Corrosion behavior of DLC-coated NiTi alloy in the presence of serum proteins

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ABSTRACT

Uniform and adherent diamond-like carbon (DLC) coatings are deposited on NiTi alloy by arc enhanced magnetron sputtering (AEMS). The effects of serum proteins, bovine serum albumin (BSA) and fibrinogen (Fib) on the corrosion behavior of DLC-coated NiTi alloy in phosphate buffer saline (PBS) solution are investigated at 37 °C using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The results show that DLC coatings, which enhance the corrosion resistance of the NiTi alloy especially in the presence of BSA, move the OCP to the positive direction, increase the polarization resistance, lower the corrosion current density, and enhance the breakdown potential. The presence of fibrinogen shows the similar effect but less notable than BSA. The associated mechanism is also discussed.

1. Introduction

Nearly equiatomic NiTi alloy has attracted much attention as biomedical implants on account of their unique shape memory effect and superelasticity [1,2]. The physiological environment is a complicated electrochemical system and so the corrosion behavior of implants must be considered before they can be used clinically. Many studies have been carried out to investigate the corrosion behavior of NiTi alloy in simulated body fluids [1,3,4]. The good corrosion resistance of NiTi alloy is generally ascribed to the formation of passive films consisting mainly of titanium oxide. However, in some aggressive environments such as chloride solutions, breakdown of the passive films can occur readily and healing of the passive films can be a difficult and slow process. Moreover, as Ni is a major element in the alloy, if the passive films break down, Ni ions will leach from the alloy into surrounding tissues inhibiting cell proliferation and differentiation through changing the expression level of related genes [5]. Therefore, further improvement in the corrosion resistance of NiTi alloy in a physiological environment is crucial.

Diamond-like carbon (DLC) coatings are promising candidates because of their excellent corrosion resistance [6–8] and biocompatibility [9,10]. Much research [6,7,11] has been performed to investigate the corrosion behavior of DLC coatings in simulated body fluids (SBF) such as Hanks’ or Ty rode’s solution. However, as aforementioned, the physiological environment is a complicated electrochemical system that contains not only inorganic species but also organic molecules such as serum proteins. The impact of serum proteins on metallic implants has been studied, for instance, by interacting with the charged double layer established at the metal/electrolyte interface [12,13] as well as the chelating effect with metal ions, which can accelerate the corrosion of metallic implants [14–16]. Unfortunately, little work has been done on the influence of serum proteins on DLC coatings which may be important to clinical applications.

The present work studies the influence of two major serum proteins, bovine serum albumin (BSA) and fibrinogen (Fib) on the corrosion behavior of DLC-coated NiTi alloy fabricated by arc enhanced magnetron sputtering (AEMS). The corrosion behavior of the DLC-coated NiTi samples is assessed by electrochemical methods at 37 °C in PBS, PBS+BSA and PBS+Fib, and the results are compared to bare NiTi alloy.

2. Experimental Details

Arc enhanced magnetron sputtering (AEMS) was utilized to deposit the DLC coatings. A columnar titanium target (460 mm × 660 mm) was used in the chamber to produce the arc discharge. It was hollow and a permanent magnet was placed in the center of the hole. Ultra-pure graphite targets (two pairs of targets with dimension of 435 mm × 94 mm × 8 mm) were used to prepare the DLC coatings on mirror polished NiTi (50.7 at.% Ni) substrates with dimension of 15 mm × 15 mm × 2 mm. The substrates were ultrasonically washed with acetone, alcohol, and distilled water for 15 min sequentially and then dried in a nitrogen atmosphere before introduction into the deposition chamber. The sputtering gas was Ar. When the pressure reached 6.0×10⁻² Pa, the heating system was turned on. After chamber temperature reached 150 °C (The substrate temperature might a little higher than the chamber temperature because the holder of the sample was between the heater and thermocouple.),
Ar⁺ plasma sputtering was first conducted for 30 minutes at -1 kV to remove undesirable surface oxide and contamination. The cleaning was conducted at deposition temperature rather than room temperature in order to inhibit further oxidation of the substrate during the heating interval because of the vacuum chamber wall outgases during heating. Afterwards, a Ti interlayer was deposited using the columnar Ti target (50 A) in the arc discharge mode for 5 min to improve the adhesion between the substrate and coatings. Then the deposition parameters of DLC coatings, which are based on our previous large numbers of experiments, are as follows: pulsed DC bias voltages of -100 V (duty factor of 40% and pulse frequency 40 kHz), graphite target power of 3 kW, chamber temperature of 150 °C, working pressure of 0.3 Pa in Ar (flow rate of 24 sccm) and deposition time of 60 min.

