Effects of tungsten pre-implanted layer on corrosion and electrochemical characteristics of amorphous carbon films on stainless steel

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Abstract

Amorphous carbon (a-C) films have been deposited on untreated and W pre-implanted (20 kV, $3 \times 10^{17}$ ions/cm\textsuperscript{2}) stainless steel substrates by plasma immersion ion implantation and deposition (PIII&D). X-ray photoelectron spectroscopy indicates that the transition layer consists of tungsten carbide (WC) and C. The corrosion behavior of the coatings is investigated electrochemically in 37±1 °C simulated body fluids. In comparison with the a-C films, the a-C films with a W pre-implanted layer exhibit more positive open-circuit potentials, lower corrosion current density, and higher protection efficiency as indicated by potentiodynamic polarization tests. Electrochemical impedance spectroscopy reveals that the W pre-implantation layer increases the corrosion resistance of the a-C coatings in test solutions. The continuous structure caused by W pre-implantation layer is believed to not only offer good adhesion between the a-C film and steel substrate but also act as a barrier to mitigate penetration of water molecules and ions.

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1. Introduction

With the development of biomedical titanium and cobalt alloys, austenitic stainless steels have been gradually relegated to temporary implants such as fracture plates, bone screws and hip nails because of their inferior \textit{in vitro} and \textit{in vivo} corrosion properties [1]. However, stainless steels have certain advantages but localized corrosion attack and releasing of metallic ions from the materials must be reduced. Possible approaches to improve the corrosion resistance include bulk alloying or surface modification. In order to create a surface that facilitates bioreactions and possesses the desired biofunctional properties, a suitable coating with good biocompatibility and adequate protection is a viable means. Amorphous carbon films have generated great interest as protective coatings in orthopedic and other medical implants because of their good biocompatibility [2] as well as favorable physical and chemical properties [3]. However, the adhesion with most metal implant materials is usually poor due to high residual internal stress thereby hampering wider applications [4]. Up to now, thermal treatment and incorporation of metallic and non-metallic elements have been used to reduce the internal stress in amorphous carbon films [5,6]. However, these methods may alter the properties of amorphous carbon films. Therefore, there is a need to improve both the adhesion and corrosion resistance simultaneously [7]. Compared to the gaseous ion beam treatments [7], non-metallic and metallic intermediate layers are more widely employed for adhesion improvement [8–13]. The application of metallic interlayers such as Cr, Mo, Cu, Zr, Al or W has been shown to yield good adhesion between steels and diamond-like carbon films [12,13]. Compared to the other elements, tungsten is mechanically tougher than Si and more resistant to oxidation than Ti, and so the oxidation problem when using W as an
intermediate layer can be more easily alleviated [14]. According to our previous study utilizing plasma immersion ion implantation (PIII), the W pre-implantation layer shows the presence of WC and C–C bonds and defects dramatically enhance the nucleation density. The WC and C–C bonds increase the chemical affinity and adhesion between the amorphous carbon films and stainless steel [15,16]. Although the improvement of adhesion strength by a W transition layer has been reported, there has not been much work conducted on the corrosion behavior of a-C films with W transition layers. In the present work, we investigate the anti-corrosion properties of amorphous carbon films with a W pre-implanted layer (20 kV, 5 × 10^{17} ions/cm²) fabricated on stainless steel substrates by plasma immersion ion implantation and deposition (PIII&D).

2. Experimental details

Commercial AISI 316 stainless steel coupons with dimensions of 10 mm × 10 mm × 2 mm were prepared. The specimens were polished mechanically and then ultrasonically washed in acetone for 10 min. A multi-purpose plasma immersion ion implanter equipped with several plasma generating tools including RF discharge, hot filament discharge, and vacuum arc metal plasma sources was used to prepare tungsten by plasma immersion ion implantation (PIII) [17,18]. The base pressure in the vacuum chamber was 1 × 10^{-5} Torr. Tungsten pre-implantation was conducted using the following parameters: negative high voltage = −20 kV, frequency = 30 Hz, pulse width = 300 μs, ion fluence = 5 × 10^{17} ions/cm², and implantation time = 2 h. After tungsten pre-implantation, mixed Ar and C₂H₂ gases were introduced into the plasma chamber. Plasma immersion ion implantation and deposition (PIII&D) was conducted to deposit amorphous carbon films on the stainless steel samples pre-implanted with W. The mixed Ar/C₂H₂ plasma was sustained by 1 kW hot filament discharge and PIII&D was performed using the following conditions: negative high voltage = −20 kV, pulse width = 200 μs, and frequency = 40 Hz. The processing time was 2 h without heat treatment. Samples designated Sub-WC1 and Sub-WC2 were prepared using Ar to C₂H₂ flow rate ratios of 5:10 and 5:15 (sccm), respectively. Sub-C designates the sample directly deposited on the stainless steel substrate at an Ar to C₂H₂ flow rate ratio of 5:10 (sccm).

