles can be seen at high magnification (inserted images in Fig. 3b). After immersion in SBF at 37 °C for 240 h, the uncoated WE43 alloy (Fig. 4d) is seriously corroded with significant corrosion products and relatively large pits on the surface. On the contrary, a small quantity of corrosion products are observed on the surface of coated sample. The corrosion products analyzed by EDS mainly consist of silicon and magnesium with calcium phosphate (Fig. 3f), this corrosion products combined with silicon film can further slow down the degradation rate. The cross-sectional SEM images and the corresponding EDS (line scanning mode) of the coated samples (Fig. 3c) indicate that the coating with thickness about 5 μm, adhere well to WE43 substrate, and mainly consist of silicon. It was reported that the coating thickness has a significant

![Fig. 1. (a) GAXRD patterns of the uncoated and the Si coated WE43 alloys; (b) the survey XPS spectra (inserted: the Si2p and O1s core level spectra) and (c) the AES analysis of the Si coated WE43 alloys.](image-url)
influence on the degradation behavior of the substrate, and a thicker coating could result in a slower degradation rate [27]. The protective effect of silicon film in our study is in agreement with hydrogenated amorphous silicon coating prepared by magnetron sputtering deposition for magnesium alloy [15].

3.3. In vitro cytotoxicity and hemocompatibility of the Si coated samples

The cell viability of L929 cells after 1, 3 and 5 days incubation in the uncoated and Si coated specimens extraction medium are illustrated in Fig. 4(a). The extract of the Si coated samples exhibits higher cell viabilities in comparison with that of the uncoated ones (p < 0.01), and slightly differences of cell viability can be seen after 1, 3, and 5 days incubation, implying that silicon film has no inhibitory effect on L929 cell. Fig. 4(b) shows the hemolysis percentage of the uncoated and the Si coated samples, it can be seen that the hemolysis value reduce to 2.9% ± 0.7% for the Si coated sample from 6.1% ± 0.4% of the uncoated ones (p < 0.01). Therefore the Si coated WE43 alloy will not cause severe hemolysis to blood system according to ISO 10993-4 standard. Representative SEM images of platelets adhering to the samples are shown in Fig. 4(c) and (d). The platelets on both samples are at the inactivated stage with a round shape [28], and no spread dendritic platelets can be observed. As reported by Roy et al. [29] that the extracts of silicon showed no cytotoxicity to L929 cells and silicon did
not exhibit hemolysis. Muthusubramaniam et al. [30] reported the results of hemocompatibility studies using bare silicon, polysilicon, and modified silicon substrates, and the tests revealed that all the silicon substrates displayed low coagulation and complement activation.

4. Conclusions

(1) The amorphous Si film was successfully prepared on the surface of WE43 alloy by PECVD.
(2) The immersion test suggests that the amorphous Si film could effectively slow down the degradation rate and alleviate local alkalization of WE43 alloy in SBF at 37 °C.
(3) The indirect toxicity experiment results showed that the extract of Si coated WE43 alloys exhibits no inhibitory effect on L929 cell growth.
(4) The hemolysis percentage of WE43 alloy decreased after being coated by Si film.

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