Raman spectroscopy (ALMEGA) was conducted to determine the chemical structure of the DLC coatings. A 532 nm argon laser was used as the source and the power was 25 mW. The atomic structure of the DLC coatings were determined by high-resolution transmission electron microscopy (HRTEM, JEM-200CX) at an accelerating voltage of 200 kV. Field-emission scanning electron microscopy (FE-SEM, JSM-6700F) was utilized to observe the surface and cross-sectional morphologies of the DLC coatings at an accelerating voltage of 20 kV. The adhesion strength between the coatings and substrate was assessed on a scratch tester equipped with a diamond indenter (cone angle 120° and tip radius 0.2 mm). The speed was 2 mm/min and the normal load was linearly increased from 0 N to 100 N at a rate of 50 N/min. The critical scratch load (Lc) at which the coatings exhibited spalling or flaking was determined by SEM.

A phosphate buffer saline (PBS, pH = 7.4) solution was used as the electrolyte in the measurements. The BSA and Fib (Sigma Chemical Co.) solid reagents were dissolved in PBS at concentrations of 35 mg/ml and 3.5 mg/ml, respectively. The concentrations are similar to those found in human serum [17,18]. The electrochemical measurements were conducted in a traditional single compartment three-electrode cell of 50 ml. A saturated calomel electrode (SCE) was used as the reference electrode and platinum wire as the auxiliary electrode. All the potentials reported here are referenced to the SCE. The electrochemical measurements were carried out using CHI660C electrochemical workstation (Chenhua Co. Shanghai, China).

The corrosion behavior of the DLC-coated and uncoated NiTi alloy in different solutions was evaluated at 37±0.5 °C by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization without deaerating by assuming that the dissolved oxygen content was regulated by exposure to the air atmosphere. A copper wire was attached to one side of bare NiTi electrode by tin soldering, and epoxy resin was used to seal it to expose an area of 0.5 cm². After solidification, it was wet grinded with silicon carbide paper of 1500 grit and then polished with 2 μm diamond paste. To avoid the exposure of interface between film and substrate, the DLC-coated sample was mounted in epoxy resin with the entire DLC-coated surface exposed to air. After keeping it for overnight, a smooth cuneal block with bottom area of 0.5 cm² was attached to the center of DLC surface by double-side adhesive and put it into the mould inverted, and then fresh epoxy resin filled into the mould was followed. After solidification, the block was taken away and the exposed surface of the DLC coatings was ultrasonically rinsed in acetone to remove organic contamination. All the electrodes were ultrasonically rinsed in acetone, alcohol, and distilled water for 15 min successively before measurements. The OCP of the electrode was continuously monitored for 600 min, starting immediately after immersion in the electrolyte and followed by EIS at OCP over a frequency range of 1 mHz to 100 kHz with a sinusoidal perturbation potential amplitude of 10 mV. After the EIS measurement, potentiodynamic polarization was carried out at a scanning rate of 0.0167 mV/S from the initial potential 250 mV negative to OCP and swept towards the anodic direction until a current density 1 mA/cm² was reached.

3. Results and Discussion

3.1. Coatings characterization

The Raman spectrum acquired from the coatings is displayed in Fig. 1. There is a wide peak between 1100 cm⁻¹ and 1800 cm⁻¹ that can be deconvoluted into two peaks identified as D and G, respectively. The D peak centered at about 1350 cm⁻¹ corresponds to the breathing mode of sp² C only in the rings, whereas the G peak centered at about 1580 cm⁻¹ can be attributed to the stretching vibration of any pair of sp² C in the chains or rings [19]. The D and G peaks are typical characteristics of DLC. The HR-TEM micrograph in Fig. 2 shows that the coatings have random atomic arrangement and therefore is completely amorphous as also confirmed by the corresponding electron diffraction pattern in the inset photo showing a dim halo. The Raman spectrum and HR-TEM image of the coatings indicate the presence of diamond-like amorphous carbon coatings.