X-ray photoelectron spectroscopy (XPS, PHI 5802) was employed to determine the composition and chemical structure of the W implanted layer. Elemental depth profiles were obtained by XPS using argon ion sputtering at an approximate sputtering rate of 6 nm/min. The surface view of the specimens before and after corrosion was observed by scanning electron microscopy (SEM) on a JEOL-JSM-5600LV and optical microscope.

The corrosion tests were carried out at 37 ± 1 °C in simulated body fluids (SBF) [19]. The corrosion test apparatus consisted of a conventional three-electrode cell comprising a working electrode, saturated calomel electrode (SCE) as the reference electrode, and pure carbon stick as the counter electrode. The specimens were prepared by connecting a copper plate to one side of the sample covered by cold setting resin. The opposite surface of the specimen was exposed to the solution. The exposed area was about 1 cm². Variations in the free corrosion potential were monitored as a function of time under open-circuit conditions for approximately 1800 s. Potentiodynamic polarization tests were carried out at a scanning rate of 1 mV/s. The initial potential was 300 mV below E_{corr}. An EG&G 263A potentiostat/galvanostat was used for the electrochemical measurements. The electrochemical impedance spectroscopy (EIS) measurements were conducted on a GAMRY PCI4/300 at a stable OCP. The perturbing signal had an AC amplitude of

<table>
<thead>
<tr>
<th>Samples</th>
<th>E_{corr} (mV)</th>
<th>i_{corr} (nA/cm²)</th>
<th>β_a</th>
<th>β_b</th>
<th>Protection efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>−0.299</td>
<td>29.926</td>
<td>0.2217</td>
<td>0.1149</td>
<td>−</td>
</tr>
<tr>
<td>Sub-C</td>
<td>−0.182</td>
<td>14.549</td>
<td>0.1737</td>
<td>0.2259</td>
<td>51.4</td>
</tr>
<tr>
<td>Sub-WC1</td>
<td>−0.149</td>
<td>0.406</td>
<td>0.1943</td>
<td>0.1365</td>
<td>98.6</td>
</tr>
<tr>
<td>Sub-WC2</td>
<td>−0.083</td>
<td>1.829</td>
<td>0.2438</td>
<td>0.2793</td>
<td>93.9</td>
</tr>
</tbody>
</table>
10 mV and frequency range from 30 kHz to 10 mHz. The data were analyzed using the software Gamry Echem Analyst.

3. Results and discussion

Fig. 1 depicts the XPS depth profiles of Fe, W, and C. The outer layer on the Sub-WC samples is mainly composed of C particles. The intermediate layer is rich in W, Fe, and C as shown by a broken-line circle in Fig. 1. A graded zone with gradual changes in the composition exists at the interface. The pre-implanted tungsten profiles still retain the near Gaussian shapes in the transition layer. The chemical states of W, Fe, and C in the transition layer are also investigated. No Fe–C compounds are formed but WC appears, as indicated by the W4f7/2 peak at 31.79 eV and C1s peak at 283.3 eV. The gradual changes revealed in the tungsten PIII sample demonstrate structural continuity from the substrate to the film, thereby reducing internal stress concentration in the vicinity of the interface [20]. Besides, the expected radiation damage by the energetic ion implantation and formation of WC and C–C bonds may lead to the formation of more compact and high-quality amorphous carbon films [15].

The electrochemical stability of the systems in the test solution is investigated by the open-circuit potentials. The greatest $E_{corr}$ value of 0.093±0.012 V is observed from Sub-WC2, followed by Sub-WC1, Sub-C, and the substrate. The negative OCP values for the Sub-C samples may be caused by the penetration of the test solution [21].

The electrochemical parameters obtained from the potentiodynamic polarization curves (Fig. 2) and Tafel polarization curves are given in Table 1. The corrosion current density ($i_{corr}$) of 14.549 nA/cm$^2$ for the Sub-C sample is about 1/2 of that of the substrate. Moreover, the $i_{corr}$ value (0.406 nA/cm$^2$) of the Sub-WC samples is further lower indicating lower corrosion rates. The protection efficiency [3] also indicates that Sub-WC1 offers the best protection among the coated samples up to 98.6%. With further polarization at the anodic direction, the corrosion density of stainless steel increases rapidly at about 0.3 V. In contrast, a potential of 0.9 V from the Sub-C samples and approximately 1.6 V from the Sub-WC samples are obtained. The two kinds of Sub-WC samples have similar corrosion behavior, indicating that the variation of the Ar to C$_2$H$_2$ flow rate ratios (5:10 and 5:15) has little influence. The improvement in the breakdown potential values means the extension of the passive region in the coated system and a higher polarization is necessary to trigger the onset of anodic dissolution of the system [22]. After potentiodynamic polarization tests, the Sub-C samples are selectively damaged and corroded holes as large as approximately 60 μm are found. In contrast, only minor corrosion attack is observed from the Sub-WC samples.