Fig. 3 shows the surface morphology of the DLC-coated NiTi alloy as well as the cross-sectional morphology of the DLC coatings on a Si substrate in the inset photo. The DLC coatings are smooth and uniform and no macro-particles can be observed. The inset photo reveals uniform DLC coatings about 800 nm thick together with a Ti interlayer.
No pores can be observed in the coatings and at the interface and this is expected to provide good corrosion protection for the NiTi alloy.

3.2. Adhesion strength

Good adhesion between the DLC coatings and NiTi alloy substrate is important to biomedical implants. Fig. 4 shows the morphology of the scratch track on the DLC-coated NiTi alloy and the local magnified photo near the place where spalling initially occurs (indicated by a black arrow). The critical scratch load, $L_c$, where spalling first occurs is about 60 N, which is a high scratch load [20] and therefore an indication of good adhesion strength. This is because the Ti interlayer formed by arc discharge releases the internal stress between the DLC coatings and NiTi alloy.

3.3. Open circuit potential measurements

Evolution of the OCP with time observed from the DLC-coated and uncoated NiTi alloy is shown in Fig. 5. It is clear that the OCP of the DLC-coated sample is higher than that of the uncoated one. The OCP of the uncoated sample in PBS rises rapidly at the beginning and then decreases gradually finally reaching a steady state. For the DLC-coated sample in PBS, the OCP exhibits no evident variation throughout the measurement, whereas after the addition of BSA and Fib, the OCP increases in the beginning and then reaches a stable value gradually. Addition of protein increases the OCP values, especially for the BSA.

The system is electro-neutral during the electrochemical reaction and so the decrease in the anodic dissolution current will move the OCP to a positive direction in order to decrease the cathodic reduction current [21]. After immersion in the electrolyte, a passive film consisting of mainly Ti oxides forms on the surface of NiTi electrode [1,22] and inhibits the conduction of ions at the electrode/electrolyte interface. As a result, the anodic dissolution current decreases as indicated by the rise in the OCP. After a balance between dissolution and formation of Ti oxides has been established, a stable anodic dissolution current and thus a steady OCP value result. As the DLC coatings are chemically inert, many chemical reactions involving inorganic species in the PBS cannot occur, and so the anodic dissolution current is very stable, albeit small. The OCP shows no obvious variation and is higher than that of the uncoated NiTi.
alloy during the measurement time. However, after immersing in the protein containing PBS solution, the protein adsorbs onto the surface of the electrode gradually and spontaneously to act as a barrier against conduction of ions. As time elapses, protein adsorption increases and the anodic dissolution current diminishes gradually. The decrease in the current raises the OCP in the beginning and after the adsorption process anodic dissolution current diminishes gradually. The decrease in the conduction of ions. As time elapses, protein adsorption increases and the micro pores resistance due to the formation of ionic paths across the coatings.

Table 1 summarizes the fitted resistance and capacitance values of the DLC-coated and uncoated NiTi alloy samples. The \( R_p \) value of the DLC-coated one is approximately two orders of magnitude higher than that of the uncoated sample, indicating that the DLC coatings can inhibit charge transfer at substrate/electrolyte interface consequently enhance the corrosion resistance effectively. After the addition of proteins, the CPE1 decreases while \( R_p \) increases compared to that in the PBS. CPE1 in PBS comprises the oxide film capacitance \( \left( C_f^1 \right) \) in series with double layer capacitance \( \left( C_{dl} \right) \) in the micro pores of the coatings. The capacitance can be expressed as follows:

\[
CPE_1 = \left[ \left( C_f^1 \right)^{-1} + \left( C_{dl} \right)^{-1} \right]^{-1}
\]

As described by V. P. Hoven [23] after immersion in a protein solution, the proteins adsorb onto the surface of the materials immediately (on a time scale of milliseconds). The adsorbed protein layer (\( C_{pore} \)) is always porous rather than compact [24] and two parallel current paths are present, namely \( C_f \) in series with \( C_{dl} \) and another one being the series combination of \( C_p \) \( C_f \) and \( C_{layer} \) [25]. Setting \( \theta \) as the close contact coverage of proteins to NiTi substrates, the CPE1 can be given by:

\[
CPE_1 = \left( 1 - \theta \right) \left[ \left( C_f^1 \right)^{-1} + \left( C_{dl} \right)^{-1} \right]^{-1} + \theta \left( C_f^1 \right)^{-1} + \left( C_{dl} \right)^{-1}
\]

After addition of proteins, CPE1 value decreases as shown in Table 1, if \( \theta = 0 \), the CPE1 is equal to that in PBS, which is 3.68 \( \mu \text{Fcm}^{-2} \). If \( \theta = 1 \), the CPE1 is equal to that of the homogenously and compactly covered surface. The theoretical capacitance value of the adsorbed compact protein layer can be estimated by P. Bernabeu’s equation [25] to be about 0.51 \( \mu \text{Fcm}^{-2} \) for BSA and 0.71 \( \mu \text{Fcm}^{-2} \) for Fib. Since the three capacitances in Eq.(2) are in series, the total capacitance value will be less than any of them. In other words, if the adsorbed protein layer is homogenous and compact, the CPE1 will be smaller than 0.51 \( \mu \text{Fcm}^{-2} \) and 0.71 \( \mu \text{Fcm}^{-2} \) for BSA and Fib, respectively.

As shown in Table 1, the CPE1 values after the addition of protein are between 0.51 (or 0.71) and 3.68 \( \mu \text{Fcm}^{-2} \), and so the protein layer adsorbed on the substrate is porous rather than compact. Hence, substituting the CPE1 value into Eq. (2) yields the adsorbed protein layer coverage \( \theta \) of the substrate in BSA and Fib solution equal to be 47.8% and 42.7%. The adsorbed protein layer with good contact can act as a barrier to inhibit the conductivity of ions at the substrate/electrolyte interface and so \( R_p \) increases after the addition of proteins as shown in Table 1. The different coverage \( \theta \) and \( R_p \) in BSA and Fib solutions may originate from the different structure. BSA is an oval compact globular protein with dimensions of 9 nm\( \times \)9 nm\( \times \)7 nm and molecular weight 66 kDa, whereas Fib is a fibrous protein with dimensions of 5 nm\( \times \)5 nm\( \times \)47 nm and molecular weight 340 kDa [26]. The compact structure and small size of BSA may be more efficient in covering the surface.

### Table 1

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Test solutions</th>
<th>( R_s ) (( \Omega \text{cm}^2 ))</th>
<th>( CPE_2 ) (( \mu \text{Fcm}^{-2} ))</th>
<th>( n )</th>
<th>( R_p ) (( k\Omega \text{cm}^2 ))</th>
<th>( CPE_1 ) (( \mu \text{Fcm}^{-2} ))</th>
<th>( n )</th>
<th>( R_p ) (( k\Omega \text{cm}^2 ))</th>
</tr>
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<tbody>
<tr>
<td>NiTi alloy</td>
<td>PBS</td>
<td>70.8 ( \pm ) 0.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>19.12 ( \pm ) 1.61</td>
<td>0.92 ( \pm ) 0.00</td>
<td>106 ( \pm ) 5</td>
</tr>
<tr>
<td>DLC-coated NiTi alloy</td>
<td>PBS</td>
<td>60.1 ( \pm ) 0.3</td>
<td>13.96 ( \pm ) 0.10</td>
<td>0.91 ( \pm ) 0.00</td>
<td>86 ( \pm ) 4</td>
<td>3.68 ( \pm ) 0.26</td>
<td>0.75 ( \pm ) 0.02</td>
<td>25000 ( \pm ) 1814</td>
</tr>
<tr>
<td></td>
<td>PBS + BSA</td>
<td>63.3 ( \pm ) 0.1</td>
<td>12.86 ( \pm ) 0.11</td>
<td>0.90 ( \pm ) 0.01</td>
<td>232 ( \pm ) 12</td>
<td>1.92 ( \pm ) 0.14</td>
<td>0.69 ( \pm ) 0.02</td>
<td>40500 ( \pm ) 2226</td>
</tr>
<tr>
<td></td>
<td>PBS + Fib</td>
<td>63.4 ( \pm ) 0.1</td>
<td>13.72 ( \pm ) 0.10</td>
<td>0.90 ( \pm ) 0.01</td>
<td>142 ( \pm ) 7</td>
<td>2.11 ( \pm ) 0.21</td>
<td>0.74 ( \pm ) 0.03</td>
<td>33500 ( \pm ) 2902</td>
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</tbody>
</table>