The Bode plots determined by the EIS technique in Fig. 3 show the different corrosion behavior of the Sub-C and Sub-WC systems after immersion in simulated body fluids. In order to illustrate the corrosion behavior of these two kinds of systems, the equivalent circuit $R_s\lbrack CPE1\{R_{pore}(CPE2R_{ct})\}\rbrack$ is utilized to model the EIS spectra [3]. Here, $R_s$ corresponds to the solution resistance of the test solution between the working electrode and reference electrode, and CPE1 ($C_{coat}$) is the
capacitance of the coating including pores in the outer layer coating. \( R_{pore} \) represents the pore resistance resulting from the formation of ionic conduction paths across the coating. CPE2 (\( C_{dl} \)) is the double-layer capacitance of the coating within the pit and \( R_e \) is the charge transfer resistance of the coating/substrate interface. Because of the existence of inhomogeneity between the double layer and nonuniform diffusion, the non-ideal behavior is taken into account by introducing a constant phase element (CPE) [23]. The data fitted by means of the above equivalent circuit are listed in Table 2.

It is interesting to note the high value of \( R_{pore} \) in the a-C film. After initial immersion, the \( R_{pore} \) values of the Sub-WC samples show slight decrease during the 168-h exposure in SBF, and decrease suddenly at about 360 h due to the permeation of corrosive electrolytes through the coating/substrate interface. In contrast, the sudden decrease in \( R_{pore} \) in the Sub-C samples appears at approximately 168 h, which is lower than that of the Sub-WC sample. The results indicate that the Sub-WC system inhibits in-leakage of corrosive electrolyte more effectively during immersion. The variation of CPE1 also corresponds to the changes in the \( R_{pore} \) values. In the Sub-C samples, the CPE1 increases more quickly than that of the Sub-WC samples, and it may be caused by more ions and water molecules reaching the interface [3]. The Sub-WC samples show higher \( R_e \) values than the Sub-C samples at the same immersion time. The higher \( R_e \) value indicates better corrosion resistance for the Sub-WC system than Sub-C system. Besides, the variation in the \( R_e \) values also reflects the degree of penetration of the water molecules and ions. Mansfeld et al. have introduced a method to measure the amount of delamination area and water uptake of coatings exposed to the test solution [3,23,24]. The gradual increase in the \( A_d \) and \( V \) values indicates that long-term immersion causes the continuous increase in the in-leakage of the corrosive electrolytes through the pre-existing defects in the coatings, followed by penetration along the interface between the DLC and buffer layer as well as between this region and the substrate. In comparison with the Sub-C samples, the coatings on the Sub-WC samples exhibited no significant damage after 360-h immersion. However, the Sub-C samples suffer more corrosion attack and obvious damage can be monitored by SEM. This may be because the number of defects after penetration of water molecules and ions into the interface between the DLC and substrate is higher. As far as the Sub-WC system is concerned, the W pre-implantation layer inhibits damage and cracks in the a-C layer. This may be attributed to the following possible reasons. Firstly, the W pre-implantation layer decreases the compressive residual stress, lessening the opening of pores and cracks. Secondly, the diffusion-controlled process, such as chemical reactions or capillary-driven penetration of corrosive electrolyte [25], will occur at a smaller rate due to the existence of the W transition layer. The delamination area is affected by the volume fraction of water uptake through the open defects because the in-leakage of water molecules and ions causes possible debonding and cracking of the coatings. The results in Table 2 show that the Sub-C samples tend to absorb more corrosive electrolyte due to the lack of a barrier, i.e. transition layer, which can offer good adhesion and obstructing effect for further penetration of the corrosive electrolyte. The \( A_d \) and \( V \) values are in good agreement with the protection efficiency obtained from the potentiodynamic polarization tests. For the protective coatings, the lower the \( A_d \) and \( V \) values, the better is the corrosion resistance. Moreover, penetration of corrosive electrolyte at a lower rate does less harm to the coated samples. It can be seen that the Sub-WC samples have more positive OCP values, indicating better electrochemical stability during the long-term exposure in simulated body fluids.

4. Conclusion

The Sub-WC samples show more positive open-circuit potentials and breakdown potentials than the Sub-C samples without W pre-implantation, indicating better corrosion resistance. Exposure of the Sub-WC and Sub-C samples to simulated body fluids leads to different corrosion behavior. The Sub-WC system shows a lower variation in the delamination area \( (A_d) \), volume fraction of water uptake \( (V) \), and greater \( R_{pore} \) values during the immersion period. The mechanism by which W pre-implantation layer improves the corrosion resistance of the coatings may be the formation of a transition layer consisting of tungsten carbide (WC) and C. It inhibits further penetration of the corrosive electrolyte through the pre-existing defects in the coatings via a diffusion-controlled process.

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References