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Fig. 6. Bode plots of: (a) uncoated and (b) DLC-coated NiTi alloy at OCP and 37 °C as well as their corresponding equivalent circuit.
After the addition of proteins, $R_{pore}$ increases as shown in Table 1. As soon as the DLC-coated electrode is immersed in the protein containing PBS solution, the protein starts to adsorb not only onto the surface of the DLC coatings but also the micropore walls. The adsorbed insulating protein layer decreases the effective diameter of the micropores that conduct charged ions. Hence, $R_{pore}$ increases after the addition of protein in PBS as shown in Table 1. The results are consistent with the OCP measurements. The increased $R_{pore}$ lowers the anodic dissolution current and raises the OCP value.

### 3.5. Potentiodynamic polarization measurements

Fig. 7 depicts the potentiodynamic polarization curves acquired from the DLC-coated and uncoated NiTi alloy in different solutions. The measured corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), and breakdown potential ($E_b$) are listed in Table 2. The passive region of the uncoated sample is about 600 mV from -200 mV to 400 mV because of the formation of Ti oxides on the electrode surface. At the end of the passive region, the current density shows a sudden increase which represents the breakdown of the oxide film and onset of pits. The DLC coatings on the NiTi alloy lowers the current density and increases the breakdown potential in PBS compared to the uncoated one. The corrosion current density measured from the DLC-coated sample is lowered further in the presence of BSA and Fib. As the isoelectric points of BSA and Fib is pH 4.5 and 5.9 [27], respectively, all of them are negatively charged in PBS (pH = 7.4). As the scan is performed towards the anodic direction, after the electrode is positively charged, the negatively charged proteins adsorb on the surface of the electrode and the micropores of the DLC coatings where short circuit current can be formed. The insulated adsorbed protein layer can inhibit mass transportation of the corrosion species. As aforementioned, BSA has a small size and compact structure, which may block the micropores and cover the reaction sites efficiently, as indicated by the low current density and high breakdown potential shown in Fig. 7. It is very interesting that the breakdown process shows a gradual increase in the current after the addition of protein rather than a sudden increase in PBS as shown in Fig. 7. This may originate from the competitive interaction between adsorption of proteins onto the reaction sites and dissolution of the electrode at a high potential.

### 4. Conclusion

Uniform and adherent DLC coatings are successfully deposited on NiTi alloy by arc enhanced magnetron sputtering to enhance the surface corrosion resistance. The presence of proteins can enhance the corrosion resistance of porous DLC coatings remarkably, especially for BSA. This is attributed to the adsorption and forming of a protein layer on the substrate/electrolyte interface in the micropores and on micropore walls. It can cover the surface and inhibit mass transportation of the corrosion species. The close contact coverage of the protein layer in the micropores benefits the corrosion resistance. The coverage of micropores for BSA and Fib is 47.8% and 42.7%, respectively. The breakdown process pertaining to the DLC coatings is a gradual process because of the competitive interaction between adsorption of proteins onto the reaction sites and dissolution of the electrode at a high potential. The thickness of DLC coatings is about 800 nm under the given deposition conditions. However as it is known, different film thickness may influence the adhesion strength and corrosion resistance of NiTi/DLC system, which we will study in more detail in the future.

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### References


### Table 2

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Test solutions</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (A/cm²)</th>
<th>$E_b$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiTi alloy</td>
<td>PBS</td>
<td>-314</td>
<td>$4.0 \times 10^{-6}$</td>
<td>376</td>
</tr>
<tr>
<td>DLC-coated NiTi alloy</td>
<td>PBS</td>
<td>-96</td>
<td>$2.8 \times 10^{-6}$</td>
<td>812</td>
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<tr>
<td>DLC-coated NiTi alloy</td>
<td>PBS+BSA</td>
<td>-60</td>
<td>$3.5 \times 10^{-6}$</td>
<td>1181</td>
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<tr>
<td>DLC-coated NiTi alloy</td>
<td>PBS+Fib</td>
<td>-83</td>
<td>$1.3 \times 10^{-6}$</td>
<td>1154</td>
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